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http://earthref.org/GERM/

IGPP

UCSD

GERM Workshop

La Jolla, California
March 6-9, 2001

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Welcome to the Geochemical Earth Reference Model Workshop

The **Geochemical Earth Reference Model** (GERM) initiative defines itself as a grass-roots effort working towards a better understanding of the chemical makeup of the earth with all its chemical reservoirs, from core to atmosphere. It is important that this is a community-based initiative, and this GERM conference hopes to support this community involvement. GERM focuses on setting a global geochemical scientific theme with the goal of an optimum characterization of the chemical earth, and GERM attempts to provide useful resources on the way towards this goal.

In this workshop we focus on these two goals with a series of keynote addresses with extended discussion periods, and some more technical sessions that address a series of current problems in geochemistry. At this meeting these technical sessions will include electronic publishing and databases; specifically databases on subduction zones, the lower lithospheric mantle, and rivers. The more technical portion of the conference will be the focus of break-out sessions on Wednesday and Thursday, and a concluding plenary session on Friday ("GERM – quo vadis")

To document the results of this workshop we have planned several activities. (1) The graduate students attending this conference will take notes for all keynote presentations and discussions. Eight students are assigned to cover eight keynotes and they will work with the speakers and copy some or all of the displayed diagrams. The notes and diagrams will be posted on our website for the use by conference participants. The student notes will also be used for a short report of this conference to be published in the next issue of Geochemical News. (2) The break-out session chairs will be responsible for producing documents that summarize the results of these sessions. All chairs will have the opportunity to present their conclusions for discussion in the final plenary session on Friday. Ultimately, these documents may also take on the form of white papers, published commentaries and technical papers, or initial discussion papers for the more contentious issues. (3) The editor of G-cubed, Bill White, has authorized a theme volume of G-cubed devoted to GERM that will summarize the results of this conference. On Saturday, we have reserved five rooms, and ordered a catered lunch, for the ones who help write up these documents.

Enclosed find the conference program and abstract volume, together with your personal schedule for the break-out sessions that we hope you will attend. This program (in PDF form) will also be posted on our website, where all abstract illustrations can be found in color.

Thank you for joining us here at GERM.

Hubert Staudigel

… for the convenors of this workshop and the GERM Steering Committee

Thank You

This conference and the GERM effort is funded through the NSF-EAR Facilities and Instrumentation program. We acknowledge additional funds by the SIO Director's office, the Quest for Truth Foundation and Micromass Corporation. The Institute for Geophysics and Planetary Physics (IGPP) has provided a supportive and stimulating scientific home for GERM with excellent support facilities. Probably the most important person to thank here is Patty Keizer, who tirelessly worked on this conference for the last five months. She put together this conference volume and was the main responsible person for all of the logistics. However, this conference could not have been done without Anthony Koppers, the main developer of the new GERM website, and who helped with about every aspect of the organization of this conference.

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Program Summary Modeling Course

March 6 in 2001

9:00 – 10:30
Hubbs Hall

Energy Conserving Fractionation and Assimilation
Frank Spera and Wendy Bohrson

Coffee Break 10:30 – 11:00

11:00 – 12:30
Hubbs Hall

MELTS
Mark Ghiorso

Catered Lunch 12:30 – 1:30 at the Martin Johnson House T-29

1:30 – 3:00
Hubbs Hall

Using the Online U-series Calculator
Mark Spiegelman and Vincent Salters

Coffee Break 3:00 – 3:30

3:30 – 5:00
Hubbs Hall

Modeling on the Geochemical Evolution of the Earth with TnT2000
Anthony Koppers and Jason Phipps Morgan

Icebreaker at the Martin Johnson House T-29 starting at 5:00

Program Summary Workshop

March 7 in 2001	March 8 in 2001	March 9 in 2001
8:30 – 10:00 Hubbs Hall	8:30 – 10:00 Hubbs Hall	8:30 – 10:00 Hubbs Hall
Meeting Introduction Hubert Staudigel **Welcoming Remarks** Charles Kennel, Director SIO John Orcutt, Director IGPP **Publishing Crises in Geochemistry** Al Hofmann, Friso Veenstra, Bill White **Information Technology of GERM** John Helly	**Element Partitioning and Earth's Core Composition** Bernie Wood **Discussion Leader** Bill McDonough	**Dynamics and Fluxes of Fresh Water Input into the Oceans** Billy Moore **Discussion Leader** Art Spivack
Coffee Break 10:00 – 10:30		
10:30 – 12:00 Hubbs Hall	10:30 – 12:00 Hubbs Hall	10:30 – 12:00 Hubbs Hall
The Silicate Earth Claude Allegre **Discussion Leader** Don Anderson	**Global Chemical Fluxes in Rivers** Jerome Gaillardet **Discussion Leader** Lou Derry	**D/H Constraints on Mantle-Ocean Hydrogen Fluxes** Dan Schrag **Discussion Leader** Jeff Severinghaus
Lunch Break 12:00 – 1:30 at the Martin Johnson House T-29		
1:30 – 3:00 Revelle, Munk Lab, Hubbs Hall	1:30 – 3:00 Hubbs Hall	1:30 – 3:00 Hubbs Hall
Group Sessions and Symposia	**Mass Balances of Subduction** Tim Elliot **Discussion Leader** Jim Gill	**Does Tomography say Anything about Geochemistry?** Guy Masters **Discussion Leader** Al Hofmann
Coffee Break 3:00 – 3:30		
3:30 – 5:00 Hubbs Hall	3:30 – 5:00 Revelle, Munk Lab, Hubbs Hall, Board Room	3:30 – 5:00 Hubbs Hall
Thermodynamics of Mantle Melting Marc Hirschman **Discussion Leader** Jason Phipps Morgan	**Group Sessions and Symposia**	**GERM - Quo Vadis** Hubert Staudigel Bill McDonough Lou Derry Al Hofmann Henry Shaw
5:00 – 8:00 Munk Lab	5:00 – 8:00 Munk Lab	6:00 Head of Tecolote Canyon
Poster Session and Reception	**Poster Session and Reception**	**Conference Dinner**

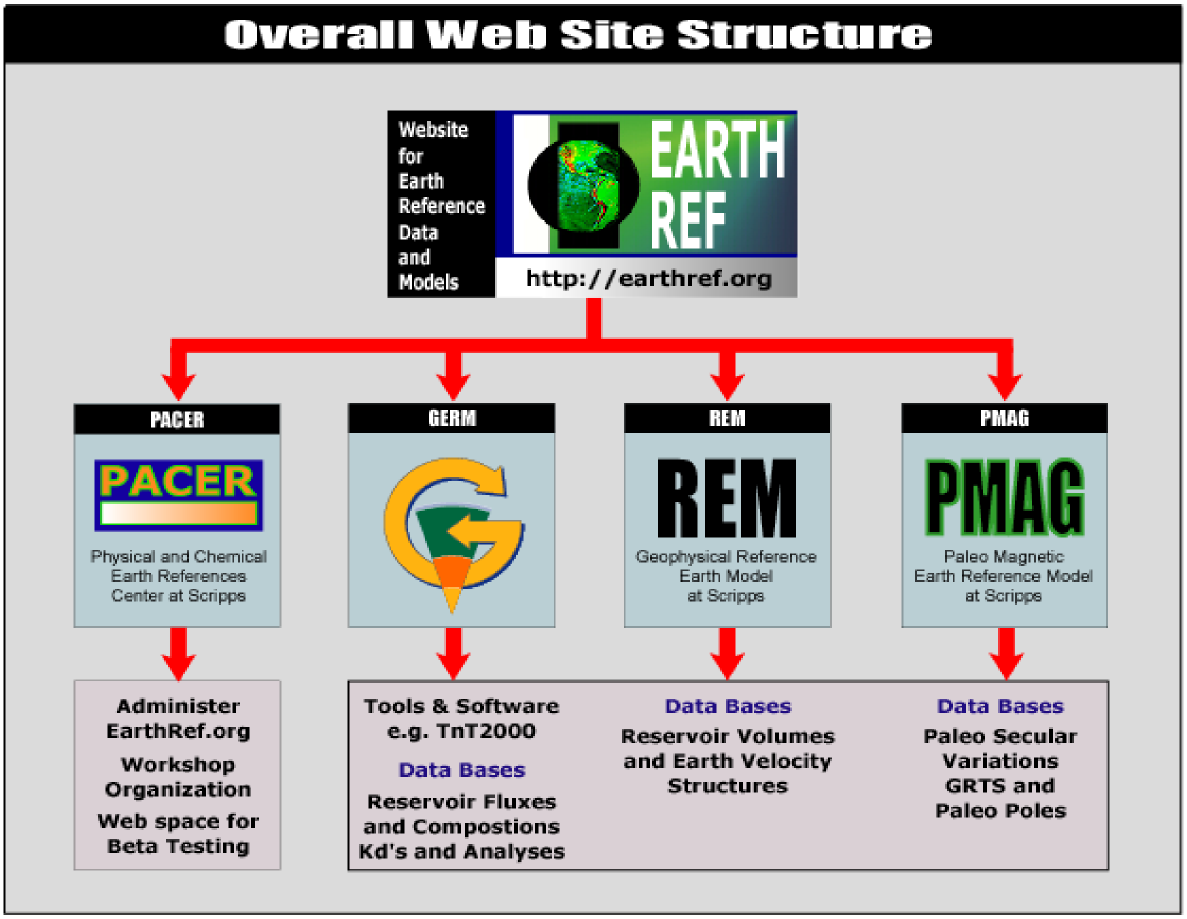
Program Group Sessions

March 7 in 2001	March 8 in 2001
1:30 – 3:00 Hubbs Hall	1:30 – 3:00 Hubbs Hall
Group Session 1 **Part 1** **GERM Databases** Anthony Koppers; John Helly	**Group Session 1** **Part 2** **GERM Databases** Anthony Koppers; John Helly
1:30 – 3:00 Munk Lab	1:30 – 3:00 Munk Lab
Group Session 2 **Part 1** **Workshop on Electronic Publication** Al Hofmann	**Group Session 2** **Part 2** **Workshop on Electronic Publication** Al Hofmann
1:30 – 3:00 Revelle Hall	1:30 – 3:00 Revelle Hall
Group Session 3 **The Subcontinental Mantle** Rick Carlson	**Group Session 4** **GERM Subduction-Zone Fluxes** Gray Bebout; Tim Elliott
	1:30 – 3:00 Board Room
	Group Session 5 **River Fluxes** Lou Derry; Jerome Gaillardet

The New GERM Website

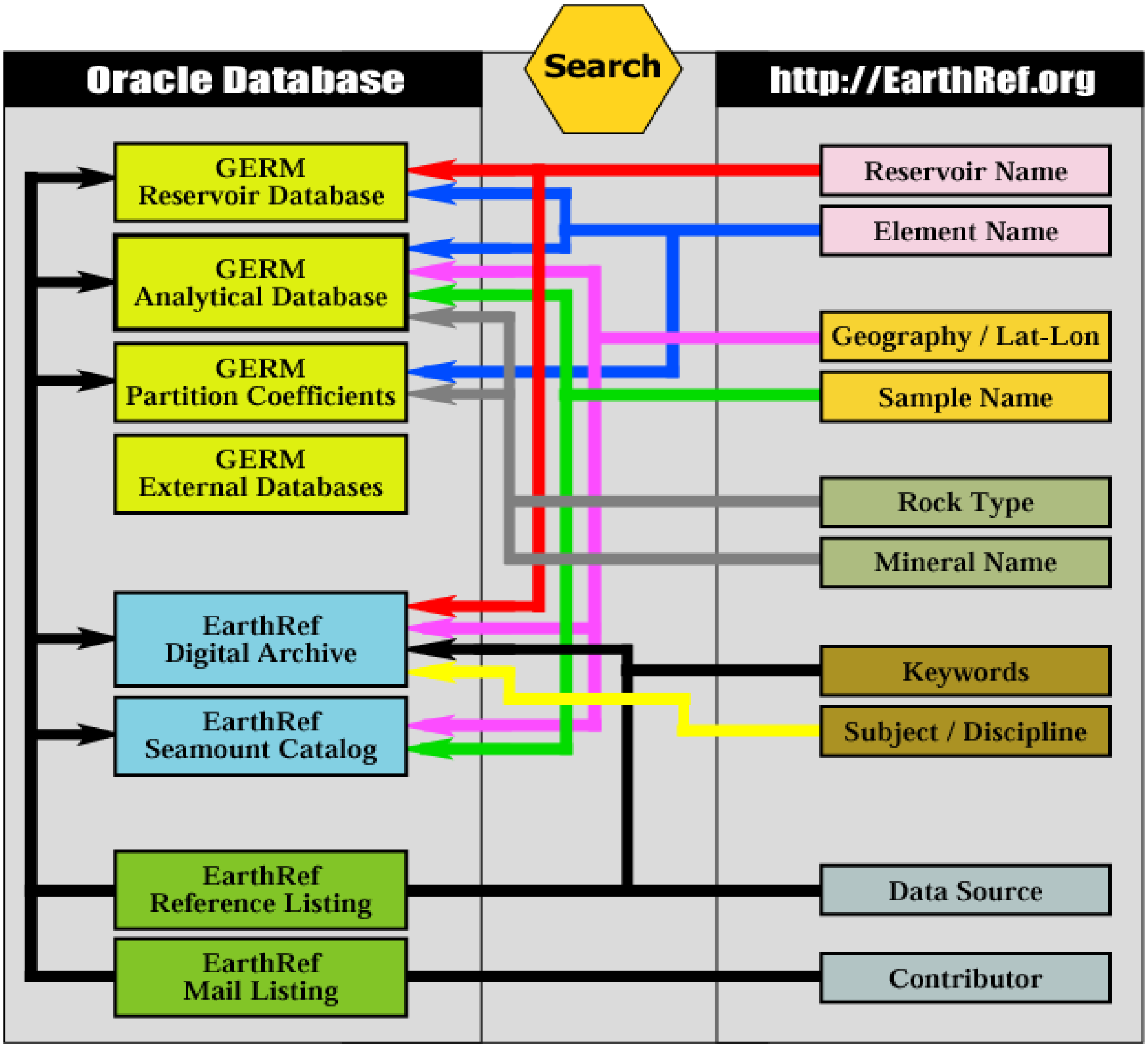
Anthony Koppers and Hubert Staudigel

The GERM website was established as the result of the first, 1996 GERM meeting in Lyon. Henry Shaw of the Lawrence Livermore National Laboratory built and maintained this site for until a year ago. The core of this website was a series of (static) web pages that provided all available information on the world's major chemical reservoirs, with downloadable chemical data files. This website became quite popular, with an increasing amount of data and an increasing number of scientists downloading data from it (~5000 hits per year). However, as the website grew, it became obvious that the website became difficult to keep up-to-date and that its functionality could be greatly improved by changing it into a relational database. We are presenting this new GERM website at the 2001 GERM meeting in La Jolla, California.



The new GERM website is hosted at the Scripps center for Physical and Chemical Earth References (PACER) in concert with the Geophysical Reference Earth Model (REM) website. Even though these two websites are currently not linked, it is our hope to be able to do so in the intermediate future. Even though the data are fundamentally different, the geophysical and geochemical Earth reference models are related and have to be reconciled with each other. There are many data that can be shared for model calculations. The same is true for many databases in the Earth sciences. For this reason, PACER has established the "EarthRef.org" URL http://earthref.org as a common host for Earth sciences reference data.

The EarthRef.org website maintains various online databases that permit for data queries using a wide range of metadata. These online databases are designed in Oracle 8.0.5 and they are maintained by Anthony Koppers (IGPP/Scripps) at the San Diego Supercomputer Center, in consultation with John Helly (SDSC), Henry Shaw (LLNL/DOE) and Hubert Staudigel (IGPP/Scripps). They can be directly accessed through the http://earthref.org/databases.htm link.



The philosophy behind the EarthRef.org databases is to have a flexible architecture that allows for the archiving, searching and downloading of any type of Earth science digital data. The archived data may support all of the major components of EarthRef.org (e.g. the Reference and Mailing List database) or specific sections (e.g. the GERM Reservoir Database and GERM KD's Datbase). Ultimately we hope to directly link these data sources with on-line modeling tools that allow for a variety of calculations, relating these Earth science data. Our development of the TnT2000 global-geochemistry modeling tool (see http://earthref.org/tools/tnt.htm) is a first attempt at this.

Data archived in Earthref.org may include individual data points (such as chemical analyses and age determinations) or any other arbitrary digital objects (ADO). These ADOs can serve as original data resources (an image of a data table or illustration) or, more so, as any resource useful in research and teaching (such as maps, correlation diagrams and modeling codes). ADOs can be searched for on basis of their metadata and subsequently be downloaded as data files.

GERM Relational Databases

The GERM Reservoir Database is the original GERM database that contains summary data on the geochemistry of each reservoir in the Earth. These geochemical data can be searched for based on reservoir name, element, reference and availability of data. This relational database only includes peer-reviewed literature data. As a result, numerous interesting but unpublished data sources are now omitted that originally were available on the GERM website. In the long run, and in case these data do ***not*** get published in the peer-reviewed literature, they may still be made available through the EarthRef Digital Archive (see below). At the moment we are working on the GERM Fluxes Database, which will be online in the near future. We also maintain links to external databases, such as the GEOROC and PETDB analytical databases.

The KD’s Database contains partition coefficient data for all types of rocks and minerals and for every element. All KD values can be searched for using combinations of rock name and mineral, element and reference. Up to this moment all data has been compiled by Roger Nielsen (Oregon State University) and includes both experimental and empirical data.

Digital Archives

The EarthRef Digital Archive (ERDA) is the archiving backbone of EarthRef.org. It can accommodate any "digital" contribution ranging from data tables to diagrams to reports to geological maps to videos. We are also developing a Seamount Catalog containing bathymetry maps, dredge locations and data on seamount morphology. The major goal of these archives is to supply the Earth scientist with simple means to have access to the widest possible variety in digital data files, with a direct relevance to research and teaching. Data files may be archived as strictly peer-reviewed contents, or as an open exchange of useful resources as shared between scientists without review. The EarthRef Digital Archive is designed as general medium for the exchange and access to a very rich and diverse range of geo-information.

ERDA data objects are extensively described in terms of metadata. These metadata are used when Earth scientists search through this online database in order to download their desired data files. The metadata ***minimally*** include keywords (e.g. sediment, REE, argon), descriptions and the data file specifics. However, there are many optional types of metadata, which (when made available with each data contribution) would significantly increase the success of finding these data files in the online data queries. For example, the ERDA contributions can also be characterized for their latitude-longitude, geography (e.g. Alps, Massif Central), age range in Ma or geological age (e.g. Cretaceous, Archean), science discipline and subject (e.g. mineralogy and petrology, igneous petrology) and project name.

ERDA provides the basic database structure and is capable of handling an extremely diverse set of data types. To demonstrate this diversity, we have setup a Seamount Catalog that contains bathymetry maps from seamounts surveyed with the Seabeam 2000 system. The Seamount catalog serves as a support structure for sample locations in the GERM geochemical databases, and it provides a basic database on dredge locations and seamount morphology. In order to generate complete maps of the seamounts (when the Seabeam surveys were incomplete) we have merged the Seabeam data with the bathymetry database of Sandwell & Smith (1996, 1997). All maps are available for downloading in high and low JPG formats next with their gridded bathymetry data and the original Seabeam 2000 data files.

Reference Database

Key to each EarthRef database is the Reference Database. By searching for reference one can find its way into each different database (Figure 2). More importantly, each data table or text passages included in the databases can be downloaded as PDF and Microsoft Excel background data files in their original layout.

Mailing List

A mailing list will be maintained. Scientists who wish to add themselves to this list or who need to make an address change can do so via data forms on the EarthRef.org web site (which will be operational shortly after the workshop). This mailing list will also be used to identify each data contributor to the EarthRef databases.

Future Database Initiatives

Even though GERM and REM are mature sites, there are plans for additional sections. Currently we are planning a Paleomagnetic database (PMAG) and a Geological Timescale Archive (GTA). Suggestions are welcome.

The GERM Initiative

Steering Committee

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Editors

The following people are responsible for coordinating the collection and editing of geochemical data that comprise the GERM data set in the Online Databases. If you would like to contribute to the GERM effort, please contact the appropriate person listed below.

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Detailed Program Tuesday 6 March

► 9:00–10:30 Hubbs Hall

Energy-Constrained Recharge, Assimilation, and Fractional Crystallization (EC-RAFC): an energy-constrained model for tracking the trace element and isotopic composition of melt in open systems

Frank Spera and Wendy Bohrson

Geochemical data for igneous rocks provide definitive evidence for the occurrence of open-system evolution including **R**eplenishment or **R**echarge of 'primitive' magma, **A**ssimilation of anatectic wallrock melt, and cumulate formation by **F**ractional **C**rystallization. A general model (**E**nergy **C**onserved-RAFC or EC-RAFC) has been constructed which enables forward-modeling of trace element and isotopic trajectories of magma undergoing simultaneous replenishment, assimilation and fractional crystallization during the approach to thermal equilibrium. In thermodynamic terms, the model consists of a three-part composite system (pristine magma body, country rock and recharge magma reservoir) isolated from the environment. Walls between the sub-systems making up the composite system are diathermal and open with respect to the exchange of melt. EC-RAFC is formulated as a set of $3+t+i+s$ coupled differential equations, where the number of trace elements, radiogenic and stable isotope ratios modeled are t, i and s, respectively. The differential equations express conservation of energy (enthalpy), total mass and trace elements as the composite system approaches thermal, trace element and isotopic equilibrium. Partial melting of wallrock, modeled as fractional melting, is incorporated, as is the energetics of sensible and latent enthalpy exchange between the various sub-systems. Non-linear melt productivity relations for country rock, original magma and recharge magma are accommodated. Addition of recharge magma increments (each of arbitrary mass) is accomplished continuously or episodically (arbitrary number of pulses). Temperature-dependent trace element partition coefficients are used to describe trace element distributions. Solution of the set of differential equations, with magma temperature (T_m) as the independent variable, provides values for the average wallrock temperature (T_a), mass of melt within the magma body (M_m), mass of cumulates formed, mass of wall rock involved in the thermal interaction (M_a^o) and the mass of anatectic melt assimilated (M_a^*). In addition, the concentration of t trace elements (C_m) and $i+s$ isotopic ratios (ε_m and δ_m) in melt and cumulates are computed as the melt temperature evolves from its initial value, T_m^o to the user-defined equilibration temperature, T_{eq}. Input parameters needed to generate a solution include the initial temperatures and compositions of magma, recharge magma, and wallrock, bulk distribution coefficients and their temperature dependencies, heats of fusion and crystallization and isobaric specific heat capacities of the various constituents. The *a priori* defined magma recharge mass function, $M_{rm}(T_m)$ (user-supplied) specifies the addition of recharge magma to the magma body (e.g., episodically, continuously, a crescendo of pulses, recharge events of different duration and magnitude, etc). The present incarnation of EC-RAFC incorporates a weak coupling to major element mass balance and phase relations by means of a set of user-defined 'melt productivity' functions based on laboratory experiments or Gibbs Energy minimization simulations (e.g., MELTS; Ghiorso and colleagues). Melt productivity functions are defined for end-member bulk compositions characterizing the local geologic picture including wall rock, pristine magma and recharge magma. These functions prescribe the relationship between melt mass fraction and temperature. This composite system model, while clearly a simplification of complex natural systems, serves to illustrate the most significant interactions expected during RAFC evolution. Comparison of EC-RAFC predictions with trends from natural systems where independent evidence exists for complex RAFC evolution shows that some otherwise inscrutable composition-time trajectories are plausibly explained given the particulars of the magmatic-hydrothermal-recharge system under investigation.

Modeling course outline

During the workshop, the theory of EC-RAFC will be reviewed, practical aspects of the program will be described, and half-dozen EC-RAFC simulations will be performed to illustrate the flexibility and limitations of the model.

How to get the program

A program to perform EC-AFC calculations is available at http://magma.geol.ucsb.edu/.

► 10:00–10:30 Coffee Break

► 11:00–12:30 Hubbs Hall

MELTS

Mark Ghiorso

MELTS/pMELTS is a software package that models major element solid-liquid phase equilibria in magmatic systems. The algorithms are based on thermochemical models of constituent phases and results are obtained by minimization of suitable thermodynamic state functions. Calculations can be performed under a variety of specified pressure/temperature conditions and for a range of bulk compositions corresponding to natural magmas. The MELTS/pMELTS package is available as a standalone executable for UNIX systems and as a Java Applet interface to a server compute engine located at the University of Washington. Both implementations will be demonstrated at the short course. Either version of the package will deliver calculations based upon the original calibration designed for low pressure simulations (MELTS) or the newer model optimized for pressure in the 1-2 GPa range (pMELTS). The Java Applet also delivers an interface to a thermochemical properties calculator for constituent solid phases utilized in the package.

Modeling course outline

1. MELTS and pMELTS - What are they and what do they do?
2. Implementation and delivery
   a. UNIX versions of MELTS/pMELTS - Availability and documentation
   b. Java Applet versions of MELTS/pMELTS and Calc - access and system requirements; online documentation
3. Uses of MELTS/pMELTS - Some examples
   a. Low pressure models (MELTS)
      - Equilibrium crystallization of MORB
      - Fractional crystallization of MORB
      - Response to variation in oxygen fugacity
   b. Higher pressure models of mantle melting (pMELTS)
      - Subsolidus phase equilibria
      - Adiabatic, decompression melting
4. Questions and answers (an opportunity for participants to suggest calculations and explore other aspects of the modeling)
5. Summary and future directions of the MELTS/pMELTS effort

How to get the program

MELTS is available at http://melts.geology.washington.edu/.

► 12:30–1:30 Catered Lunch at the Martin Johnson House T-29

► 1:30–3:00 Hubbs Hall

Using the Online U-series Calculator

Mark Spiegelman and Vincent Salters

Measured departures from secular equilibrium in the uranium series decay chains provide important constraints on the rates of recent mantle and crustal processes. Nevertheless, the inferences drawn from these observations depend upon the models used to interpret them. While several useful models for U series exist, they are not all equally easy to use, and it is often the ease of use, rather than the utility of the model, that determines which models are applied. UserCalc levels the playing field by making some of the more general U series transport models accessible to a wider community through the UserCalc Web site available from Lamont-Doherty Earth Observatory. These models calculate the effects of both melting and melt transport on two U series chains ($^{238}U \rightarrow ^{230}Th \rightarrow ^{226}Ra$ and $^{235}U \rightarrow ^{231}Pa$) and allow the user to input their own petrological insight and data to explore the behavior of this model. The purpose of the site is to provide a tool that can spur additional collaborations between geophysicists and geochemists as well as drive more rapid exploration/evolution of U series models.

Modeling course outline

Hands-on use is the best way to familiarize oneself with Usercalc. The workshop will discuss the details of using the calculator, the various ways to enter the input parameters for the program, step-by-step use of the program, and will explain the various parameters calculated by the program. Furthermore, we will explore the limits of the program by varying the input parameters for the calculator. Lastly, best estimates of input parameters will be given for melting at different depths and U-series excesses will be calculated using these best estimates.

How to get the program

UserCalc is available at http://www.ldeo.columbia.edu/~mspieg/UserCalc/Banner.html

► 3:00–3:30 Coffee Break

► 3:30–5:00 Hubbs Hall

Modeling on the Geochemical Evolution of the Earth with TnT2000

Anthony Koppers and Jason Phipps Morgan

TnT2000 is a MATLAB toolbox for modeling both simple and sophisticated scenarios that mimic the geochemical differentiation of the Earth (see also the Koppers, Phipps Morgan and Staudigel abstract in the back of this volume). This is achieved by an easy-to-use graphical user interface that facilitates the definition of multiple reservoirs and their intrinsic properties in order to approximate global reservoir geometries, their evolution and the mass fluxes between them.

TnT2000 will be distributed both as a stand-alone program (compiled in C^{++}) and as its original MATLAB software code. The program can thus be used without the MATLAB 6.0 license, but it also allows geochemists to work with the original software code, if required. Improvements and additions to the TnT2000 software code are strongly encouraged, but with the restriction that any new code will be shared openly (similar to the open-source Linux distribution). For this purpose, TnT2000 has a modular design that readily allows for the expansion of different algorithms of partial melting, alteration, mixing, entrainment, recycling and mantle convection.

Course outline

In this short course we will demonstrate a range of different models that we already have defined in TnT2000. We will begin with a ***classical*** box model that ignores any effects of increased heat loss in the early Earth's history. We will end with a set of three ***complex*** whole mantle and two-layered mantle convection models that concurrently adjust the heat loss evolution over geological time:

1.	Steady state Upper Mantle model	Galer & O'Nions, 1985
2.	Post-Archean Uranium Recycling model	Elliott et al, 1999
3.	Two-Stage Melting	Phipps Morgan & Morgan, 1999
4.	Dense Deep Layer	Kellogg et al, 1999

Through these demonstrations we would like to illustrate the diversity in differentiation patterns evolving from these different models. However, more significantly, we would like to show what the effects are of different heat loss models on the Earth's differentiation. Due to time limits, we will focus mainly on the Rb-Sr, Sm-Nd and U/Th systematics.

How to get the program

TnT2000 has been developed in MATLAB 6.0 for Microsoft Windows 95/98/NT/2000 but can be used under Linux and UNIX operating systems as well. TnT2000 will be available as freeware from the EarthRef.org ***Modeling Tools*** website at http://earthref.org/tools/tnt.htm. At this website one can download the program itself, but also find documentation, example files and online help files to provide you with up-to-date support.

References

Elliott, T., Zindler, A. & Bourdon, B. (1999, Earth and Planetary Science Letters 169:129-145)
Galer, S.J.G. & O'Nions, R.K. (1985, Nature 316:778-782)
Kellogg, L.H., Hager, B.H. & van der Hilst, R.D. (1999, Science 283:1,881-1,884)
Phipps Morgan, J. & Morgan, W.J. (1999, Earth and Planetary Science Letters 170:215-239)

► 5:00 Ice Breaker at Martin Johnson House T-29

Detailed Program Wednesday 7 March

► 8:30–10:00 Hubbs Hall

Meeting Introduction
Hubert Staudigel

Welcoming Remarks
Charles Kennel, Director SIO
John Orcutt, Director IGPP

Publishing Crisis in Geochemistry?
Al Hofmann; Friso Veenstra; Bill White

Information Technology of GERM
John Helly

The ability of investigators to share data is essential to the progress of interdisciplinary, integrative scientific research. There are many difficulties in doing this both within and across disciplines. This paper presents a brief review of the main issues in achieving effective data sharing based on previous efforts within the ecological community. We also discuss a range of information architectures for effecting differing levels of standardization and centralization.

► 10:00–10:30 Coffee Break

► 10:30–12:00 Hubbs Hall

The Composition of the Earth and Earth's Reservoirs
Claude Allègre; Eric Lewis; Stephane Escrig

The difficulties for computing the composition of the Earth is the fact that it is a differentiated planet and we have no access to the deep interior. The general balance equation: [Bulk Earth] = [Mantle] + [Continental Crust] + [Core] + [Atmosphere-Hydrosphere] is the key to solve the problem. [Bulk Earth] values can be accurately estimated by comparing some key elemental ratios between meteorites and upper mantle materials. We have shown that [Bulk Earth] plots on the carbonaceous chondrite line in different [A/R, B/R] diagrams, R, being a refractory but at a different place depending on the volatility. [A/R] ratios, where R is a refractory element plot close to (CM) for medium refractory elements (Mg, Si, Hf) and below CV for volatiles (K, Rb, Cl, I). These systematics permit the calculation of a Bulk Earth chemical composition.

The budget equation [Continental Crust] + [Depleted Mantle] = [Primitive Mantle] can be worked out for all trace elements using ratios in various ways. The global inversion has been done by blocks, each block corresponding to a chemical family: alkali, alkaline-earth, rare earth, strongly incompatible metals (SIMs), transition elements, platinoids, metalloids, thiophils, halogens. The blocks are then combined two by two, then four by four, etc. and the process is iterated.

We then get the composition of the continental crust, depleted mantle, and the primitive mantle. By subtraction from the Bulk Earth, we obtain the composition of the core. The core contains 80% Fe, 4.5% Ni, 7% Si, 4% O, 1.4% S, siderophiles, thiophils (like sulfur), but also some elements like Mn, V, Cr, P, and also Nb (not Ta). Strong constraints about the formation of the core can be obtained. Using extinct radioactivities Hf-W and Mn-Cr, we can put precise constraints and timing about condensation-accretion in the solar nebulae and metal segregation in planetary interiors.

Discussion Leader

Don Anderson

One can point to several key issues which are holding up progress in understanding Earth chemistry and dynamics, and in interdisciplinary communication. Often, in the history of science one can point out the stumbling blocks, or assumptions, and when these are identified, rapid progress can be made. In the past these were phlogiston, Ptolemy, geocentricity, fixed continents and so on.

Currently some workers make the following assumptions to may be questioned

1. Is the mantle immediately below the lithospheric plates (the MORB mantle) homogeneous, well-stirred and depleted? Does OIB require a deeper, distinct reservoir? Should a “common” reservoir be above the others?
2. Are all seismological subdivisions (such as upper and lower mantle, transition region, D") also accessible geochemical reservoirs?
3. Is whole mantle convection implied by geophysical data (geoid, some tomographic cross-sections, synamic topography, radial correlations, spectral heterogeneity maps)?
4. Is the upper mantle almost isothermal and subsolidus except at ridges and hotspots?
5. Are samples from the "lower mantle" (Bullen's Region D starting at 1000 km) routinely available to geochemists?
6. Are the recent findings of ancient material in the ocean basins significant?
7. Density contrasts of 1% are required to isolate the deeper parts of the mantle, and to “irreversibly” stratify the mantle; what impact does this have on our thinking? Does it make sense to talk about whole mantle convection?
8. A low-radioactivity lower mantle is consistent with much geophysical data, including accretional differentiation, implying that most of the U, Th, K is in the crust and shallow mantle and most of ^{40}Ar is in the crust-atmosphere system. This is the opposite of the “undegassed” primordial lower mantle scenario. How can this be tested?
9. Convection modeling with plates, and continents, suggest that the plates drive themselves; the plates are part of the upper thermal boundary layer and they drive plate tectonics and mantle convection. The mantle is passive. The lithosphere also controls the rate of mantle cooling, not the mantle viscosity itself, as once thought. Does any geophysical or geochemical data require “active” upwelling and temperatures outside the normal mantle range of 1400±200°C?
10. The effect of P on thermal expansivity and viscosity shows that lower thermal boundary layer instabilities are giant (10^4 km) and long-lived (10^9 years). Such "megaplumes" show up in seismic tomography as 2 large red regions in the deep mantle, under Africa and the central Pacific. Can we date these megaplumes by geology, tectonics, geochemistry or geophysics? Are they isolated?

11. The absence of a heat flow anomaly (McNutt) and thermal swell (seismology) at various hotspots, including Hawaii and Siberia, seems to rule out a thermal explanation. What are the options?
12. Can a reservoir in the convecting Earth be both isolated and accessible? Do we need to talk about "aurevoirs" as well as "reservoirs"?

► 12:00–1:30 Catered Lunch at the Martin Johnson House T-29

► 1:30–3:00 Hubbs Hall

Group Session 1: GERM Databases -- Part 1

Anthony Koppers; John Helly

Recently several geosciences databases (GEOROCK, PETDB, EarthRef) have come to a useful state and, as a community, we should think about how we would like them to evolve into the future. The goals of this group session are (1) to critically review these data bases, (2) to evaluate the potential for future developments of data bases (3) discuss data formats and metadata standards, and (4) to develop a data input format that may be proposed to electronic journals as a preferred data publication format. From this assessment we can help to foster a new method of data publication that may ultimately allow us to directly download data into databases from a peer-reviewed electronic publication.

There will be two sessions, one on Wednesday and one on Thursday, both of them located in Hubbs Hall, where we will have access to the Internet and a computer projector. In the first session we will focus on discussion and in the second on writing and on practical development of metadata standards and a digital data input format that is optimized in terms of compatibility to the current databases. To accomplish the writing we may split up into smaller working groups.

The agenda for these two sessions includes

1. Presentation of the currently available databases in terms of their contents, access and future plans. GeoRock (Sarbas) and RidgePet (Lehnert); Earthref (Koppers); 10-15 minutes each.
2. Discussion of these databases: What are their strengths and weaknesses? Can any of the weaknesses be remedied? Are there any plans for time-stamping the databases? What is the access to the original references? Are the search results cited with a reference? What are the plans for backup, mirroring, distribution on CD, or over the Internet? Can these databases be made interoperable with each other and other databases? How to interoperate different types of databases such as Oracle and Microsoft Access? How to interoperate specialized versus generalized databases?
3. Where do these geochemical databases need expansion and by whom? Why focusing solely on hard rock geochemistry without including sediments, water, ice and air analyses?
4. Short presentation by John Helly: What is the electronic future of databases? What do other sciences do? Is there anything we can learn from outside Earth sciences?
5. Metadata. What are metadata? And, what can we do to define some metadata standards that are consistent across different databases and database structures? How to come to one global and general Earth Science metadata library?
6. The recent establishment of g-cubed, the all electronic journal for geochemistry, geophysics and geosystems, offers unique opportunities for combining database activities with peer-reviewed data

publication activity. One of the major goals of this section is to create a data publication template that could be included into G-cubed and can be downloaded from the Earthref/GERM website in order to upload already-published literature data?

► 1:30–3:00 Munk Lab

Group Session 2: Workshop on Electronic Publication -- Part 1

Al Hofmann

The growth of geochemistry and dramatic improvements in analytical equipment are leading to dramatic growth in the production of geochemical data. This raises new questions about quality control, documentation and publication of geochemical data. Authors, editors, reviewers, and "consumers" need to pay more attention to these questions, if we want to maintain or improve the quality of our science.

Present bad practices include

1. Publication of geochemical diagrams without data tables
2. Publication of "representative" data selected by the author
3. Published statements to the effect that the "full set of data may be obtained from the author by request"
4. Published statements to the effect that the "full set of data will be published separately";
5. Publication of concentration ratios instead of concentrations
6. Failure to publish essential "metadata" (Metadata include information on sample location, sample description, analytical techniques, laboratory in which the analyses were performed, information on data obtained for reference materials ("standards"), documented or at least estimated analytical uncertainties, failure to explain how the stated uncertainties are defined).

The present situation is not satisfactory. It will rapidly deteriorate in the future, as the rate of data production grows further, unless new guidelines are adopted by the community about the publication and management of geochemical data.

► 1:30–3:00 Revelle Hall

Group Session 3: The Subcontinental Mantle

Rick Carlson

Importance of the Subcontinental Mantle Lithosphere

Continental crust contains the majority of Earth's highly incompatible lithophile elements. Mass balance calculations based on calcium and aluminum abundances allow the whole volume of continental crust to be generated from a volume of mantle roughly equal to that now found as subcontinental lithospheric mantle (SCLM). In contrast, the abundance of incompatible trace elements (e.g. Rb, Ba, Pb, etc) in continental crust requires extraction of these elements from a much larger volume of mantle than just the SCLM. Samples of the SCLM generally show the depletion of Ca, Al, and Fe expected for residues of melting, but their incompatible trace element abundances tend to be enriched compared to those expected for any residue, and in some cases are even more enriched than found for fertile mantle. Clearly, the subcontinental lithospheric mantle plays a critical role in the formation and longevity of the continents as well as in the transfer of incompatible elements from the main volume of mantle to the crust. Several key questions remain regarding the role the SCLM plays as a chemical reservoir on Earth.

These include …

1. How is the SCLM related to continent formation? Source? Product of tectonic accretion unrelated to crust formation?
2. Is the SCLM sufficiently enriched in incompatible elements to represent a major reservoir of incompatible elements in the Earth?
3. What role do non-peridotitic lithologies (eclogite/pyroxenite/glimmerite) play in determining the bulk composition of the SCLM and in continental magma genesis?
4. How many "oceanic" plateaus are actually built on SCLM? Kerguelen, Azores, others?
5. What is the flux of melts/fluids into and out of the SCLM?

Composition of Subcontinental Mantle Lithosphere

1. Numerous xenolith analyses available
   a. Need both bulk-rock analyses and ability to reconstruct bulk compositions from mineral analyses
   b. Many mineral geothermobarometry results published, but individual probe analyses of phases generally not published
   c. Need method to evaluate and correct for host-rock contamination to define "in mantle" compositions
2. Quantitative estimate needed of "average" level of metasomatic enrichment
3. Estimate needed of abundance and composition of non-peridotitic lithologies via concentrate analyses
4. Relation of seismic velocity and electrical conductivity to composition, including bulk composition, volatile abundance, presence of non-peridotitic lithologies.

Role of Subcontinental Mantle Lithosphere in Continent Formation, Continental Magma Genesis, and Continent Longevity

1. Thermal filter for transiting magmas
2. The place where melt-wallrock interaction occurs

3. Melt productivity of a wet, polylithology mantle
4. Role of volatiles (H_2O, CO_2) in melt productivity and reactivity
5. Physical properties as a function of bulk composition, volatile abundances and siting (i.e. hydrous phases or dissolved in anhydrous phases), and abundance of veining

What is Needed? How can GERM Help?

1. Comprehensive database of xenolith composition
   a. Bulk compositions
   b. Mineral compositions
   c. Ages
   d. Models to construct bulk compositions from mineral compositions and modes
2. Better models of melt-wall rock interaction

3. Experimental petrology of hot magmas from fertile peridotitic sources interacting with cold, wet, polyphase lithosphere.
4. Promote better experimental understanding of metasomatic phases
   a. Stability under varying P, T, oxygen fugacity, H_2O and CO_2 abundance
5. Experimental petrology of pyroxene/garnet/phlogopite/amphibole melting at mantle pressures
6. Partition coefficients for metasomatic phases
   b. phlogopite, ilmenite, carbonate, amphibole, apatite, rutile, alkali-titanites, etc.
7. Relation of physical properties (density, strength, seismic velocity, electrical conductivity) to bulk composition, oxidation state, volatile abundance

► 3:00–3:30 Coffee Break

► 3:30–5:00 Hubbs Hall

Thermodynamics of Mantle Melting

Marc Hirschman

It is well known that the sources of oceanic basalts vary in their isotopic and trace element composition, but the extent of lithologic heterogeneity is more controversial. Enriched mantle reservoirs (HIMU, EM, etc.) may plausibly be carried by normal peridotite, by peridotite enriched in major or minor components (FeO, TiO_2, alkalis, H_2O, CO_2) or by pyroxene-rich lithologies. Understanding the lithologic character of geochemically distinct mantle reservoirs would place strong constraints on the origin of such reservoirs. Also, if exotic lithologies are shown to play a significant role in basalt genesis, interpretations of the dynamics of the mantle may be affected. For example, if plumes carry easily melted components, then excess potential temperatures required to explain oceanic island volcanism are less pronounced.

Establishing the presence or absence of lithologic heterogeneity in basalt source regions requires understanding of the energetics of melting and phase equilibria constraints established by experiment. Beneath oceanic ridges and islands, partial melting is driven primarily by adiabatic pressure release. I will review the basic energetics behind pressure-release melting, emphasizing the key variables that influence the production of melt during this process, solidus location and the isobaric productivity, and use this as a basis for understanding the effect of mantle heterogeneity on melt production in upwelling mantle. I will also review theoretical models and experimental evidence (both old and new) that provide constraints on the production of partial melts from both peridotite of variable composition and from pyroxenite.

Discussion Leader

Jason Phipps Morgan

1. Do observational constraints on the extents and rates of melting beneath hotspots and ridges agree with experimental determinations of melt productivity?
2. Is there convincing evidence for or against lithologic heterogeneity in basalt source regions?

3. If different lithologies have different solidii, and variations in volatile content strongly affect the high-pressure (initial) solidus of a given lithology, then how different are upwelling temperatures beneath hotspots and ridges? Or, is most of the observed difference between OIB and MORB due not to differences in starting temperature, but to differences in initial lithologic composition and the different shallow depth-limits to OIB and MORB melting?
4. Chemical isolation can easily occur in the solid mantle. Different lithologies created by different near-surface melting and alteration processes are likely to have distinct isotopic evolution when recycled back into the mantle. Do distinct, long-lived mantle 'reservoirs' even exist within the mantle in their mixing-theory definition as homogenous spatially distinct regions with different chemistries and isotopic evolution? Or, instead, are we seeing the effects of lithologically variable mantle that is being sampled by a selective, component-solidus-dependent, melting process?
5. In addition to lithologic heterogeneity (peridotite, eclogite), are mantle components characterized by other variations in peridotite composition such as volatile-content that effect their partial melting behavior? Can such effects be distinguished from those of olivine-poor heterogeneities?
6. Do the scale-lengths of mantle heterogeneity have important observable effects on melting and basalt chemistry? How do melt-inclusion observations fit within our thoughts on the characteristic scale-lengths of local mantle heterogeneity?

► 5:00–8:00 Munk Lab Poster Session and Reception

Detailed Program Thursday 8 March

► 8:30–10:00 Hubbs Hall

Element Partitioning and Earth's Core Composition

Bernie Wood

Despite the uncertainties inherent in any estimate of core composition, the latter can, for many elements, be constrained by comparison of bulk silicate earth composition with those of carbonaceous chondrites. If we consider those elements, which are nonvolatile and siderophile and were hence separated into the metal during core formation then their concentrations in the core are readily derived from the difference between bulk earth (carbonaceous chondrite-based) and primitive upper mantle compositions. Thus we obtain, in the core, about 80% Fe, 5% Ni, 0.25% Co and so on. It has been known for a long time that core-mantle equilibrium at low pressures would produce a silicate earth too depleted in these and other siderophile elements. Recent experiments demonstrate that partitioning behavior is more consistent with high pressure core-mantle equilibration (25-30 GPa) plausibly at the base of a magma ocean. Volatile siderophile elements such as C and S are of uncertain abundance in the earth, but are important because of their potential contribution to the light element content of the core.

The low atomic number light element which constitutes, from density considerations, about 10% of core mass is most likely a mixture of Si, S, C and H. A combination of high-pressure experiments and cosmic abundances suggests around 2% S and <1% each of C and H. This leaves Si, which according to some estimates (based on the low Si/Mg ratio of the mantle) should constitute 7% of core mass. Si as the dominant light element is, however, only consistent with the high-pressure (25 GPa) core segregation model. At the low pressures (1-5GPa) favored in some core-formation scenarios, separation of an Fe-Ni-Si metal would also extract most of the V, Cr and Nb,. At high pressures, Si becomes much more siderophile and could form a significant part of the light element constituent without dramatically depleting the mantle in V and Cr.

Discussion Leader

Bill McDonough

1. What is the uncertainty of the amount of light element component in the outer core? Is it 10±4 wt% according to Brown et al (1994)?
2. Is the inner core an Fe-Ni alloy, or does it also contain a light element component such as carbide, phosphide, nitride, hydride?
3. Are “simple” single element solutions for the light element component in the outer core viable any longer? Is it S?
4. If the light element component in the outer core is a mixture, how’s this “core cocktail” concocted?
5. To what extent is there mass transfer across the CMB? Today? In the past?
6. We know where are the CMB and D” but what is the composition of the D” and what is the thickness and chemical gradient at the CMB?
7. If the D” layer is a zone of melt, then is there any evidence for this condition in our geological samples?

8. Are we required to conclude that inner core crystallization leads to an outer core with a radiogenic Os composition, or might the radiogenic Os isotopic signatures of some OIBs explained by other plausible processes?
9. The time at which core formation was completed (>99% metal extracted) is not well constrained (e.g., >3.6 Ga).
10. Core formation models involving low pressure conditions no longer appear viable for the Earth and thus, either pre-differentiated accreted planetismals were "re-equilibrated" with the whole earth, or accreted planetismals were NOT differentiated.

► 10:00–10:30 Coffee Break

► 10:30–12:00 Hubbs Hall

River Geochemistry: From the Continental to the Marine Point of View

Jerome Gaillardet; Bernard Dupré; Damien Lemarchand; Sylvain Levasseur, Pascale Louvat; Romain Millot; Claude Allègre

For several years, our group has focused on the sampling and geochemical investigation of rivers draining large portions of the continents as well as smaller rivers draining more simple geological areas. The techniques and methods developed earlier for the study of mantle geochemistry have been applied to these new samples. They include trace and major element analysis of all phases transported by rivers (sands, suspended and dissolved), isotopic tracing, data inversion and large-scale mass budgets. Here, two examples of significant results inferred from our river systematics are presented. The first one shows how river chemistry allows us to constrain carbonate and silicate weathering (and associated air CO_2 consumption) of the continents, the second one shows that refined riverine budgets of elements are a first and necessary step for understanding ocean chemistry and modeling their secular evolution.

Fluxes and control of silicate weathering

Isotopic and chemical natural tracers in river-dissolved load are interpretated as a mixing of rainwater and the dissolution products of the main lithologies present on the continents: carbonates, evaporites and silicates. It appears that the silicate box has to be divided into first cycle silicates and recycled silicates as shown by first order mass budgets between dissolved and solids riverborne products. Clearly, the continental crust submitted to chemical weathering do not have the conventional chemical composition of the upper continental crust and need to be completed by a silicate recycled component. Os isotopes may potentially be a tracer of part of the recycled continental crust. The inversion of large river chemistry data leads to the quantification of chemical weathering rates of the different reservoirs exposed to chemical weathering. It is particularly interesting to determine silicate weathering rates due to the net consumption of atmospheric CO_2 associated silicate weathering reactions and to find out the principal factors that control silicate weathering. From our large scale (big rivers) and small-scale (granitic and basaltic rivers) studies, we found that a coupling between mechanical erosion rates and chemical weathering rates exists at various scales showing that climatic parameters are not the over-riding parameters controlling silicate weathering.

Boron oceanic cycle

The largest rivers of the world have been sampled and analyzed for boron concentrations and isotopic composition. This is the first attempt to determine the boron flux from continent to ocean. The result is that the main oceanic input of boron to the ocean is the riverine input, making B a powerful tracer of continental weathering. In addition, the main oceanic output fluxes are associated to low temperature oceanic crust weathering, adsorption on sediments produced by mechanical erosion of the continents and precipitation of carbonates. A model has been developed to predict the secular evolution of Boron isotopes in the ocean, given that the secular evolution of oceanic crust production, mechanical erosion and precipitation of marine carbonates (an indirect function of continental chemical weathering) are reasonably known. Conversely to Sr isotopes, so far, there is no data showing the secular evolution of B isotopes in seawater. B isotopic ratio in carbonates has been measured by different authors, but is sensible to both marine pH and isotopic evolution of the ocean. However, keeping pH constant over the Cenozoic, our modeled curve follows the trend of increasing B isotopic ratios in carbonates.

References

[1] Gaillardet J., Dupré B., Louvat P. , Allègre C. J. (1999a) Global silicate weathering of silicates estimated from large river geochemistry. Chem. Geol., Special issue Carbon Cycle.7. 159, pp 3-30.

[2] Gaillardet J., Dupré B., Allegre C. J. (1999b) Geochemistry of large river suspended sediments: silicate weathering or crustal recycling ? Geochim. Cosmochim. Acta. Vol 63 (23/24), pp 4037-4051.

[3] Lemarchand D, Gaillardet, J., Lewin, E. and C. J. Allègre (2000) Boron isotopes river fluxes : limitation for seawater pH reconstruction over the last 100 Myr. Nature, de 2000, pp 951.

Discussion Leader

Lou Derry

1. The evolution of the upper continental crust is affected by interaction with the hydrologic cycle, which in turn effects the carbon cycle. Can we trace the history of crust-hydrosphere interactions by looking at the chemical and isotopic evolution of the upper crust? This history feeds back to the mantle via subduction of hydrated material, and generates elemental and isotopic ($\delta^{18}O$, etc.) anomalies. What is the evidence for temporal progression of these processes?
2. The only successful Earth system models are those built around the CO_2 climate-weathering feedback. Yet, although some evidence for a direct climate control on weathering rates exists, good evidence for lithological and tectonic controls also exist. How can we reconcile the need to have a stable Earth system over the long term with this "mixed bag" of controls on weathering rates, some of which are not obviously involved in a stabilizing feedback loop?
3. The sensitivity of boron isotope ratios to oceanic pH has generated substantial interest in the use of the $^{11}B/^{10}B$ ratio as a paleo pH indicator. What other evidence can be brought to bear on the problem of separating flux effects from pH effects on marine boron isotope signatures?

► 12:00–1:30 Catered Lunch at the Martin Johnson House T-29

► 1:30-3:00 Hubbs Hall

Mass Balances of Subduction

Tim Elliot

Subduction of sediment and altered ocean crust is a first order global flux and potentially a dominant control on mantle composition. Between subduction and deep recycling into the mantle lies the subduction zone. Subducted material may continue to depth unhindered, or maybe short-circuited and rapidly returned to the crust. Attempting to constrain an elemental mass balance at the subduction zone is therefore of prime importance in modeling the of Earth evolution.

As in many “GERMesque” calculations, there are major problems in obtaining a reliable estimate. A combination of good subduction inputs (full sediment stratigraphy and analyses, as well as an estimate of the composition of altered oceanic crust) together with fluid, volcanic front and back-arc compositions and volumes are required. There are few places where all such information is available. Maybe the best candidate is the Marianas, where reasonably comprehensive data is available on most of these components.

A mass-balance has been attempted for a number of the incompatible elements (that define the major differences between crust and mantle and likewise control long-lived radiogenic isotopic variation). It appears that a best estimate is that some 30-50% of the net subducted continental budget is returned to the surface at the Mariana arc. Importantly much of this flux is evident in the back arc (a factor of 2-4 times more important than the arc front). The ultimate fate of this material of back-arc crust is thus crucial- presumably it is also ultimately subducted.

Additional aspects of the calculation are the effects of the arc processing on the composition on the deep subducted material. Does it resemble any of the components in OIB frequently inferred to be recycled material? In terms of many highly incompatible ratios it is hard to reconcile the composition of the deep recycled material with components in OIB. Either additional reaction occurs at depth undetected or there is a large hidden reservoir (a slab graveyard) as proposed from other geochemical constraints.

Discussion Leader

Jim Gill

1. How important to the geochemistry of magmatic outputs (± 25% or ±100%) are spatial (along-strike and down-dip) and temporal variations in each of the three key subduction input parameters: the mantle wedge, sediment, and altered basaltic crust? If important, how should this be addressed by GERM?
2. What are the key factors affecting the composition of the subduction zone “mass transfer agents” (fluids or melts), what are representative values for these factors, and how well are they known? For example, factors may include partition coefficients, residual mineralogy, and fluid/melt fractions applicable to basalt dehydration or sediment melting, Are there consensus values?
3. What are the key subduction input and output processes that fractionate elements of importance to global geochemistry, and how well are they known? Examples may include separation of Hf from Lu during sediment subduction, Pb from U and Ce during slab dehydration, Nb from Th during slab melting, and rare gases from CO_2 during all of the above.

4. For any specific arc or globally; what is the relative value to geochemistry of single “representative analyses” (typical subducting sediment, altered crust, forearc fluid, volcanic front magma, rear-arc magma, backarc [spreading] magma) versus databases for the same?
5. OIB and IAB differ more than N-MORB. For OIB there is consensus about the geochemical (isotopic ± elemental) end-members. What are similar end members for arcs? For example, should one separate arcs clearly affected by: fluids mostly from altered crust; fluids from sediments; melts from altered crust (adakitic?); and melts from sediments? What are the most useful geochemical discriminants?
6. How different are volcanic and plutonic rocks in arcs geochemically, and what is the significance of the difference for crustal evolution? For example, are any plutonic rocks in non-collisional Cenozoic arcs demonstrably second-stage?
7. How does the composition of the crustal output of the Mariana (or other non-collisional) arc compare to Bulk Continental Crust, and what do the differences imply?
8. Subduction zones differ in geophysical as well as geochemical parameters. What are the strongest linkages between geophysical and geochemical differences? What if any key geophysical parameters about subduction zones are missing from GERM databases?

► 3:00–3:30 Coffee Break

► 3:30–5:00 Revelle Lab

Group Session 1: GERM Databases -- Part 2

Anthony Koppers; Hubert Staudigel

Continued from Part 1 …

► 3:30–5:00 Munk Lab

Group Session 2: Workshop on Electronic Publication -- Part 2

Al Hofmann

Electronic publishing and data storage are finally reality and are finding gradual acceptance by the scientific community. The worldwide web offers the possibility of unprecedented access to publications and data to the international scientific community. The initial cost of "going electronic" is high but is likely to drop in the future through technological improvements.

This brave new world raises many new questions

1. Who will get access to the electronic data and at what price?
2. Who guarantees permanence of record keeping?
3. Can publishers provide unlimited, free access to web-published papers after a period of grace (6 months to 2 years), which should protect the library market?
4. What role will copyright questions play in the future?
5. Will electronic publishing undermine the current peer review system?

6. What role will electronic “preprint servers” play?
7. How will the economics of the publishing enterprises (commercial publishers and professional societies) be affected?
8. Can web-based databases and data sources be linked through the internet?

► 3:30–5:00 Revelle Hall

Group Session 3: GERM Subduction-Zone Fluxes

Gray Bebout; Tim Elliott

Observations and Constraints

Reservoirs in simplified arc model

1. Depleted mantle
2. Subducting slab
3. Sediment section
4. Variably altered oceanic crust

Chemical reservoir characterizations

1. Depleted mantle (mantle peridotite and xenolith suites - how informative?)
2. Sediment Section (GLOSS a good start, and SubFac driving acquisition of core from outboard of two focus arcs; DSDP/ODP database)
3. AOC (heterogeneous but some constraints; composites integrating heterogeneity)

Physical / thermal characterizations

1. Geophysical observations
2. Thermal models constrained by geophysical observations

Tangible fluxes

1. What goes in (relatively well known sediment and AOC subduction rates)
2. Trench-to-subarc (diagenetic/metamorphic pathway; fragmentary information)
    a. studies of paleoaccretionary complexes representing <50km
    b. investigation of trace elements and volatiles in eclogitic suites
    c. representing 50-120 km (problem with exhumation overprinting)
    d. extremely limited experimental constraints on element partitioning
3. Slab-to-mantle (inferred via geochemical studies of arc lavas)
    a. mismatch of empirical and experimental partitioning data
    b. fluid metasomatizing agent(s) not well characterized
4. Mantle wedge-to-crust/surface (arc lava production rates; a problem central to mass-balance efforts)
5. Mantle/crust-to-atmosphere (global estimates exist based on volcanic gases; estimates underway for individual arc-trench systems)

THEME 1: Toward true mass-balance (mass in vs. mass out)

On what to concentrate? Remembering that vast majority of mass subducted enters the deep mantle (small amounts of material removed from slab and added to subarc mantle, whereas most of overall arc -mass- is from the mantle wedge)

1. selected trace element and isotopic tracers
2. volatile components (H, C, N, etc.)
3. others?

Factors/parameters in physical model

1. slab+sediment sampled by individual volcanoes (how to begin calculating?) (how to define slab sectors sampled by spaced volcanoes)
2. role/effect of structural heterogeneity in subducting oceanic crust (e.g., transform faults, seamounts)
3. forearc modifications (some components), estimated "fluid compositions" and any constraint on the amount of "fluid" added to wedges
4. how to estimate arc production rates?
5. allied tracer studies, including along-arc and across-arc investigation (identify forcing functions)
6. characterizing the "fluids" from sediment and AOC - combination of experiments, further arc study, calculations using available partitioning data, and work on metamorphic suites

What have we done (been doing) thus far?

Discussions at previous meetings (GERM workshops, SubFac planning meetings)

1. simple conceptual model (three stages, see below)
2. identification of key reservoirs (see above)
3. decision to concentrate efforts on 8 arc-trench systems showing desirable range in physical and chemical characteristics:
    a. Izu-Bonin-Marianas (SubFac Focus Experiment)
    b. Central America (SubFac Focus Experiment)
    c. Tonga
    d. Aleutians
    e. Cascadia
    f. Banda
    g. Lesser Antilles
    h. South Andes
4. **PLAN** - provide "clearing house" for particularly illuminating databases and synthesis or theoretical papers (linked to from G^3, and elsewhere?) and ultimately, produce straw-man mass-balance for each system, pointing to missing information and previously unrecognized fluxes?
5. further web page development would result in production of individual pages for each of the 8 systems, each linked to additional resources for the respective systems (Centam and IBM linked to MARGINS)

Conceptual Model (Idealized Ocean-Ocean Convergent Margin)

Subduction Zone Input

1. Pore Fluids
2. Seafloor Sediment (see GLOSS; Global Subducted Sediment estimates).
3. Altered Oceanic Crust (see GERM web page with estimates of AOC compositions).

Stage I (Forearc Processes)

Compaction-related dewatering of sediment; forearc prograde mineral devolatilization reactions in sediment and oceanic crust. These processes favor the liberation of aqueous fluids which can then be delivered to the seafloor along structural heterogeneities or into the forearc mantle wedge, the latter potentially resulting in hydration and production of serpentinite seamounts. Forearc accretion and erosion processes will also be considered.

Stage II (Subarc Processes)

Magma production at the main volcanic arc, resulting from delivery of slab+sediment chemical components to mantle wedge, in addition to AFC processes in the arc crust. Contributions to crustal growth and atmosphere (the latter through volcanic degassing).

Stage III (Backarc Processes)

Magma production during back-arc rifting

Deep Subduction Zone Output

Deeply Recycled Material

THEME 2 - What can/should GERM do?

Invited synthesis papers aimed at reservoirs and pathways deemed critical

1. **GOAL** let's propose some papers and some authors to solicit, taking ideas from those at the breakout session (and considering geophysical constraints)
2. possible special sessions at upcoming meetings (Fall AGU, etc.)
3. in particular, solicit some arc-specific mass-balance attempts (to test the sensitivities, qualities of constraints, etc.)

How to encourage databases, in part connected with MARGINS/SubFac(?)

1. **GOAL** nuts and bolts (what do we want and from whom?)
2. GEOROC + SubFac/MARGINS databases (linked to)

What else to do?

1. how else to improve the GERM web pages related to subduction? What material, other than geochemical data, should be accessed on our pages?
2. promote (like MARGINS) a set of goals that could help assist planning of studies directed at specific problems (what is required to undertake subduction-zone mass-balance)
3. to what extent focus on non-arc studies (forearc fluids, metamorphic studies) (certainly include volcanic gases added to atmosphere and work on appropriate peridotite and xenolith suites with potential information regarding processes in mantle wedge)
4. possible addition of Sangihe (Indonesia) to our 8 focus arc-trench systems (Japanese studies planned)
5. other ideas?

► 3:30–5:00 Board Room

Group Session 4: River Fluxes

Lou Derry; Jerome Gaillardet

Despite significant advances in measuring fluxes of solutes and sediments to the oceans; substantial work remains to be done. While river fluxes for most elements are now known to first order, the controls on the fluxes of many of the elements remain poorly understood. Data are available for the fluxes of major elements from most major rivers, thus a "first generation" database already exists (although it could certainly use improvement).

Understanding the geological and climate controls on river fluxes is a more complex issue, and the data to address those questions are not systematically available. Development of a second-generation integrated river database may help. Such a database could include information on both dissolved and suspended load fluxes, seasonal variability, and isotopic compositions. Further, river basins are spatially heterogeneous. Geology, soils, climate, vegetation and land use vary widely across catchments and these variations directly impact fluxes. At present, data on these "boundary conditions" are either unavailable or not in any single location. Future database development may include information on both present fluxes and other attributes of river basins.

In this session, we hope to encourage the audience to help define the types of data that should be archived and how they should be archived. We hope to convince GERM participants to contribute to these databases by writing of papers that contribute to the GERM database. Such papers may include research articles, reviews, characterizations, or data briefs.

► 5:00–8:00 Munk Lab Poster Session and Reception

Detailed Program Friday 9 March

► 8:30–10:00 Hubbs Hall

Material fluxes to the ocean through coastal aquifers

Billy Moore

Continental margins are exceedingly complex regions. Here short-term interactions of tides, waves, storms and river outflow combine with longer term changes in sea level, topography, sediment supply, and land use to produce one of the most dynamic regions of the planet. Recently we have learned that changes in groundwater flow and interactions of seawater with coastal aquifers produce a complex subterranean system that delivers a heretofore-unrecognized supply of nutrients, trace metals, and carbon to coastal waters. This paper outlines our strategy to address the supply of materials to the coastal ocean through the subsurface advection of these unique fluids. Our studies have been conducted in salt marshes, along the inner shelf, and at deeper sites on the continental shelf. Most of this work has been along the southeastern coast of the US.

The fate of dissolved material delivered to the coastal ocean depends on its reactivity and the rate at which it is mixed offshore. To assess the supply of materials by subsurface fluids, we select tracers that have high concentrations in the fluids relative to surface waters and low reactivity in the coastal ocean. Our first task is to determine the residence time of coastal waters relative to exchange with the open ocean. Here we employ two short-lived radium isotopes, ^{223}Ra ($t_{1/2}$ = 11.4 days) and ^{224}Ra ($t_{1/2}$ = 3.6 days) to measure cross-shelf exchange. These tracers are introduced to coastal waters by groundwater input and desorption from sediments. The offshore tracer distributions are related to the exchange time of coastal waters through the decay of the Ra isotopes; faster exchange carries the tracer signal further offshore. Along the coast of South Carolina, shore-perpendicular profiles of ^{223}Ra and ^{224}Ra in surface waters show consistent trends which may be modeled as eddy diffusion coefficients of 300 to 900 m^2s^{-1}. For materials released near the coast, the exchange rates allow an estimate of how quickly the impact will be diluted and dispersed.

Coupling the exchange rate with offshore concentration gradients yields estimates of offshore fluxes of dissolved materials. For systems in steady state, the offshore fluxes must be balanced by new inputs from rivers, groundwater, sewers or other sources. Two tracers that show promise in evaluating subsurface fluid advection are barium and ^{226}Ra ($t_{1/2}$ = 1600 years). These tracers have relatively high concentrations in the fluids and low-reactivity in the coastal ocean. Applying the eddy diffusion coefficients to the offshore gradient of ^{226}Ra concentration provides an estimate of the offshore flux of ^{226}Ra. Measuring the concentrations of ^{226}Ra in subsurface fluids provides an estimate of the fluid flux necessary to provide the ^{226}Ra. Measuring other components of the fluids (nutrients, metals, carbon) provides an estimate of the fluxes of these materials from the subterranean system.

Discussion Leader

Art Spivack

1. The radiotracer transport model is appropriate for systems with low Peclet number (vL/D). How can importance of aquifer fluxes be estimated for other regions?
2. Are estimated groundwater fluxes based on this model consistent with hydrologic models derived from groundwater recharge estimates or Darcy law fluxes?
3. Is there an adequate understanding of what controls mixing and recirculation of salinized water? Is the notion of a "subterranean estuary" consistent with conventional physical hydrologic models?
4. Are coastal aquifer chemical fluxes significant to global budgets or are they dominantly of regional (coastal) impact? What elements or compounds (e.g., nutrients) are most likely important?

► 10:00–10:30 Coffee Break

► 10:30–12:00 Hubbs Hall

D/H Constraints on Mantle-Ocean Hydrogen Fluxes

Dan Schrag

Measurements of deuterium in deep sea pore fluids reveal a decrease in δD with depth at most locations. Numerical modeling shows that in most cases the patterns cannot be explained by preservation of paleo-seawater at depth in the sediment with a much lower δD value than today. The formation of smectite in basalt or ash layers is a major control on Ca, Mg and oxygen isotope profiles, but the influence on deuterium profiles would be minor and result in an increase rather than a decrease in δD with depth. The pore fluid profiles are best explained by a flux of deuterium from the base of the sediments into the underlying oceanic crust and upper mantle. This flux may be explained by the diffusion of low δD water into the pore fluids from the oxidation of mantle hydrogen and methane, and has implications for the global hydrogen budget.

Discussion Leader

Jeff Severinghaus

1. Large upward fluxes of methane are implied by the deuterium measurements in pore fluids, because a substantial addition of metabolic water from methane and/or hydrogen oxidation is required in order to make the observed isotopic imprint on the large reservoir of water in marine sediments. What is the oxidant (or electron acceptor) for this methane/hydrogen oxidation? Is there a sufficient supply of this oxidant, and can its depletion be observed, perhaps in the form of an anomalous profile?
2. Is this methane thought to be thermogenic or biogenic? What effect does the answer to this question have on the calculated flux, due to the differing isotopic character of these two sources?
3. How is it known that the methane and/or hydrogen is mantle-derived? Why not just get it from deeper anoxic sediments?
4. Has anyone tried extracting these gases directly from pore fluids in anoxic regions deeper down, and has their isotopic composition been measured?

5. Would this large methane flux have implications for the formation of methane hydrates in marine sediments?
6. More broadly, what is the current interpretation of deep-sea oxygen isotope records over glacial timescales in terms of temperature versus ice volume?
7. What caused the glacial-to-interglacial rise in atmospheric CO_2, observed rather consistently over the last four glacial cycles in the Vostok ice core, from 190 ppm to 280 ppm? Recent data indicate a lag of CO_2 behind central Antarctic temperature of a thousand years or so. How does this lag constrain the possible answers?
8. Is iron fertilization by atmospheric dust supplied to the southern ocean a viable candidate for the glacial CO_2 change?
9. When did atmospheric molecular oxygen accumulate, and what controls its concentration on geologic time scales?
10. Did the oceans freeze over in a runaway albedo-feedback catastrophe in the Neoproterozoic (~600 Ma), the "Snowball Earth", and what does the study of this question tell us about how the Earth system operates?

► 12:00–1:30 Catered Lunch at the Martin Johnson House T-29

► 1:30–3:00 Hubbs Hall

Does Tomography say Anything about Geochemistry?

Guy Masters

We review the structure of the mantle as determined by seismic tomography. The basic features are now well-known: in the lower mantle, the structure is characterized by large regions of slow seismic velocity (very slow in shear) beneath the central Pacific and Africa surrounded by belts of slab-like fast material. The slow regions appear to be commonly underlain by ultra-low velocity zones right at the core-mantle boundary. There is large-amplitude, long-wavelength structure near the surface and near the core-mantle boundary characteristic of boundary layers. Importantly, there is no large-amplitude long-wavelength structure near the 660km discontinuity and this is no longer considered (by seismologists) as a major barrier to convection. We discuss in detail, the evidence for and against decorrelation of structure across the 660km discontinuity.

Recently, deeper layering of the mantle has been proposed to reconcile some geochemical observations with the geophysical ones. We review in detail the evidence for and against such a layer and find that seismological evidence is lacking though scenarios can be devised where such a layer can be made virtually invisible to seismology (the "stealth" layer).

Finally, we consider how the tomographic maps can be quantitatively interpreted in terms of composition and temperature. This is the province of mineral physics and many of the needed parameters remain unmeasured for lower mantle constituents. However, reasonable guesses can be made and some reasonably secure inferences can be made -- in particular, it seems clear that seismic anomalies near the base of the mantle can not be due to sub-solidus thermal effects alone. Partial melting or chemical changes are needs with the latter being currently preferred because of the lack of attenuation anomalies observed in the deep mantle.

Discussion Leader

Al Hofmann

Food for discussion

1. Relationship between:
    a. Seismic velocity and major-element chemistry
    b. Seismic velocity and trace elements (= heat production, U, Th, K)
2. Correlations of geophysical and geochemical mapping of mantle heterogeneities
    a. ocean-wide scale
    b. hotspot-scale (plume-asthenosphere interaction)
    c. internal heterogeneities of plumes
3. Melting in the deep mantle (ultralow velocities)
4. Reservoir questions:
    a. Chemical boundary at 660 km?
    b. Deep mantle primitive reservoirs?

► 3:00–3:30 Coffee Break

► 3:30–5:00 Hubbs Hall

GERM - Quo Vadis

Hubert Staudigel; Bill McDonough; Lou Derry; Al Hofmann; Henry Shaw

► 6:00 Conference Dinner at the Head of Tecolote Canyon

Poster Abstracts
Listing in alphabetical order

Bulk Earth composition from refractory/refractory and volatile/refractory ratios
Anderson, D L

An alternative and complementary approach to bulk Earth composition is to form refractory/refractory and volatile/refractory ratios of as many terrestrial materials as deemed necessary (MORB, continental crust{CC}, ultramafic rocks{UMR}, island arc basalts{IAB}, sediments{SED}, etc. and a Q-component e.g. AOB, kimberlite) and use the refractory ratios in a generalized inverse with target ratios (e.g. CO,CI,CM,E,cosmic, solar etc.) to solve for mixing ratios. This is the approach used in Theory of the Earth. The mixing ratios then give the volatile/refractory ratios (which are not used in the inversion) and information about missing elements and hidden reservoirs. Primitive mantle then consists of CC, MORB, SED, UMR, etc. in the proportions dictated to give "cosmic" refractory ratios. The "missing" elements are related to various mass-balance paradoxes such as the Pb-paradox, the helium and Hf-paradoxes, the Th-enigma, the Nb/U etc paradoxes and so on. These identify possible errors in estimates of components or identify inaccessible "reservoirs" {aurevoirs} and 'problem' elements (Nb,Ta,W, U, Pb). This is a generalization of the 'pyrolite' approach (PM= basalt + UMR) and Allegre's approach (PM+ CC+DM) and does not involve the need to pick a few components or assign characteristics to mantle subdivisions (e.g. upper mantle = DM). For example, the MORB component need not be preassigned but all the MORB data can be put in. The sizes of the various DM reservoirs are output. In the original work Ander's estimates of PM were among the target ratios tested. Now, Allegre's PM can also be used as target ratios in order to identify missing elements and the aurevoirs of the paradoxes. If least-squares derived mixing ratios of essentially all terrestrial components do not satisfy some of the comologically based refractory ratios, then we have learned something about elements that might be sequestered in the core or in hidden reservoirs.

Plate Tectonics as a Far-From-Equilibrium Self-Organized System
Anderson, D L

A fluid heated from below becomes a far-from-equilibrium self-organized system as the temperature is raised, i.e. it goes from a quasi-stable conductive system to a well organized set of convection cells (Prigogine). A self-organized system in the Prigogine sense occurs when there is an open system with a large steady supply of energy. Nothing organizes the system- there is no template or tuning- it organizes itself. In standard models of mantle dynamics and geochemistry it is usually assumed that the mantle controls the plates (via convection, hotlines, massive overturns, megaplumes and so on) but when continents and plates are placed on top of the system, they become the organizing agent for mantle flow. A convecting system cooled from above is driven by the descent of the cold boundary layer; there are no active upwellings. The mantle is passive. It can no longer organize itself. But the plates satisfy the requirements for a self-organized system. The energy source is the gravity and heat from the mantle but the buoyancy and dissipative forces are in the plate-slab system, not in the mantle. Mantle convection with a stress-free boundary and no plate tectonics is driven by buoyancy and viscous dissipation internal to the fluid. This is quite different from plate tectonics. It is now known that the lithosphere controls the cooling rate of the mantle and that the self-governing viscosity feedback of Tozer is pre-empted by dissipation in the outer shell (Conrad, Hager, Christianson). Dissipation includes continent-continent collision, transform fault resistance, slab bending and the toroidal component of plate tectonics. Such a system will episodically reorganize to minimize dissipation. Global plate reorganizations are the result. These involve new plates, new volcanic chains and mountain belts, new plate boundaries, and a different pattern. Driving forces can only change gradually but dissipative forces can change rapidly and are instantly communicated throughout the system and different self-organization results. It is no coincidence that the Pacific hemisphere completely reorganized as the Pangea hemisphere broke apart. This was a plate tectonic catastrophe, not a mantle overturn. The system is sensitive to small fluctuations in stress, just as Rayleigh-Benard convection is sensitive to small fluctuations in temperature. The plates are not only a self-organizing system but they organize the mantle flow, as has been shown by numerous simulations (Gurnis, Pekeris, Lowman, Jarvis, Elder, Gable, Hager, O'Connell). The plates not only drive the "plate-scale" flow (G. Davies) but inhomogeneities in the plates (lithospheric architecture, continents, corners, edges, slots, rifts) drive small-scale convection, increasing magma delivery rates at these places (King, Mutter, Keen, Korenaga). Plates drive themselves and also generate the stresses that can break them and therefore they control the locations of volcanic chains. Convection-plate simulations to date have not revealed this self-organization tendency because plate configurations, velocities and interactions are prescribed by the modeler, not by the system. The plume hypothesis, to a large extent, is based on 2D simulations, free boundary or prescribed plate boundary conditions, Boussinesq assumptions (no pressure dependence of coefficient of thermal expansion etc.), rigid plates and so on. When mineral physics is taken into account (even of Birch 1952 vintage), plus realistic boundary conditions (internal heating, self-organized plates, 3D, continents on top, lithospheric architecture) the mantle and the plates behave in a completely different way than assumed in The Standard Model of mantle geodynamics and geochemistry. The deep boundary layers do not have the features attributed to them in plume cartoons. Only recently have geodynamic models included the effect of pressure, plates and internal heating. These show, along with first principles (Birch, 1952) that any lower thermal boundary layer is thick and instabilities are sluggish. There is a 3 to 4 order of magnitude decrease in the local Rayleigh number between the top and bottom of the mantle, precluding narrow thermal instabilities (Tackley). Lower TBL instabilities are broad, consistent with tomography, and long-lived. The P dependence of alpha means the mantle can be, and should be, irreversibly stratified .The geophysical data is most consistent with a chemical boundary below 1000 km, perhaps a deeper one as well. The data is geoid, topography, decorrelations, slab modeling and quantative analysis of tomographic models. The recent assertions that the mantle operates in the whole mantle convection mode are based on Boussinesq and heated from below simulations, ideal shear coupling, radioactive-rich deeper layers, and selected tomographic cross-sections. Most papers against layered convection treat only the 650 km discontinuity (a known phase change), not the general problem of chemical stratification . It is relevant that most of the authors of the recent whole-mantle-convection flap are now pushing layered convection, but they still accept the geochemical assertion that geochemists have samples of the lower mantle ,or "primordial undegassed" mantle". But the chemically distinct layers, or phase change boundaries, do not define the geochemical reservoirs. Mass balance shows that all the geochemical components can be stored in the shallow mantle. Whether the inhomogeneity is plume pudding, marble cake, or layers (perisphere) is still debatable but the assumption that the lower mantle is sampled by volcanoes is just an assumption and leads to the numerous well-know geochemical paradoxes, and asserted discrepancies between geophysics (tomography, modeling, geoid) and geochemistry. Geochemical signatures are inherited from the shallow Earth (crust, sediments, lithosphere, perisphere, mantle wedge, fracture zones). Cross-disciplinary communication has been hampered by seismologists claiming whole mantle convection based on a few color-saturated cross-sections, by geochemists asserting that low-^{3}He samples are really high-^{3}He samples because they have "high" ^{3}He/^{4}He ratios and that all seismological subdivisions are geochemical reservoirs, and by modelers putting in unphysical boundary conditions. Assumptions should not be mistaken for data but this can easily happen across the cross-disciplinary barrier.

Toward Constraining Metamorphic Chemical Fluxes in Convergent Margins

Bebout, G E

Any comprehensive model of subduction-zone chemical cycling would logically need to consider the potential significance of forearc (and deeper) metamorphic processes in altering the chemical composition of deeply subducting sedimentary and oceanic crustal rocks (e.g., affecting global budgets of volatiles, including the global CO_2 cycle; trace element contents in arc lavas). However, such processes have yet to be adequately incorporated into models of convergent margin chemical cycling. This is despite the demonstration that profound alteration in trace element and isotopic composition can in some cases accompany even the initial fluid-rock interactions at depths <1 km in forearcs. In studies of suites representing somewhat deeper subduction (5-50km), it has been demonstrated that devolatilization can (depending on thermal history) result in significant further fluid-rock fractionation that one would expect to observe in arc lavas from margins with differing thermal structure.

For suites for which it is not possible to investigate chemical change over a range in grade (and in similar lithologies), studies are plagued by lack of constraints on protolith composition. Simple comparison with lithologies on the modern seafloor is problematic as, for many chemical systems, the range of seafloor compositions and heterogeneity has not been adequately demonstrated. Experimental studies should ideally be reconciled with the record of devolatilization and trace element distribution in subduction-zone metamorphic suites. Many of the experiments are conducted at pressures and temperatures higher than those appropriate for “normal” modern forearc metamorphism, but are useful for considering subarc and beyond-arc fractionations and estimating compositions of slab-derived “fluids” entering the mantle wedge. Other fluid-rock experiments investigating shallower, lower-T alteration appear to have been conducted at unrealistically high fluid: rock ratios relative to those believed to prevail in most natural fluid-rock settings.

Some conclusions based on our recent work on Pacific paleo-accretionary suites (Catalina Schist, Franciscan Complex, Western Baja Terrane), all of which contain units representing a range in metamorphic grade in similar, mostly sedimentary, lithologies:

1) In relatively cool subduction zones (those in which subducting rocks near the slab-mantle interface are at lawsonite-blueschist-facies conditions at 1.0 GPa), despite loss of large amounts of pore fluid (up to >50 vol. %) and significant other devolatilization involving structurally bound components (mostly loss of H_2O and CO_2 , the latter in carbonate cement), metasedimentary rocks can be subducted to depths approaching 50 km without noticeable trace element loss (even for more fluid-mobile elements such as B, Cs, As, and Sb; data for suites other than the Catalina Schist from Sadofsky, 2000, Ph.D. dissertation).
2) Subducting rocks metamorphosed along somewhat higher-T prograde paths (those in which subducting rocks near the slab-mantle interface are at epidote-blueschist-facies conditions at

1.0GPa) experience differential, but significant, disturbance of trace element and stable isotope compositions (Bebout et al., 1999; see EBS on **Fig. 1**), exhibiting the greatest loss for As and Sb (relative to B, Cs, and N). Rocks subducted along the higher-T paths (epidote-amphibolite-andamphibolite-facies conditions at 1.0 GPa) show large shift in trace element and stable isotope compositions as a result of devolatilization (Bebout et al., 1999, EPSL; see EA and A on **Fig. 1**). Ion microprobe study of HP metasedimentary rocks in the Catalina Schist demonstrates systematic mineralogical residency and, for elements showing evidence of whole-rock loss, parallel decreases in those elements in their respective mineral hosts (e.g., B and Cs in white-mica).

3) Shallow subduction-zone metamorphic, even seafloor diagenetic, effects must be considered in any comparisons of seafloor lithologies with similar lithologies in paleosubduction suites. We have, for example, noted considerable shift, with depth, in whole-sediment $\delta 15N_{air}$ in the ODP Site 1149 sediment section from high values in the shallow section (higher than those observed in paleosubduction suites) to lower values at depths that approach those of the whole-rock Nisotope compositions of subduction suite metasedimentary rocks. Similarly, B isotope compositions of low-grade subduction-zone metasedimentary rocks point to selective loss, during shallow subduction, of more loosely adsorbed, isotopically heavier B.

It appears that, in cooler subduction zones (see 1 above), much of the inventory of the volatile components (other than pore fluids) is preserved in subducting sedimentary rocks to depths of at least 50 km. This inventory would presumably be available at greater depths to contribute to cross-arc chemical trends demonstrated for some convergent margins, and the study of metamorphic suites representing subduction to greater depths (>50 km) is thus desirable. Our early work on UP to UHP suites in the Italian Alps (Schistes Lustres, Lago di Cignana) indicates that, for these more deeply subducted rocks (which experienced varying degrees of mineralogical and chemical overprinting during exhumation), and particularly for the metasedimentary rocks, whole-rock investigations are likely to yield less useful or incorrect) results. Microanalytical work is necessary in order to separate the chemical alteration attributable to the prograde (subduction-related) and exhumation-related (collisional) histories. In some rocks, meaningful analytical results can be obtained for only the several particulary "robust" phases

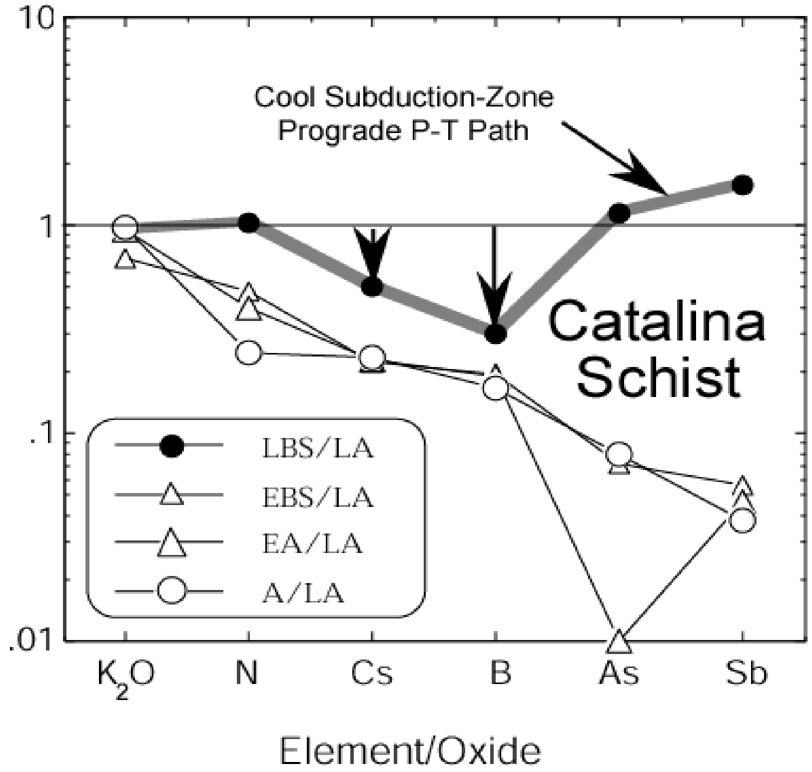


Figure 1. Plot of mean element concentrations in lawsonite-blueschist (LBS), epidote-blueschist(EBS), epidote-amphibolite (EA), and amphibolite (A) facies metasedimentary rocks normalized to the concentrations of the same components in lawsonite-albite (LA) facies metasedimentary rocks (all in the Catalina Schist). These comparisons show apparent varying susceptibilities of the components to depletion during metamorphism along increasingly higher-T prograde P-T paths (see schematic paths on Fig. 2 on next page). The data for the lawsonite-albitefacies metasedimentary rocks (peak metamorphism at <300°C at P < 0.5 GPa) are used here as a proxy for seafloor sediment, as the LA rocks strongly overlap with seafloor sediment compositions. Note that the comparison of the LBS to the LA metasedimentary rocks (broaderline) indicates possible preferential depletion of Cs and B relative to K2 O, N, As, and Sb along a relatively low-T prograde metamorphic path (from Bebout et al., 1999; EPSL).

surviving the later overprinting (e.g.,garnet, dolomite, tourmaline, apatite at Lago di Cignana) and for mineral inclusions contained within these phases. Tourmaline B isotope (ion microprobe) and major element data show potential for providing detailed records of prograde (and exhumation-related) B redistribution in these deeply subducted rocks (Bebout and Nakamura, abstract for EUG meeting, April, 2001).

It would be desirable to establish flux efficiencies for individual volatile components through subduction-zone metamorphism, or at least, to provide estimates of relative efficiency of deep subduction. This pursuit is hampered by many uncertainties related to the heterogeneity of both the

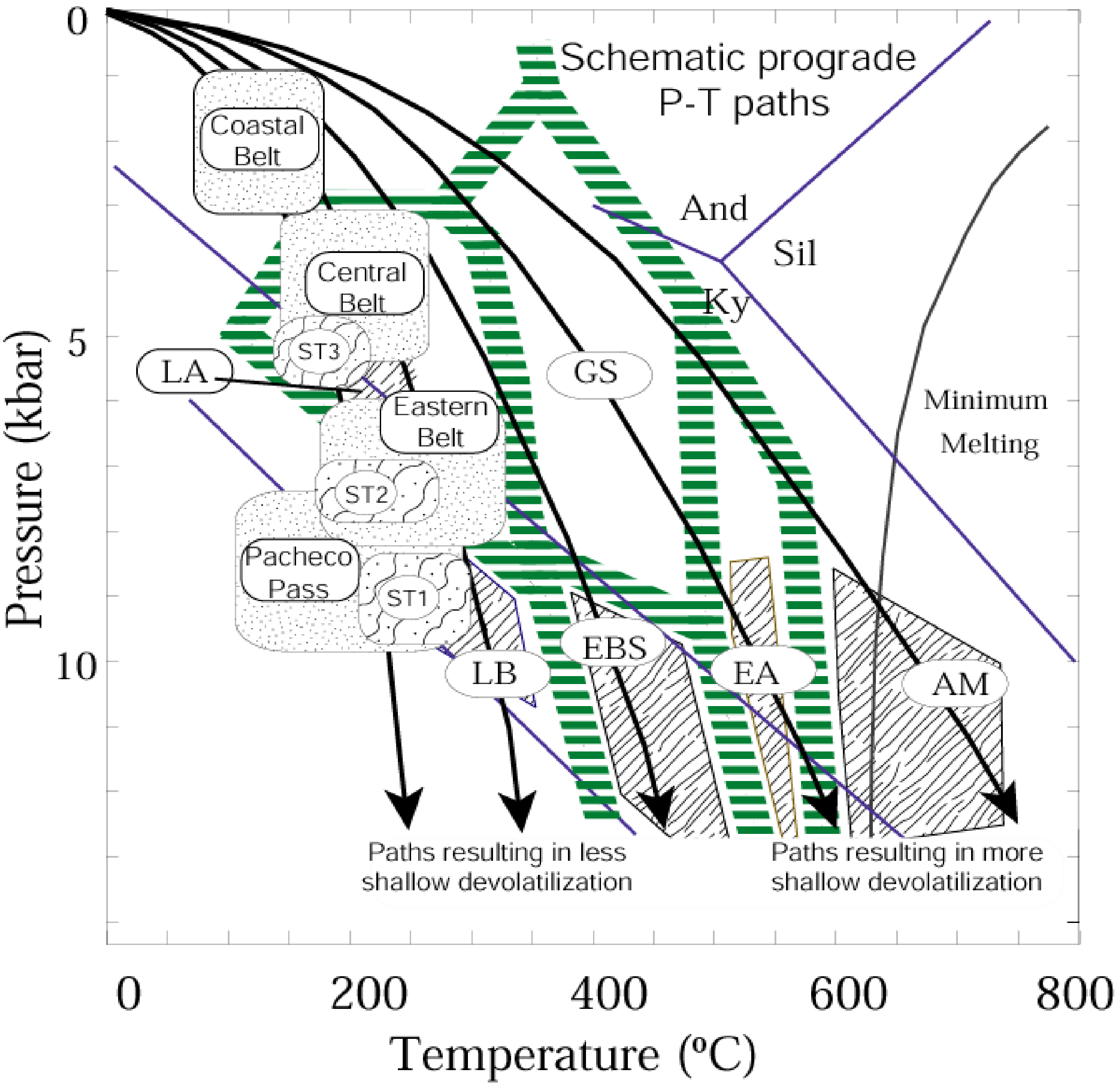


Figure 2. Pressure-temperature diagram showing estimates of peak metamorphic recrystallization of each of the Franciscan units (Coastal, Central, and Eastern Belts in the Coastal Ranges; Pacheco Pass area in the Diablo Range; all in California), the subterranes of the Western Baja Terrane (ST1, ST2, and ST3, exposed on Cedros Island, Baja California), and the units of the Catalina Schist (exposed on Santa Catalina Island, California; LA, LBS, EBS, EA, and A). Adapted from a figure in Grove and Bebout (1993; Tectonics).

incoming section and the metamorphic products, and also by the obscuring effects of exhumation-related overprinting in most paleosubduction suites (particularly the UHP suites). Still, such estimates could be combined with information regarding the incoming element budget and compared with the outputs in the corresponding arcs (or globally), perhaps providing insight regarding the overall subduction cycle of the elements. As an example, incorporating sediment flux and compositions from GLOSS, CO_2 content in altered oceanic crust, and estimates of organic C contents of subducting sediments, and considering recently published estimates of global C flux from subduction zones, one arrives at an estimated 40 ± 15 % return of subducted C via arcs on a global basis. The remainder of the subducted C is presumably either returned to the oceans and other forearc reservoirs, or enters the deeper mantle. Hopefully, focused study on individual well-studied margins (i.e., the MARGINS Subduction Factory approach in Central America and the IBM system) will result in improved mass-balance for individual components. In addition, and somewhat more easily, trace element and isotopic fractionations related to subduction-zone metamorphism (identified through study of paleosubduction suites) can be identified and further compared with the geochemical record in arc lavas and other mantle-derived materials.

The Distribution of Niobium, Uranium, Cerium, and Lead in the Earth and its Constraint on the Mass of the Depleted Mantle and Solar Nebula Temperature.

Calderwood, A R

Previous studies have demonstrated that Nb/U and Ce/Pb ratios for both mid-ocean ridge basalts (MORBs) and ocean-island basalts (OIBs) are globally uniform. These values differ from Nb/U and Ce/Pb ratios inferred for both the primitive mantle and the continental crust, and this difference has been exploited in a prior study (Hofmann et al., 1986) using a simple two reservoir mass balance model to estimate the mass of the present day depleted mantle. They concluded that only ~50% of the whole mantle had been depleted by the extraction of the continental crust from the primitive mantle, a result which is in conflict with results from recent mineral physics models, high resolution, seismic tomography models, and updated Sm-Nd crust-mantle evolution models. These other studies are in agreement that to first order, the whole mantle is uniform in both major and trace element composition, with mantle flow extending from the surface to the core-mantle boundary. The resolution of the discrepancy between mass balance models involving Nb/U and Ce/Pb ratios and these other studies is the focus here.

First, updated estimates for the concentrations of Nb, U, Ce, and Pb in the major reservoirs of the Earth (continental crust, lithosphere, depleted mantle, and core) are used to construct a new elemental mass balance model for these elements in the Earth. The model satisfies the twin constraints that accepted concentrations and ratios are adopted for the various reservoirs and that the calculated Bulk Earth must sum to values consistent with C1 chondrite values. From the resultant model, updated concentrations for the Nb, U, Ce, and Pb concentrations in the primitive mantle (PM), equivalent to the Bulk Silicate Earth, are derived. For lead, the Primitive Mantle and core concentrations are independently checked by calculating these concentrations using an experimental high temperature (2,585 C) and pressure (6 GPa) experimental partition coefficient. For an initial C1 chondritic Pb concentration of 2,471 ppb, the partition coefficient predicts Primitive mantle and core concentrations of 72 ppb and 7.46 ppm, respectively, compared with 108 ppb and 7.39 ppm from the mass balance model. Interpolating between higher pressure partitioning experiments and the 6 GPa one indicates that equilibrium fractionation of Pb between a magma ocean and molten metal at ~10 GPa would exactly match the mass balance derived Primitive mantle and core concentrations. Nevertheless, the difference in predicted core lead concentrations is only ~1% for the 6 GPa partition experiment and supports the assumption that the Earth accreted with the full C1 chondritic lead abundance and that the majority of primordial lead was sequestered into the core during core formation.

Second, the new primitive mantle values, together with the latest values for the Nb/U and Ce/Pb ratios for oceanic basalts and the U and Pb concentrations in the continental crust are used to revisit the estimate of the mass of the present day depleted mantle. Contrary to previous work, the oceanic Nb/U and Ce/Pb ratios are consistent with the whole mantle being depleted by the extraction of the continental crust from a primitive mantle. Numerical experiments show this conclusion is not sensitive to the preferred primitive mantle concentrations adopted here. Therefore, when the latest values for both concentrations and ratios are adopted, there is no discrepancy between estimates of the mass of the depleted mantle derived from the present day Nb/U and Ce/Pb ratios for oceanic basalts and the latest results from independent mineral physics, seismological, and isotope geochemical studies.

The conclusion that the Earth contains the full C1 chondritic abundance of Pb indicates that the global temperature in solar nebula, at ~1 AU heliocentric distance from the Sun, was below 519 K, the 50% condensation temperature of lead. This low temperature refutes conventional wisdom that the solar nebular at 1 AU was globally hot, with an ambient temperature above ~1,200 K, a temperature hot enough to completely vaporize potassium silicates. In contrast, it is concluded here that the Earth should have accreted with the full C1 chondritic abundance of so-called moderately depleted elements (e.g. K, Na, Rb, Cs, S, I) since all these elements possess 50% condensation temperatures in excess of lead. This finding will effect geochemical models for the composition of the Earth's core.

Geothermal fluxes of solutes, heat, and carbon to Himalayan rivers

Evans, M J; Derry, L A; France-Lanord, C; Anderson, S P

Rapid uplift and erosion of the Himalaya have brought hot rocks to the near surface, where interaction with surface-derived water produces hot springs (Craw, 1990; Galy and France-Lanord, 1999; Grabczak and Kotarba, 1985). This geothermal activity is common along the Himalayan front and near the Main Central Thrust shear zone, with numerous hot springs, or "tatopanis", found in the deeply-incised river valleys (Bhattarai, 1980; Kotarba et al., 1982). The location of the hot springs suggests a significant tectonic control on the advection of heat and fluid circulation. The fluids deliver heat and solutes to the surface with measured temperatures up to 70°C and TDS up to 7000 mg/L (Bhattarai, 1980; Evans et al., 2000; Galy and France-Lanord, 1999; Grabczak and Kotarba, 1985).

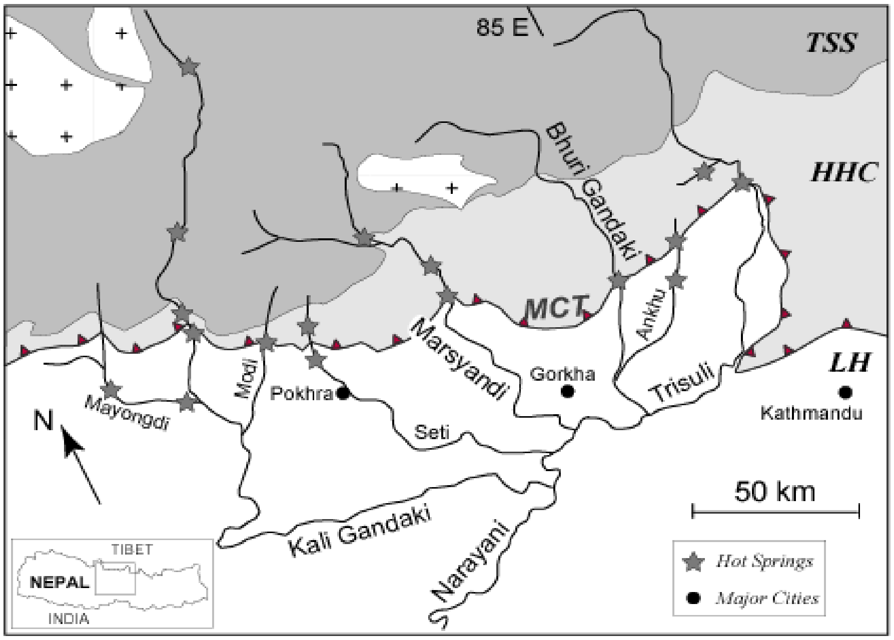


Figure 1. Locations of hot springs (stars) within the Narayani River drainage of central Nepal. Locations from Kotarba (1985), Galy et al. (1999), Evans et al. (2000), Bhattarai (1973), and Copeland (1991).

We have carried out a detailed study of the Marsyandi River of central Nepal (basin area 4800 km^2) and its hydrothermal system. In addition we have sampled a number of streams and hot springs in the Narayani River basin (basin area 35,000 km^2), the major drainage of the central Nepal Himalaya (Figure 1) and a major tributary to the Ganges. These data show that the fluxes of solutes, heat, and carbon dioxide carried by Himalayan hot springs are very likely significant for Himalayan river chemistry and their strontium isotopic budgets, for thermal models of the Himalayan orogen, and for the long term carbon cycle.

In the Marsyandi, stream chemistry is clearly affected as the river flows through the zone of hot spring activity beginning just above the STD detachment and continuing through the HHC. Spring inputs drive anomalies in Cl^- , Na^+ , K^+ , Sr^{++} concentrations and $^{87}Sr/^{86}Sr$ ratios in the Marsyandi main stem (Figure 2). Concentrations of these elements in the river rise in a region where the tributary streams are all more dilute than the main stem, and remain high downstream until the confluence with the Trisuli. Two springs contribute most substantially to the river anomalies, and both are located near the MCT shear zone. These springs have up to 58,000 µM Cl^-, 10,000 µM K^+ and 115 µM Sr^{++}, with $^{87}Sr/^{86}Sr \approx 0.77$, and are supersaturated with respect to calcium carbonate and quartz. A problem in the Sr mass balance for Sr in Himalayan rivers is “excess” Sr or high Sr/Ca ratios, with 1000Sr/Ca often 3-4 (molar), significantly higher than known bedrock ratios (1000Sr/Ca ≈ 0.5 - 2) (English et al., 2000; Galy et al., 1999). Marsyandi hot spring fluids have 1000Sr/Ca from 7 to 16 and hydrothermal input can therefore help explain why some Himalayan rivers have anomalously high Sr/Ca ratios relative to their source rocks, although other processes such as dissolution-precipitation cycles must contribute as well.

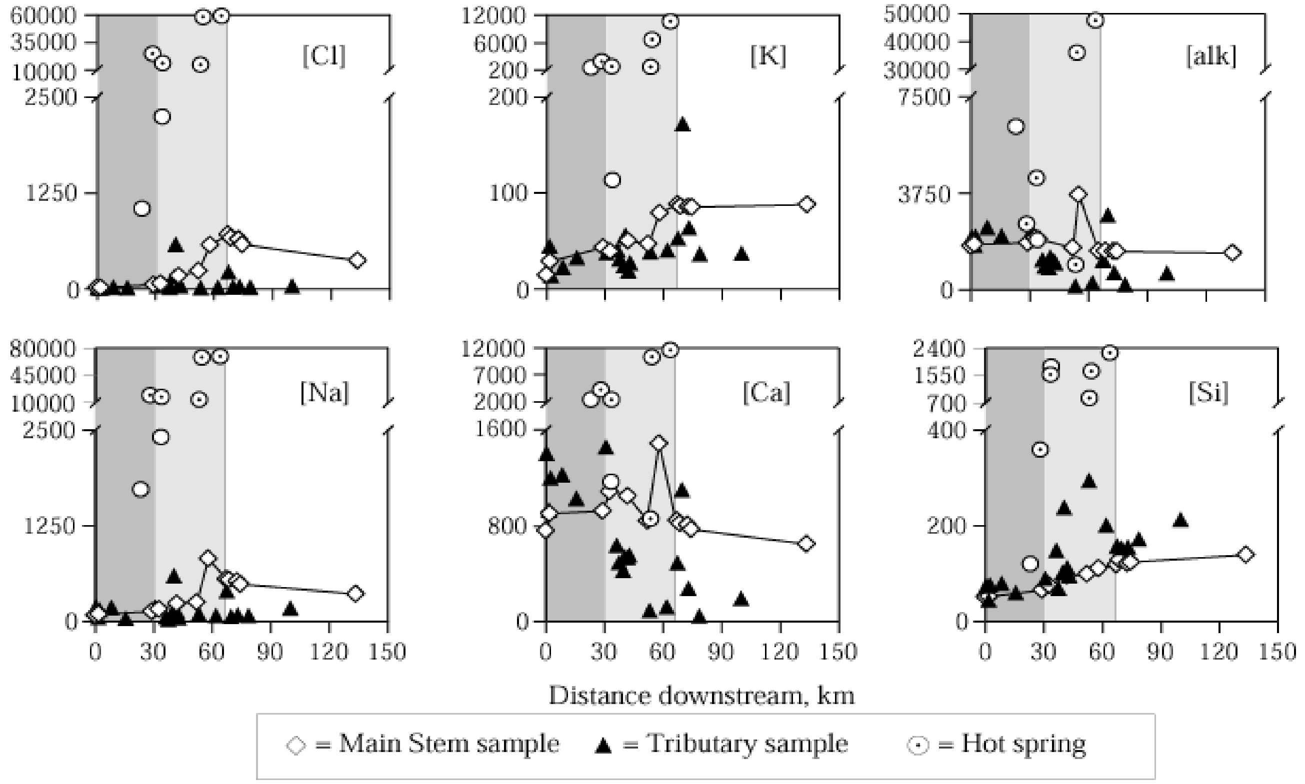


Figure 2. Concentrations in micromoles/kg for the Marsyandi river. Note key is different from Figure 1 and scale break on all vertical axes to accommodate high concentrations in hot spring waters. Shading corresponds to map units in Figure 1. K, Na and Cl are particularly anomalous in the hot springs and clearly affect the main stem chemistry down to its confluence with the Trisuli.

Hydrothermal Fluid Flux

Given the conservative nature of Cl^- in the Marsyandi, we can estimate a hydrothermal fluid flux with a Cl^- mass balance. Using tributary and spring Cl^- concentrations as well as discharge at the mouth of the Marsyandi, we calculate a hydrothermal fluid flux of 1-2 m^3/s, or ca. 1% of the total Marsyandi discharge. This fluid flux translates to a hot spring contribution of ca. 90% of the Cl^-, and 20-30% of the K^+ and Sr^{++} to the Marsyandi.

The Cl^- based fluid flux estimate is feasible in the Marsyandi because the effect of the high [Cl^-] springs is more "visible" here than other streams of central Nepal. Ge/Si ratios, however, should provide a consistent method for fluid flux estimation in all the central Nepal rivers. The thermal springs yield Ge/Si ratios from 4 to 650 µmol/mol. These values are comparable to or higher than those reported from both ocean floor vents (Ge/Si ≈ 8 to 23 mmol/mol) and hot springs and wells from Iceland (Ge/Si ≈ 9 to 150 mmol/mol) (Arnorsson, 1984; Mortlock et al., 1993). Ge/Si values in the main streams range from 1.5 to 5 µmol/mol, much higher than other non-polluted world rivers (Ge/Si <1.5 mmol/mol) (Mortlock and Froelich, 1987) while tributaries have Ge/Si ratios of 0.2 to 1.2 µmol/mol, as expected from low weathering intensity environments. The extreme enrichment of Ge over Si in the hydrothermal fluids may reflect simple Rayleigh fractionation associated with precipitation of low Ge/Si quartz as fluids cool. Regardless of the cause, the wide disparity in stream vs. hydrothermal values makes Ge/Si a valuable tracer of hydrothermal inputs. When applied to the Marsyandi, the Ge/Si mass balance gives a hydrothermal fluid flux of 0.6 m^3s^{-1}, comparable to the Cl^- estimate above.

Heat Flow and CO_2 Fluxes

We use the end member water flux estimate derived from the chemical mass balance to estimate convective heat loss in the Marsyandi basin. For a conservative 50°C temperature drop, the hydrothermal water flux estimate of 0.6 - 1.0 m^3/s yields a thermal power output rate of 100-200 MW, comparable with geothermal fields in the Taupo Volcanic Zone in New Zealand (Seward and Kerrick, 1996). When distributed over the HHC, the estimated hydrothermal heat flow is 80 to 160 mW/m^2. This compares to continental heat flow values (~40-90 mW/m^2) (Turcotte and Schubert, 1982) and hydrothermal heat loss of 20-35 mW/m^2 calculated for the geothermal belt across most of Tibet (Hochstein and Regenauer-Lieb, 1998) and reflects the advection of hot rocks to the surface along the MCT zone.

Many of the hot springs in our study area are characterized by positive $\delta^{13}C_{DIC}$ suggesting a metamorphic source of CO_2 to the system (Craig, 1967; Evans et al., 2000; Friedman and O'Neil, 1977; Galy and France-Lanord, 1999; Shieh and Taylor, 1969). We can obtain a *minimum* estimate of the metamorphic CO_2 flux in the Marsyandi by assuming that the carbon present in the in the spring fluids as alkalinity represents a mixture of metamorphic C with $\delta^{13}C \approx +10‰$ and locally derived groundwater C with $\delta^{13}C \approx -6‰$, estimated from nearby tributaries. Taking the observed maximum spring value in the Marsyandi of $\delta^{13}C = +5.9‰$ and using the water flux obtained above, we estimate a metamorphic CO_2-derived alkalinity flux in the Marsyandi system of 5.6×10^8 mol/yr. For comparison, CO_2 fluxes from individual geothermal centers in the Taupo zone range from 0.5 to 14×10^8 mol/yr (Seward and Kerrick, 1996).

References

Arnorsson, S., 1984, Germanium in Icelandic geothermal systems: Geochimica et Cosmochimica Acta, v. 48, p. 2489-2502.

Bhattarai, D.R., 1980, Some geothermal springs of Nepal: Tectonophysics, v. 62, p. 7-11.

Craig, H., 1967, the isotopic geochemistry of water and carbon in geothermal areas, *in* Spoleto, ed., Nuclear Geology in Geothermal Areas: Pisa, Laboratorio di geologia nucleare, p. 17-53.

Craw, D., 1990, Fluid evolution during uplift of the Annapurna Himal, central Nepal.: Lithos, v. 24, p. 137-150.

English, N.B., Quade, J., and DeCelles, P.G., 2000, Geologic control of Sr and major element chemistry in Himalayan rivers, Nepal: Geochimica et CosmochimicaActa, v. 64, p. 2549-2566.

Evans, M.J., Derry, L.A., Anderson, S.P., and France-Lanord, C., 2000, A hydrothermal source of radiogenic Sr to Himalayan rivers: Geology, in submission.

Friedman, I., and O'Neil, J.R., 1977, Compilation of stable isotope fractionation factors of geochemical interest, *in* Fleischer, M., ed., Data of geochemistry, Volume 440- KK, United States Geological Survey, p. 1-114.

Galy, A., and France-Lanord, C., 1999, Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget: Chemical Geology, v. 159, p. 31-60.

Galy, A., France-Lanord, C., and Derry, L.A., 1999, The strontium isotopic budget of Himalayan Rivers in Nepal and Bangladesh: Geochimica Et Cosmochimica Acta, v. 63, p. 1905-1925.

Grabczak, J., and Kotarba, M., 1985, Isotopic composition of the thermal waters in the central part of the Nepal Himalayas: Geothermics, v. 14, p. 567-575.

Hochstein, M.P., and Regenauer-Lieb, K., 1998, Heat generation associated with collision of two plates: the Himalayan geothermal belt: Journal of Volcanology and Geothermal Research, v. 83, p. 75-92.

Kotarba, M., Sokolowski, A., and Bogacz, W., 1982, Hydrogeological investigation in the Kali Gandaki thermal springs area (Nepal Himalayas).: Bulletin de L'Academie Polonaise des Sciences. Serie des Sciences de la Terre, v. 29, p. 283-291.

Mortlock, R.A., and Froelich, P.N., 1987, Continental weathering of germanium: Ge/Si in the global river discharge: Geochimica et Cosmochimica Acta, v. 51, p. 2075- 2082.

Mortlock, R.A., Froelich, P.N., Feely, R.A., Massoth, G.J., Butterfield, D.A., and Lupton, J.E., 1993, Silica and germanium in Pacific Ocean hydrothermal vents and plumes: , v. 119, p. 365-378.

Seward, T.M., and Kerrick, D.M., 1996, Hydrothermal CO_2 emission from the Taupo Volcanic Zone, New Zealand: Earth and Planetary Science Letters, v. 139, p. 105- 113.

Shieh, Y.N., and Taylor, H.P., 1969, Oxygen and carbon isotope studies of contact metamorphism of carbonate rocks: Journal of Petrology, v. 10, p. 307-331.

Turcotte, D.L., and Schubert, G., 1982, Geodynamics. Applications of Continuum Physics to Geological Problems.: New York, John Wiley & Sons.

The Slippery Slope of Tectonochemical Signatures: Post-subduction Adakitic rocks in Baja California

Forsythe, L

It is tempting in many cases to link a particular chemical signature of a rock with a particular set of tectonic conditions in the hopes of providing a new or better key to unlock the past. Certainly the well-known ‘negative high field strength element (HFSE) anomaly' in subduction related magmatism seems to work well in this sense; at least if it is observed, one may infer the rock was formed in a subduction environment while it's absence is not proof of a non-subducting environment. On the other hand, it is important to remember that the chemistry of a magma and of the rock it produces ultimately derives from the components (sources) and conditions (temperature, pressure) present during formation and evolution of this magma. And although these may often be similar for various tectonic settings, they are not necessarily the same and may not have been the same throughout geologic time.

An example of the necessity of caution when applying tectonic interpretations to magma chemistry can be seen in Cenozoic volcanic rocks from Baja California. These volcanics have many characteristics of adakites, or magma derived in part from melting of subducted basaltic lithosphere. These characteristics include the negative HFSE anomaly mentioned above as well as positive Sr anomalies on multi-element diagrams (Fig. 1), low Y and Yb, high Sr/Y ratios (Fig. 2), and low $^{87}Sr/^{86}Sr$ isotopic ratios. These characteristics are not present in all arcs and it is believed that subduction of oceanic crust younger than 25 Ma with its accompanying higher heat flow is a requisite for slab melt production.

Yet although it is clear that active subduction off-shore Baja California did involve very young crust, many Baja rocks with these characteristics have ages that post-date the best estimates of the end of subduction (no later than 12 m.y.a.). The most probable explanation for the continuation of this effect is the initiation of rifting along the arc-axis with accompanying increase in the thermal gradient in the presence of remnant subducted slab. In this case a rifting tectonic environment provides similar conditions and sources to a subduction environment, which results in rocks of similar composition.

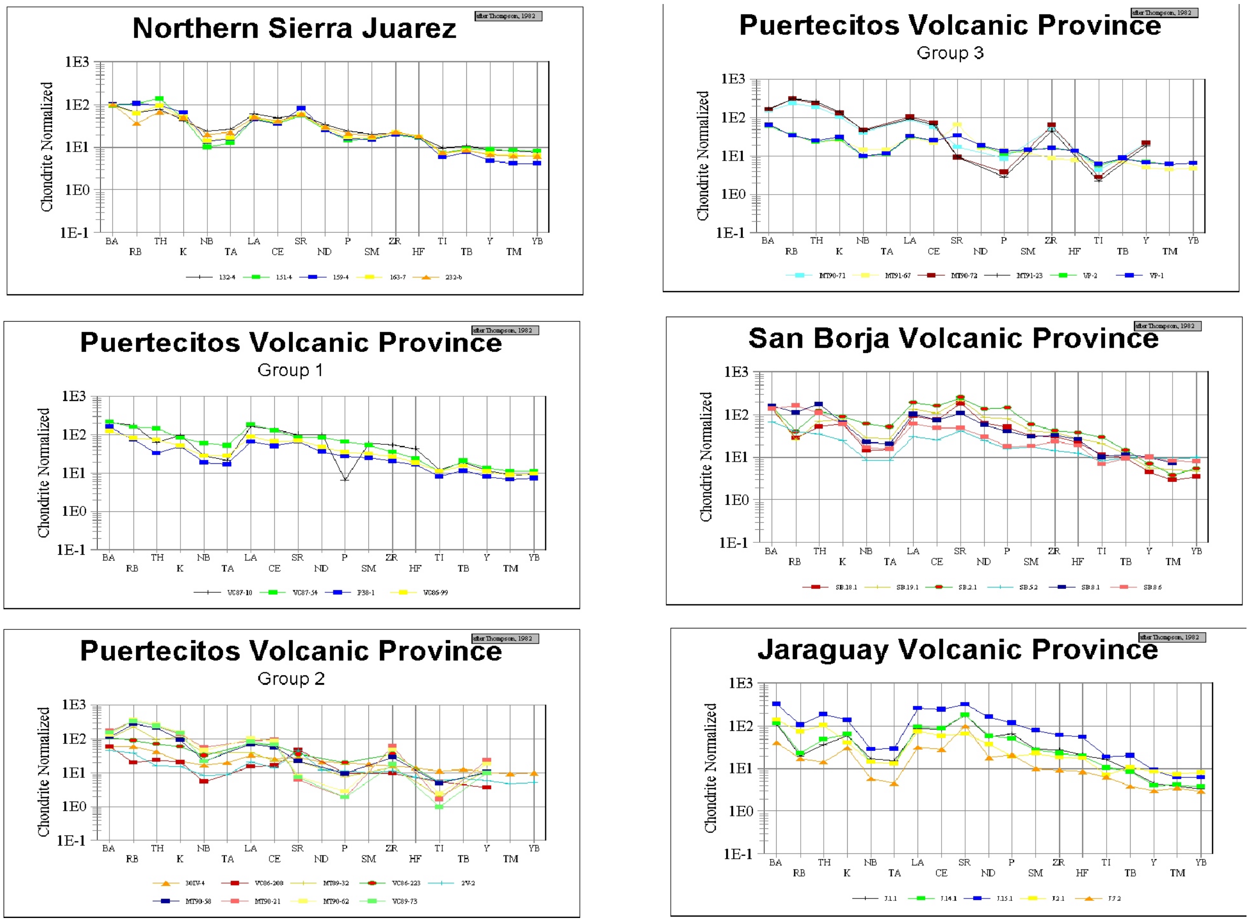


Figure 1. Multi-element, chondrite-normalized diagrams for Cenozoic volcanic rocks from Baja California with less than 65% SiO_2. Areas are lettered in approximate order from north to south (a=northernmost). The three Puertecitos groups are primarily based on age and stratigraphic relationships with 1 being the oldest (>15 Ma), 2 being around 6 Ma, and 3 being around 3 Ma.

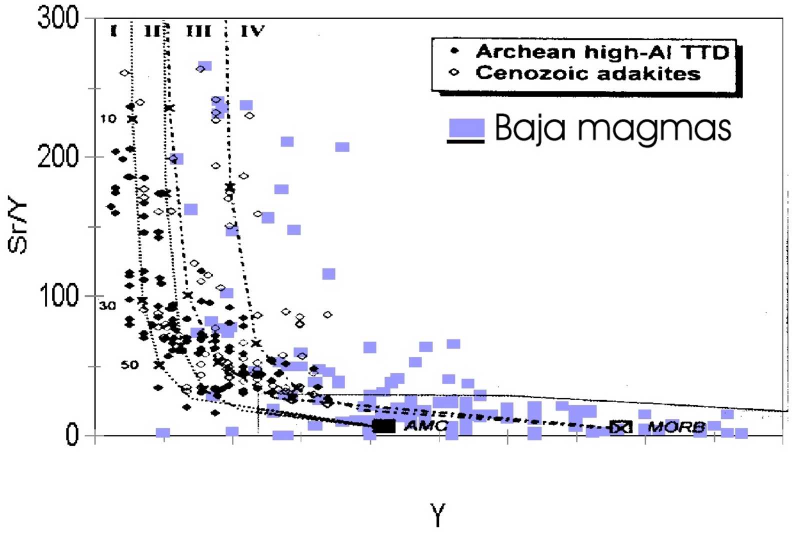


Figure 2. Sr/Y vs. Y for volcanic rocks from Baja California (top) compared to compilation of Drummond et al., 1996, Trans. Royal Soc. Edinburgh 87:205-215, fig. 4 (bottom). Baja rocks containing less than 20 ppm Y and with Sr/Y ratios more than 50 range in age from 16 Ma to 0.9 Ma. (Not all rocks shown have been dated radiometrically.)

Spatial Statistics of Isotopic Variations Along Mid-Ocean Ridges

Graham, D W; Spera, F J

How isotopic variations in basalts erupted at the Earth's surface are linked to convective mixing in the underlying mantle is a central problem in geodynamics. The range of variations in basalts from mid-ocean ridges (MORB) and ocean islands (OIB) are known to depend on mixing rates in the underlying mantle [1]. However, the size, shape and distribution of chemical and isotopic heterogeneities (clumps) within the Earth's mantle, and their evolution through geological time, still remain poorly quantified. Large amplitude heterogeneities occur at both short and long distances, ranging from the width of pyroxenite veins (<1 m) in orogenic peridotites [2] to global scales ($>10^4$km) such as the Dupal anomaly [3]. There is also evidence that scales of isotopic heterogeneity vary regionally [4].

The objective of this study is to quantify the length scale(s) of upper mantle heterogeneity through spatial statistical analyses of MORB. We have begun by defining the "scale of segregation" (L) determined from the spatial self-correlation for ^{3}He/^{4}He, ^{87}Sr/^{86}Sr, ^{143}Nd/^{144}Nd and ^{206,207,208}Pb/^{204}Pb in "zero age" lavas sampled along the globe-encircling mid -ocean ridge system. Our working hypothesis is that small scale convective patterns in the upper mantle play a significant role in dispersion of the isotopic tracers and other trace elements. Differences in L between the respective ocean basins may then be quantitatively related to unsteadiness of small-scale mantle convection, due to thickening of the oceanic lithosphere, plume impingement, and lateral temperature differences between continental and oceanic lithosphere.

The correlation coefficient R is calculated between every pair of points at separation distancer. For each point pair, R(r) is given by the ensemble average of the product of the deviations in isotope composition from the population mean, normalized to the population variance [5]. The total number of point pairs (N) for n samples is given by N=n (n-1)/2. As an example, for the global data set of Sr and He isotopes (n=1238 and 576, respectively) the number of point pairs is well in excess of 10^5 (765703 and 165600, respectively). A value of R (r) close to 1 indicates that, at a given location, an isotope ratio above (or below) the population average is likely to be associated with an above (or below) average value at a distance r away. A value of R(r) close to zero implies a random relationship, and a value close to -1 implies an anti-relationship. R(r) approaches unity at small r because points close together are from the same ‘clump’ of mantle. The value of r at which R first goes to zero is denoted as r*. On a diagram of R(r) vs. r (the correlogram), the integral of R(r) from r=0 to r=r* is the scale of segregation L, and is related to the size of a ‘clump’. Within the Earth’s interior, such clumps may vary in size and shape and their boundaries may be diffuse. Lithosphere recycling at subduction zones and plume input from the lower mantle or transition zone are two ways by which such clumps are introduced to the upper mantle. We use the L concept because it is a quantitative estimate of size which is precisely definable from spatially referenced geochemical data.

Only a narrow range of L values is found within each ocean basin (Figs. 1 & 2). In general, the isotope tracers give L values between 350-750 km for the North Atlantic, South Atlantic. and Indian Oceans. For the Pacific Ocean, L appears to be significantly less, between 100-180 km, indicating that mantle 'clumps' in this region are smaller, in agreement with inferences based on a standard (non-spatial) statistical approach [4].

Our results provide good evidence that dispersion of isotopic anomalies in the upper mantle is primarily controlled by small-scale convection. On a geological time scale, mantle flow is certainly unsteady. Small-scale convective cells, having their long axes aligned sub parallel to the plate scale flow, are one simple manifestation of this unsteadiness. In Rayleigh-Bénard convection, the amplitude and frequency of cellular wobble controls the extent of lateral mass transport (dispersion) between convective cells [6]. Based on the spatial self-correlation of isotopic tracers, this dispersion appears to be more efficient in the Pacific upper mantle than elsewhere.

References

[1] Allègre C. J. and Lewin E. (1995) Isotopic systems and stirring times of the earth's mantle. Earth Planet. Sci. Lett. 136, 629-646.

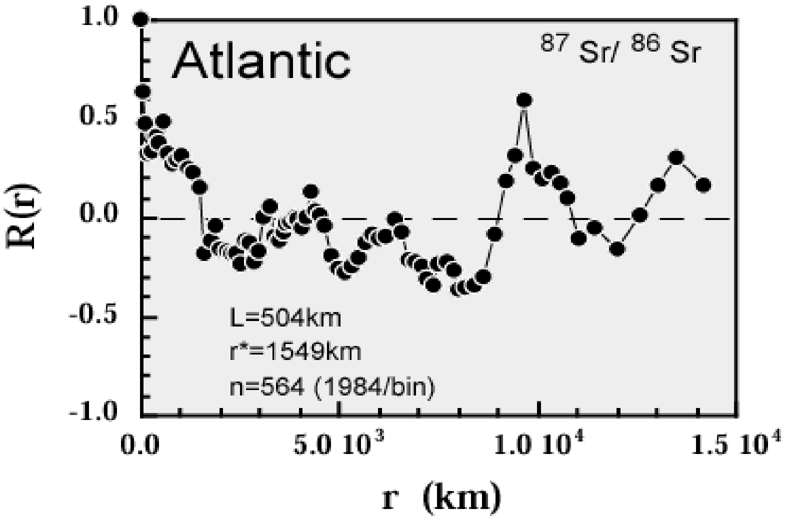
[2] Polvé M. and Allègre C. J. (1980) Orogenic lherzolite complexes studied by ^{87}Rb- ^{87}Sr: a clue to understand the mantle convection processes. Earth Planet. Sci. Lett. 51, 71-93.

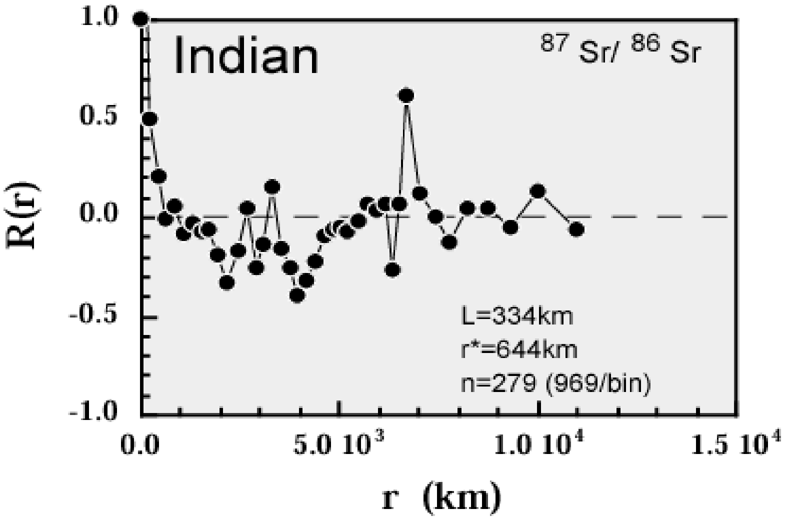
[3] Hart S. R. (1984) A large-scale isotope anomaly in the Southern Hemisphere mantle. Nature 309, 753-757.

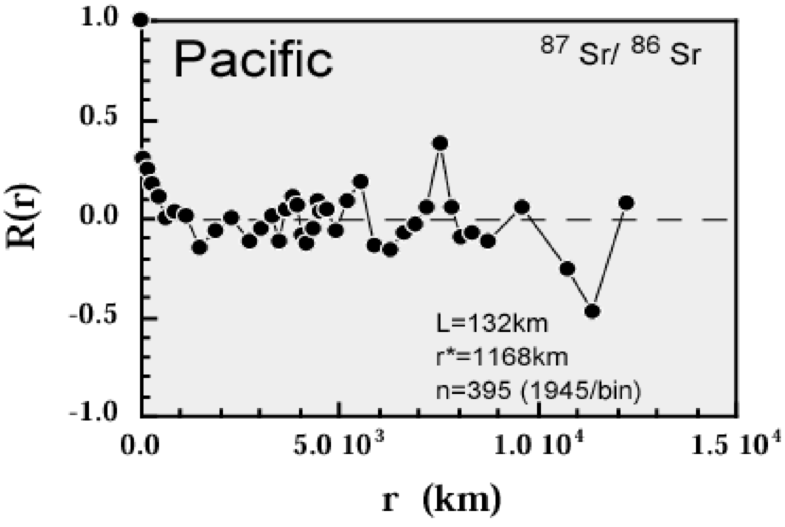
[4] Allègre C. J., Hamelin B., and Dupré B. (1984) Statistical analysis of isotopic ratios in MORB: the mantle blob cluster model and the convective regime of the mantle. Earth Planet. Sci. Lett. 71, 71-84.

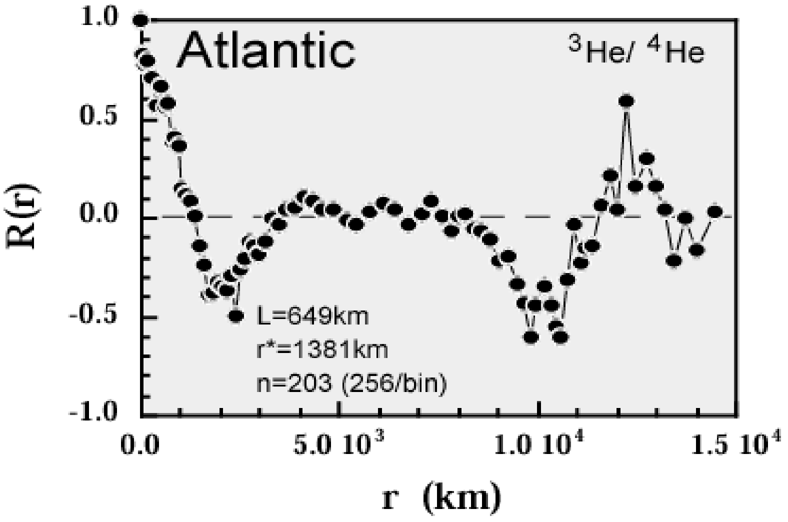
[5] Danckwerts P. V. (1952) The definition and measurement of some characteristics of mixtures. Appl. Sci. Res. 3, 279-296.

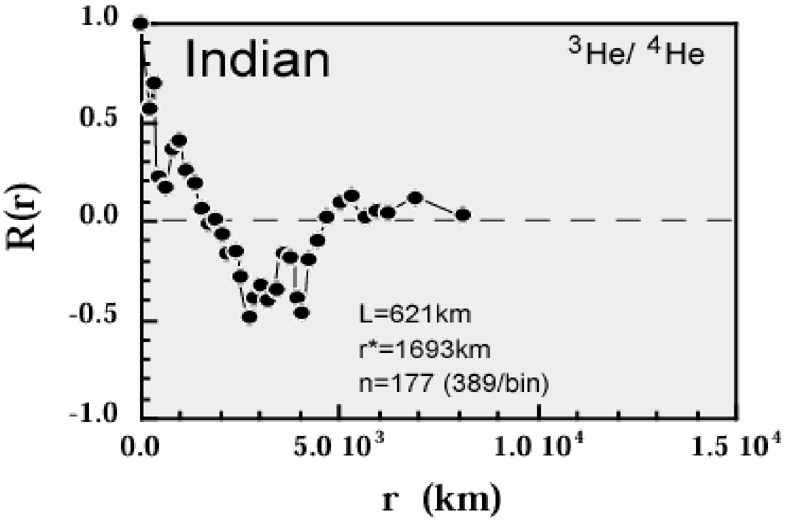
[5] Camassa R. and Wiggins S. (1991) Transport of a passive tracer in time-dependent Rayleigh-Bénard convection. Physica D 51, 472-481.

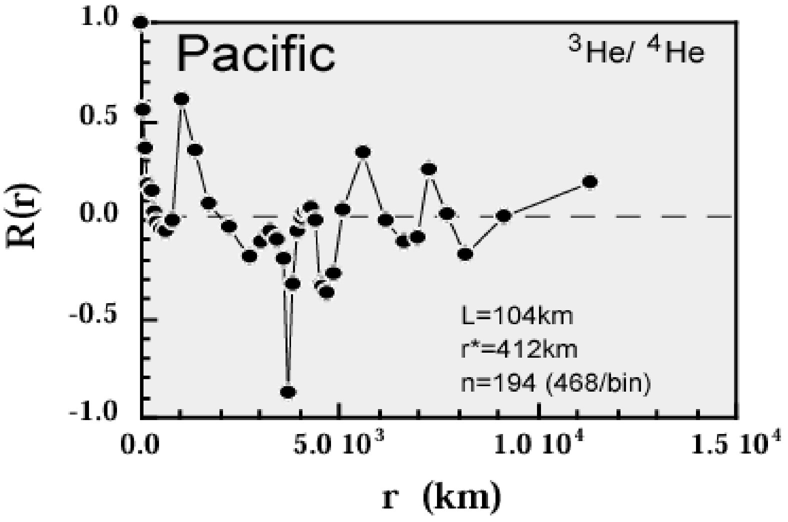

Atlantic
87 Sr/ 86 Sr
R(r)
1.0
0.5
0.0
-0.5
-1.0
L=504km
r*=1549km
n=564 (1984/bin)
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)


Indian
87 Sr/ 86 Sr
R(r)
1.0
0.5
0.0
-0.5
-1.0
L=334km
r*=644km
n=279 (969/bin)
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)


Pacific
87 Sr/ 86 Sr
R(r)
1.0
0.5
0.0
-0.5
-1.0
L=132km
r*=1168km
n=395 (1945/bin)
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)


Atlantic
^{3}He/ ^{4}He
L=649km
r*=1381km
n=203 (256/bin)
R(r)
1.0
0.5
0.0
-0.5
-1.0
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)


Indian
^{3}He/ ^{4}He
L=621km
r*=1693km
n=177 (389/bin)
R(r)
1.0
0.5
0.0
-0.5
-1.0
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)


Pacific
^{3}He/ ^{4}He
L=104km
r*=412km
n=194 (468/bin)
R(r)
1.0
0.5
0.0
-0.5
-1.0
0.0
5.0 10^3
1.0 10^4
1.5 10^4
r (km)

Hafnium and Lead isotopes from Australian-Antarctic Discordance MORB

Hanan, B; Pyle, D G; Blichert-Toft, J; Christie, D M; Albarède, F

The Australian-Antarctic Discordance (AAD), one of the deepest sections of the global MOR spreading system, is the location of a sharp boundary between Indian-type and Pacific-type upper mantle provinces (Klein et al, 1988). The Indian-Pacific mantle boundary, defined by Sr, Nd and Pb isotopes, is abrupt and has migrated westward within the last 3-4 Myr, across the easternmost segment (B5)of the AAD (Pyle et al.,1992). The deep axial depth of the AAD reflects cold underlying mantle, low melt supply and thin oceanic crust that produces a chaotic sea-floor topography. Coincident with migration of the isotopic boundary is the displacement of chaotic seafloor by normal, ridge-parallel, high melt supply, seafloor accretion (Christie et al., 1998). Here we present new Hf and high precision Pb isotope data for zero age (Pyle et al., 1992) and off-axis AAD MORB glass (Christie et al., 1998) to characterize the Hf isotopic systematics of the mantle boundary and to constrain theories for the AAD origin.

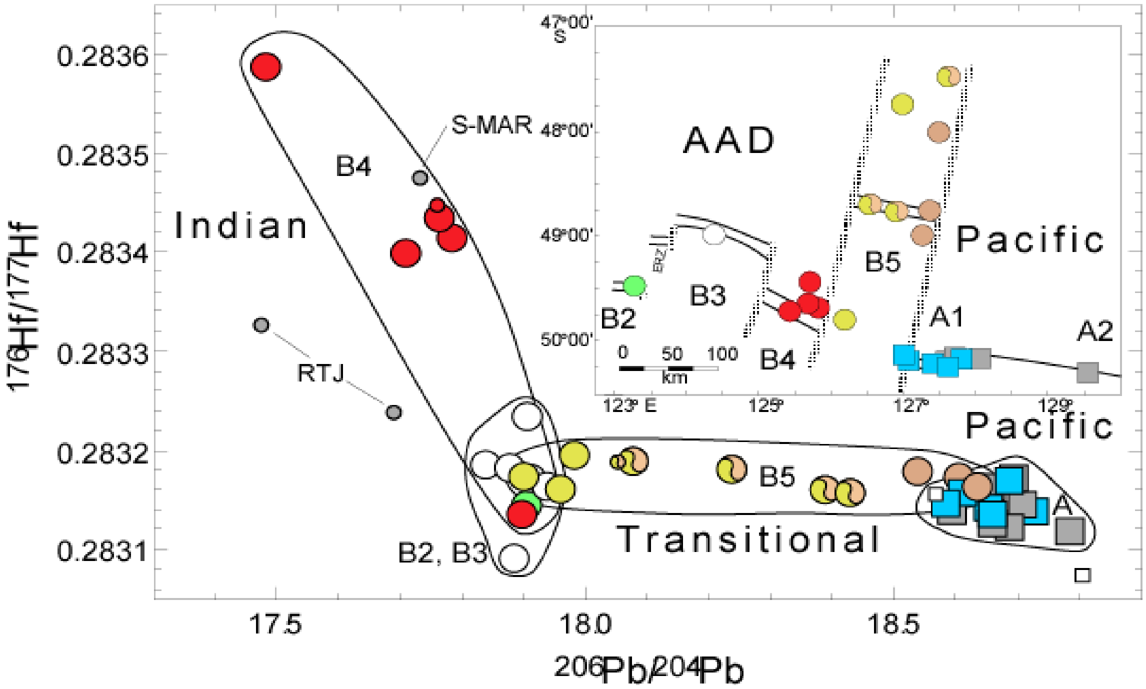


Figure 1. Hf-Pb isotope variation for AAD basalt glasses. Small symbols are from Patchett and Tatsumoto, 1980 (S-MAR)& Salters, 1996 (RTJ and AAD).

Hf and Pb isotope ratios were obtained by multi-collector plasma source mass spectrometry on the VG Plasma 54 at the Ecole Normale Supérieure de Lyon. ^{176}Hf/^{177}Hf ranges from 0.283121-0.283174 for the Pacific MORB (segments A1,A2),0.283141-0.283589 for the Indian MORB (B2,B3,B4), and 0.283121-0.283199 for the transitional ridge segment B5 (Fig.1). The Indian MORB from AAD ridgesegment B4 are ultra-depleted, with ^{176}Hf/^{177}Hf ranging 0.283140-0.283589 and ^{143}Nd/^{144}Nd = 0.513184-0.513349. Indian-type mantle has higher ^{176}Hf/^{177}Hf for a given ^{143}Nd/^{144}Nd than Pacific-type, defining separate fields in Nd-Hf isotope space. Two exceptions are: (1) segment B5 samples define a negative trend between the two fields; and (2), a single Pacific-type sample from segment A1 that plots inside the

Indian field. In the Hf-Pb, Nd-Pb, and Pb-Pb diagrams all samples from east of the AAD (segments A1 and A2) define distinct fields that represent Pacific mantle. Samples from the AAD (B2,B3,B4) west of the transitional segment B5 plot in separate fields with less radiogenic Pb, Nd, and Hf isotopes relative to the Pacific-type samples. Segment B5 forms a linear trend between the Pacific and Indian fields in the wake of westward Pacific mantle migration. Sr isotopes for AAD MORB glass are more radiogenic than those of Zone A, and B5 glasses are intermediate. Similar evidence for mantle heterogeneity and mixing between Pacific and Indian mantle is illustrated in the Hf-Pb isotope diagram (Fig.1). The Pacific mantle defines a tight field with low $^{176}Hf/^{177}Hf$ and relatively radiogenic $^{206}Pb/^{204}Pb$. The Indian mantle defines a negative trend with a regular spatial variation from high $^{206}Pb/^{204}Pb$ and low $^{176}Hf/^{177}Hf$ in the west (segments B2,B3)to lower $^{206}Pb/^{204}Pb$ and higher $^{176}Hf/^{177}Hf$ towards the east (B4). Segment B5 defines a transitional trend between the Pacific and Indian fields. It intersects the Indian trend at low $^{176}Hf/^{177}Hf$, close to the segment B3 composition. MORB with similar isotope characteristics occur at 2-7 °S on the MAR, from inter-transform spreading in the EPR Garrett FZ, and the Rodriguez triple junction (RTJ) (Hanan et al.,1986; Patchett and Tatsumoto,1980; Wendt et al., 1999; Salters, 1996). These areas represent the most depleted MORB mantle sources known.The ultra-depleted MORB from segment B4 fall along and extend the binary-like linear radiogenic isotope trends for Indian MORB to more depleted values. This suggests that the AAD MORB mantle source does not represent an exotic slab or subcontinental mantle fragment (Gurnis.et al., 1988). Melt extraction from previously melted Indian mantle like that currently beneath segments B2 and B3, possibly related to the recent ridge jumps of segment B4 adequately accounts for the isotope data.

References

Christie, D.M., West, B.P., Pyle, D.G. & Hanan, B.B., Nature 394 ,1998.
Gurnis, M., Müller, R.D. & Moresi, L., Science 279 ,1499-1504, 1998.
Hanan, B.B., Kingsley, R.H. & Schilling, J.-G., Nature 322 ,1986.
Klein, E.M. Langmuir, C.H., Zindler ,A., Staudigel, H.&Hamelin, B., Nature 333 ,623-629,1988.
Patchett, P.J. & Tatsumoto, M., Geophys.Res.Lett.7 ,1077-1080,1980
Pyle, D.G., Christie, D.M.&Mahoney, J.J., Earth Planet.Sci.Lett.112 ,161-178, 1992.
Salters, V.J.M., Earth Planet.Sci.Lett.141 ,109-123,1996.
Wendt, J.I., Regelous, M., Niu,Y., Hékinian, R.&Collerson, K.D., Earth Planet.Sci.Lett.173 ,271-284, 1999.

Helium Isotopes and Helium-Carbon Relationships in Arc Lavas and Geothermal Fluids: Implications for Constraining Volatile Fluxes.

Hilton, D R

Introduction.

One particularly successful approach to the volatile mass balance at convergent margins has been to couple major volatiles, such as CO_2, to helium measurements (isotopes and relative abundances) which allows both identification and quantitative assessment of the various contributors to the magmatic output (e.g. Sano and Williams, GRL,1996). Helium is chemically inert and a trace constitutuent in magmas yet it is an extremely useful geochemical tracer because its isotopic composition ($^3He/^4He$) is one of the most sensitive labels of a mantle-source derivation, and also because the flux of primordial ^3He from the mantle to the atmosphere is uni-directional and more reliably established than for any other species (Craig and Lupton, EPSL, 1976). This methodology of normalizing to helium is important as it holds the promise of constraining the proportion of carbon (and other volatiles) recycled between trench and arc (shallow recycling) versus the proportion that by-passes the zone of magma generation and which may potentially re-emerge via mid-ocean ridge or plume volcanism (deep recycling).

Helium isotopes in arcs.

The vast majority of arc lavas and associated geothermal features (fumaroles, solfataras, etc.) are characterized by $^{3}He/^{4}He$ ratios between 6 and $8R_A$ (where RA is the atmospheric $^{3}He/^{4}He$ ratio of 1.4×10^{-6}) i.e. very close to the MORB-helium ratio of $8 \pm 1R_A$ (Poreda and Craig, Nature, 1989). This implies that the helium is predominantly of mantle origin - presumably from the mantle wedge, and contains only a minor proportion of crustal (radiogenic)helium ($^{3}He/^{4}He$ ~$0.05R_A$). Debate has centered on the provenance of this small but significant addition of radiogenic helium: is it slab-derived and a consequence of subduction or in-growth of radiogenic helium on the down-going plate, or is it a contaminant and added immediately prior to eruption in the arc crust?

Detailed helium studies of arc magmatism have led to the conclusion that both scenarios can occur - in different tectonic settings. In the east Sunda/Banda arcs of eastern Indonesia, Poreda and Craig (Nature, 1989) and Hilton and Craig (Nature, 1989) found that $^{3}He/^{4}He$ ratios were all predominantly radiogenic - a remarkable departure from observations at other arcs. The transition from more normal ‚arc-like' ratios ($6\text{-}8R_A$) to low values was extremely sharp and coincided with the change in composition from oceanic to continental slab in the vicinity of Flores (Hilton and Craig, Nature, 1989; Hilton et al., GCA, 1992). In this case, at least, the effects of a strong radiogenic helium signal in the subducting slab were discernible through the MORB-like helium signal associated with the mantle wedge. In the Andes, MORB-like and radiogenic helium occur in close proximity at sites throughout the Central and Southern Volcanic Zones (Hilton et al., EPSL, 1993). There is no correlation between $^{3}He/^{4}He$ ratios and either Sr or Pb isotopes (as in the case of the east Sunda/Banda arcs) effectively ruling out a slab origin for the radiogenic helium isotope signal. The source of the radiogenic helium was concluded to be intra-crustal contamination with pre-eruptive degassing of near-surface magma chambers, and loss of mantle (magmatic) helium, the predominant control on the measured $^{3}He/^{4}He$ ratios. Support for this interpretation has come from further studies in the Indonesian archipelago e.g. Gasparon et al. (EPSL, 1994) who found a correlation between $^{3}He/^{4}He$ ratios and degree of shallow-level magmatic differentiation (as recorded in the Mg# of olivines). More recent work in the Lesser Antilles arc (van Soest et al., GCA 1998) corroborates these findings: the southern portion of the arc which has the thicker arc crust has lower $^{3}He/^{4}He$ ratios ($5\text{-}6R_A$) relative to the central arc (MORB-like $^{3}He/^{4}He$) which is built on thinner overlying crust. In this respect, $^{3}He/^{4}He$ ratios lower than MORB values are providing an extremely sensitive tracer of upper crustal involvement in arc petrogenesis.

He-CO_2 relationships: Flux Estimates at Subduction Zones.

Compared to MOR spreading centers ($CO_2/^{3}He$ ratios ~2×10^{9} Marty and Jambon, EPSL, 1987), subduction zones invariably have higher values - $CO_2/^{3}He$ ratios up to 10^{12} (e.g. Marty et al., Chem. Geol. 1989; Varekamp et al.,Terra Nova, 1992). Such high values have been used to argue for addition of slab carbon to the source region of arc volcanism with the implication that carbon is effectively recycled between the mantle and crust/hydrosphere/atmosphere system through subduction and magmatic degassing at arcs.

The He-C abundance and isotopic data from arcs can be approximated by a three-component mixture involving ORB mantle (M), and slab-derived marine carbonate/limestone (L) and (organic) sedimentary components (S). Sano and Marty (1995) and Sano and Williams (1996) determined the relative proportions of MORB-, L- and S-derived carbon in individual samples of arc-related geothermal fluids. Using assumed values for the endmember components (e.g. $\delta^{13}C$ values of -6.5‰, 0‰ and -30‰ and $CO_2/^3He$ ratios of $2x10^9$, 10^{13}, and 10^{13} for M, L and S respectively) they concluded that only ~10% of the carbon in the majority of arcs world-wide is MORB-derived with the bulk of the remainder (>65% total) coming from decarbonation reactions involving subducted marine limestone and slab carbonate. The $CO_2/^3He$ ratio is also pivotal to the estimate of the total mass flux of carbon released to the atmosphere/hydrosphere via arcs. For example, Sano and Williams (GRL, 1996) and Marty and Tolstikhin (Chem. Geol. 1998) use variants of the same equation:

$$\Phi C,arc = \Phi\ arc * [^3He]um * (CO_2/^3He)arc * 1/r \quad \ldots\ldots\ldots\ldots \quad (1)$$

where Φ arc = flux of magma , r = extent of partial melting (10-25%), and $[^3He]um$ is inferred upper mantle ^3He content. This methodology has led to estimates of 2.5-3.1 ($x10^{12}$ moles/a) for the carbon output via arc volcanism -in reasonable agreement with approaches integrating CO_2 fluxes from individual volcanoes world-wide (Allard, GRL, 1992; Williams et al., GCA, 1992). Although carbon flux estimates based on both the integrated and $CO_2/^3He$ approaches concur that arcs (and MOR) are the principal escape route(s) of carbon from the mantle, the absolute flux is known only to a factor of 2.

Problematic Issues affecting flux estimates using He-C relationships.

Despite the potential of He-C studies to resolve and quantify various slab-related C-fluxes to the atmosphere/hydrosphere, there are two uncertainties that limit the methodology at present.

(1) The first is whether He-C relationships measured at the surface are necessarily representative of the source region. Studies at Loihi Seamount, Hawaii (Hilton et al., Nature, 1998) have shown that magma composition exerts a strong control on resultant $CO_2/^3He$ ratios. In an equilibrium degassing scenario, the fractionation factor (α) ,defined as the ratio of $(CO_2/^3He)$ in the vapor phase to the same ratio in the melt phase, is given by the inverse ratio of their solubilities in the parental melt. For a tholeiitic basalt (SiO_2 ~48-49 wt.%), α is estimated at a value of 2.35.Therefore, for a starting $CO_2/^3He$ ratio of 2×10^9 , the melt will evolve to a much lower $CO_2/^3He$ ratio as a function of type (Rayleigh or Batch) and extent of degassing. Studies are needed to quantify the relative solubilities of helium and carbon dioxide as a function of the range of magma compositions encountered at arcs to reconstruct initial $CO_2/^3He$ ratios i.e. prior to magmatic degassing - in order to reliably assign source provenance and accurately estimate volatile fluxes.

(2) The second concerns the mass balance of carbon. Ideally, it would be useful to attempt to balance the C-input via the subducted slab with output via the volcanic arc (exsolved to the atmosphere/hydrosphere as well as underplated) with any discrepancy assigned to loss to the deeper mantle. However, the methodology of Sano and co-workers assumes that subducted marine carbonate and organic matter can be distinguished as potential input parameters based solely on their perceived C-isotopic composition prior to subduction (-0‰ versus -30‰ respectively). However, the approach ignores the anticipated evolution of organic-derived CO_2 to higher $\delta^{13}C$ as a function of diagenetic and/or catagenetic changes experienced during subduction (Ohmoto, Rev. Mineral., 1986). In the southern Lesser Antilles, for example, van Soest et al., (GCA, 1998) calculated that >50% of the total carbon would be assigned an organic origin if the S-endmember had $\delta^{13}C$ = -10‰ as opposed to <20 % for an endmember value of -30‰. In this case, the additional sedimentary input was assigned to the arc crust which is particularly thick in this portion of the arc. Clearly, attempts at a realistic mass balance are difficult without (a)

calibration of the effect of subduction on the C-isotopic signature of the sedimentary input, and (b) quantification of the effect of the crustal input.

On-going Work

Studies currently underway (to Costa Rica - see http://sio.ucsd.edu/volcano) are utilizing the He-CO_2 approach to develop a volatile mass balance for the Central America margin. In this work, we are targeting both geothermal fluids and volatile-rich minerals (mafic phenocrysts) to produce an extensive database of helium-CO_2 relationships both along and across the strike of the arc. It is planned to test the integrity of the elemental relationship between He and CO_2 to reflect source values by comparing the geothermal fluids with minerals which presumably trapped their volatile inventory prior to extensive magmatic degassing. Initial results from this study will be discussed at the GERM meeting.

Characterizing OIB Mantle Sources by Trace Element Ratios Using the GEOROC Database

Jochum, K P; Sarbas B; Hofmann A W

Concentration ratios of trace elements are suitable for characterizing the source compositions of mantle reservoirs. Some well-known examples are Ba/Rb (Hofmann and White, 1983), K/U (Jochum et al., 1983), Nb/U (Hofmann et al., 1986) and Zr/Nb (Rhodes, 1996). The highly incompatible trace elements Nb, Ta, Th, Ba, La are especially useful because their concentration ratios are similar in the basalts and in their sources. Hofmann and Jochum (1996) used Nb/Th, Ba/Th to constrain the chemistry of the Hawaiian plume. Zr/Nb, Zr/Y, Nb/Y ratios are suitable to distinguish between the Hawaiian volcanoes Mauna Loa and Mauna Kea (Rhodes, 1996).

In order to constrain systematically the chemistry of OIB mantle sources we have used the GEOROC database (http://georoc.mpch-mainz.gwdg.de/), which contains nearly all published analytical data for OIB (24500 whole rock analyses). Our investigations comprise 30 ocean islands and island groups. In a first step, we have investigated the trace elements Y, Zr, Nb, Ba, La, Ta, Th, U and the corresponding abundance ratios Zr/Y, Zr/Nb, Nb/Th, Nb/Ta, Nb/La, Ta/Th, Th/U, Ba/Th. The numbers of analytical data for the different oceanic islands vary strongly. Whereas in the case of the Hawaiian Islands, Iceland and Canary Islands more than1000 published data sets are available, there are less than 100 whole rock analyses for small islands, such as Ascension, Bouvet, Gough, Heard, St. Paul and Tristan da Cunha. The interpretation of the results of the latter islands is therefore much more difficult than for Hawaii, Iceland or the Canary Islands. To get reliable results we omitted data from the GEOROC database, which are obviously of poor analytical uncertainty.

Rock name	**Nb ppm**	**Zr/Y**	**Zr/Nb**	**Nb/Th**	**Nb/Ta**	**Ta/Th**	**Th/U**	**Ba/Th**	**Nb/La**	**Nb/U**
Hawaiian Islands										
picrites	10 ± 1	5.8 ± 0.2	11.4 ± 0.7	17 ± 1	17 ± 1	1.1 ± 0.1	3.1 ± 0.1	134 ± 14	1.16 ± 0.07	53 ±3
tholeiites	12.3 ± 0.4	6 ± 0.1	12.4 ± 0.2	16.7 ± 0.4	16.5 ± 0.4	1.14 ± 0.04	3.07 ± 0.04	137 ± 4	1.1 ± 0.02	47 ± 1
alk. bas.	37 ± 2	7.6 ± 0.3	7.4 ± 0.3	15.5 ± 0.4	16.3 ± 0.3	0.96 ± 0.04	3.6 ± 0.2	163 ± 5	1.14 ± 0.03	57 ± 4
hawaiites	47 ± 3	8.8 ± 0.4	7.8 ± 0.5	14.8 ± 0.7	15.3 ± 0.7	0.96 ± 0.04	2.9 ± 0.3	165 ± 7	1.18 ± 0.03	
neph.,mel.	67 ± 9	8.6 ± 0.4	3.5 ± 0.1	11.3 ± 0.9	16 ± 2	0.78 ± 0.14	3.8 ± 0.7	132 ± 14	1.4 ± 0.2	44 ± 13
Canary Islands										
picrites	28 ± 2	7.8 ± 0.6	6.6 ± 0.9	13 ± 3	16 ± 7	0.83 ± 0.15		71 ± 34	1.4 ± 0.3	
tholeiites	33 ± 7	6.4 ± 1.3	5.7 ± 0.7	13 ± 1	16 ± 2	0.83 ± 0.08	3.9 ± 0.2	94 ± 16	1.31 ± 0.09	59 ± 12
alk. bas.	59 ± 6	10.2 ± 0.5	5 ± 0.4	11 ± 3	16 ± 1	0.9 ± 0.2	3.9 ± 0.3	90 ± 19	1.3 ± 0.1	30 ± 20
hawaiites	65 ± 13	10.3 ± 0.6	6 ± 2	13 ± 2			4 ± 0.3	84 ± 34	1.1 ± 0.1	
neph.,mel.	91 ± 11	10.2 ± 1.4	3.5 ± 0.2	11 ± 1	15 ± 1	0.75 ± 0.06	4.1 ± 0.4	120 ± 40	1.1 ± 0.1	

Table 1: Mean Nb concentrations and concentration ratios in different rock types obtained by using the GEOROC database. Uncertainties represent 2 standard deviations of the mean.

Because concentration ratios in volcanic rocks may be affected by the degree of melting, especially in cases where the degree of incompatibility of the elements differs significantly (e.g., for Zr/Nb, Zr/Y), we determined the concentration ratios in different rock types using analyses of the Hawaiian and the Canary Islands. Volcanic rocks, such as picrites and tholeiites, are assumed to be produced by relatively large degrees of melting, whereas the melting degrees for alkali basalts, nephelinites and melilitites are much lower. Our results show that nearly all ratios for picrites and tholeiites agree within error limits (Table 1). The same is true for alkali basalts and hawaiites, but Zr/Nb ratios are 10% (Canaries) and 40% (Hawaii) lower in alkali basalts and hawaiites than in picrites and tholeiites. Nephelinites and melilitites have even lower Zr/Nb ratios. Zr/Y ratios are about 40% higher in alkali basalts and hawaiites than in picrites and tholeiites. These findings are in agreement with the generally assumed incompatibility sequence of these elements: Nb > Zr > Y. The dependence of the highly incompatible trace element ratios on the degree of melting is much lower. The mean ratios for Nb/Ta, Nb/Th, Ta/Th, Th/U, Nb/La in picrites and tholeiites differ less than15% from those in alkali basalts and hawaiites (Table 1).

To characterize OIB mantle sources we used therefore only the GEOROC data for picrites and tholeiites. As an example, Fig. 1 shows our results for Nb, Th and La in those oceanic islands where sufficient analytical data are available for tholeiites and picrites. These elements are of particular interest because

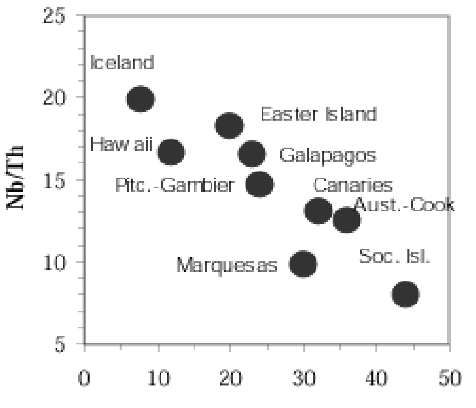


Fig. 1a

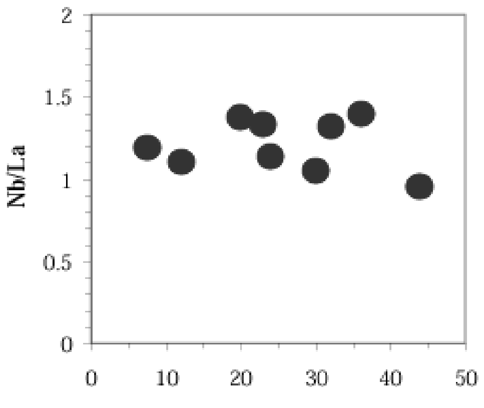


Fig. 1b

Nb is thought to be enriched in OIB mantle sources (e.g., Hofmann et al., 1986). On the other hand, a Th depletion of Hawaiian and Icelandic rock samples has been observed and interpreted in terms of a gabbroic source component (Hofmann and Jochum, 1996). Figure 1 shows that the mean Nb concentrations in the tholeiites and picrites for different OIBs vary by a factor of 5. Iceland and Hawaii have the lowest Nb contents of about 8 and 12 ppm, respectively, whereas picrites and tholeiites of the Austral-Cook, Canary and Society Islands have high Nb of 32 – 44 ppm. Nb/Th ratios are higher thanchondritic and vary from 8 to 20. They are negatively correlated with the Nb concentration. This is not surprising because Th is normally more incompatible than Nb. However, as demonstrated in Table 1, fractionation of Nb/Th due to melting processes is less than 15%. This means that the differences in Nb/Th ratios for the different oceanic islands are clearly a property of their mantle sources which may be caused by positive Nb and/or negative Thanomalies. The general Nb enrichment in OIB mantle sources (Hofmann et al., 1986) is confirmed by the higher-than-chondritic Nb/La ratios (chondritic Nb/La = 1.0). The only exception are the EM-2 type Society Islands with lower-than-chondritic Nb/La. In view of these results, we question the assertion of McDonough (1991) that most OIB (like MORB) sources have subchondritic Nb/La values. A general deficiency of the mantle can thus not be derived from these results. On the other hand, it is also clear that the high Nb/Th ratios of islands (island groups) like Iceland, Hawaii, Galapagos, and Easter, are not caused by an additional Nb excess but a deficiency of Th in their sources.

References

Hofmann, A.W. and White W.M. (1983), Z. Naturforsch. 38a, 256-266.
Hofmann, A.W., Jochum, K.P., Seufert, M. and White W.M. (1986), Earth Planet. Sci. Lett. 79, 33-45.
Hofmann, A.W. and Jochum, K.P. (1996) J. Geophys. Res. 101, 11831-11839.
Jochum, K.P., Hofmann, A.W., Ito, E., Seufert, H.M. and White, W.M. (1983) Nature 306, 431-436.
McDonough, W.F. (1991) Phil. Trans. R. Soc. Lond. A 335, 407-418.
Rhodes, J.M. (1996), J. Geophys. Res. 101, 11729-11746.

Subduction Cycling of U, Th and Pb: Perspectives from Altered Oceanic Crust

Kelley, K; Plank, T; Farr, L; Ludden, L; Staudigel, H; Alt, J

Many studies call upon subducted altered oceanic crust (AOC) to ultimately reside in the ocean island basalt (OIB) source. The existing geochemical budget of AOC from DSDP 417/418, however, generates low ^{208}Pb compositions that do not approach the OIB array (Hart & Staudigel, 1989). With this in mind, we re-evaluate the existing AOC estimate at another drill site, and consider the effect of subduction processing on the composition of the slab.

Our AOC estimate comprises ICP-MS analyses of 46 discrete and 14 composite samples from ODP Site 801, which is a large extrusive sequence (470 m) of fast-spreading Jurassic MORB east of the Marianas. Uranium determined in discrete samples correlates well with data from natural gamma logs, which both indicatea 4x enrichment of U over pristine glass (0.09 vs. 0.4 ppm). Lead is locally redistributed with no net gain or loss, and both average Pb and Th remain close to the pristine glass composition. U-enrichment creates high μ (^{238}U/^{204}Pb) (μ AOC = 56, μ DMM = 8), but leaves ω (^{232}Th/^{204}Pb) nearly unchanged from the mantle value (ω AOC = 25, ω DMM = 20).

These data yield higher μ and ω for AOC than 417/418, but would still evolve to low ^{208}Pb. AOC thus must be chemically processed by subduction before reaching the OIB source. To constrain slab losses, we use the global model of Elliott, et al. (1999), which provides permissible bounds on μ, ω and κ (^{238}U/^{232}Th) in mantle reservoirs. Assuming AOC retains Th, we subtract AOC ω and κ from Elliott, et al.'s OIB reservoir to calculate 58% of Pb and 85% of U lost from AOC during subduction. Lead loss of 58% is consistent with Ce/Pb models and hydrothermal mobility studies, but 85% U-loss is larger than predicted by current partitioning data. Mixing calculations also indicate μ of the slab-derived fluid contributing to arc volcanism is as low as 2.6-4, which suggests that much less U is lost to the arc than overall from AOC, and that sediment contribution to the arc is much higher μ than bulk sediment. Uranium loss from AOC is controlled by breakdown of its mineral host, and our data show that carbonates, which may be stable to great depths, bind significant U in AOC. Carbonate control may provide a mechanism for some U to be lost from the slab to the upper mantle, below the arc magma source, which may account for the decrease in κ with time in the depleted mantle.

References

Hart, S.R. and Staudigel, H., 1989. Isotopic characterization and identification of recycled components, in S.R. Hart and L. Gulen (eds.), Crust/Mantle Recycling at Convergent Zones, Kluwer Academic Publishers, 15-28.

Elliott, T., Zindler, A., and Bourdon, B., 1999. Exploring the kappa conundrum: the role of recycling in the lead isotope evolution of the mantle, EPSL, 169, 129-145.

Tracking Isotopic Heterogeneity in Geochemical Reservoir Models

Kellogg, J B; Jacobsen, S B; O 'Connell, R J

The average isotopic composition of the crust and depleted mantle through time can be used with classical geochemical reservoir (or box) models to infer the mean ages, mass flux histories, and residence times of the various elements of reservoirs present in the Earth (e.g. Jacobsen and Wasserburg, 1979, 1980). The isotopic heterogeneity of oceanic basalts also provides important constraints on the chemical evolution of the mantle-crust system. One fruitful approach has been to identify the mantle's major end member compositions (e.g. HIMU, EMI, EMII, DM) and then try to associate each with a particular process (e.g. Zindler and Hart, 1986). This leads us, then, to a picture of the mantle in which there are at least four distinct reservoirs that have remained isolated from each other for billions of years. Absent major differences in rheology or density, it seems unlikely that such isolation is possible in a convecting mantle.

Allegre and Lewin (1995) approached the problem of isotopic heterogeneity in another creative way, balancing the processes which create heterogeneity against those which destroy it to develop a model of mantle variability. Isotopic variance was seen to be a function of three time scales: the residence time of each species, the radioactive decay time (or mean life), and the stirring time. The inclusion of this last parameter was particularly important, as it explicitly tied the variability to a geophysical process which could be explored independently.

We present a new model for the evolution of mantle heterogeneity in which we extend the reservoir model to include subreservoirs of variable composition. Our approach improves on previous work in several important ways. In particular, it enables us to investigate the length scale dependence of observed heterogeneity. Also, it explicitly ties the development of heterogeneity to the better-understood development of the mean isotopic values of the reservoirs.

This model establishes a quantitative framework for interpreting mantle heterogeneity, providing a measure of the variability expected within a convecting, progressively differentiating system. Ultimately this will allow us to distinguish normal variability from that which requires a more exotic explanation, such as a physically distinct reservoir.

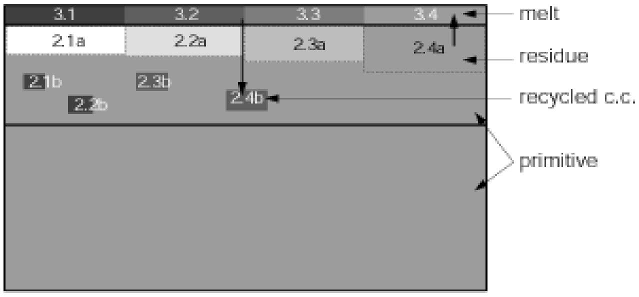


Figure 1 The creation of subreservoirs. The genesis of continental crust (e.g. 3.4) leaves behind a residue of depleted material (e.g. 2.4a). Recycling of continental crust generates another subreservoir of enriched material (e.g. 2.4b)

The Model

Our method is based on the following assumption: subreservoirs created in the mantle are never completely mixed, rather they are merely stirred mechanically by convection. This allows us to approach the problem in several distinct steps. First we establish a baseline, the mean isotopic values for each reservoir throughout Earth history. The traditional geochemical reservoir models give us precisely these values. Second, we must understand and quantify the processes which give rise to heterogeneity in the depleted mantle. Subreservoirs, volumes which have chemical characteristics which differ from the mean, are created by the input of material from other reservoirs and by the residue left behind by fluxes out of the depleted mantle. Third, we must quantify the stirring process. Numerical studies indicate that mechanical stirring in a vigorously convecting medium can be described as an exponential growth/reduction in length scale (Kellogg and O 'Connell, 2001). Finally, we address the issue of sampling. Clearly the observed variance will be much greater when sampled on a mm scale than on a km scale.

Creating Heterogeneity

In our model, mantle heterogeneity is created in two ways (illustrated in Figure 1): (a) fluxes into the mantle from the continental crust, and (b) the residue of partial melting associated with fluxes out of the mantle. (Note that we could include fluxes from the primitive/enriched mantle as well but neglect it here for simplicity.) At each time step (~100 Myr), we create one new subreservoir for each of these processes. Each of these subreservoirs has a uniform isotopic character determined by the mean isotopic values of the reservoirs, the chemical enrichment factors, and, in the case of the residue, the effective degree of partial melting, F. As such, each has its own distinct trajectory in isotope space following its creation. Figure 2 shows the range of values spanned by these subreservoirs at various stages in Earth evolution. Note that the tip of each curve, furthest from the mean reservoir evolution curve, represents the same subreservoir's isotopic composition at different points in time.

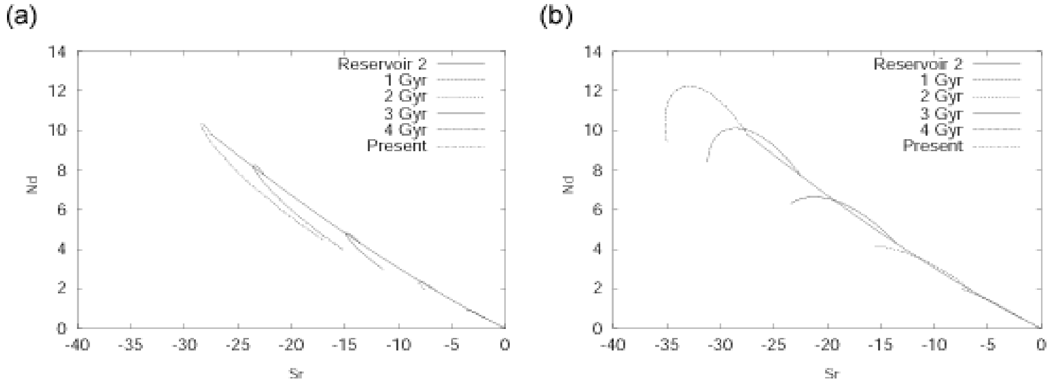


Figure 2 Evolution of heterogeneity in the depleted mantle. The solid line shows the evolution of the mean isotopic values. Dashed curves show full range of subreservoir isotopic values at (from right to left) 1 Gyr, 2 Gyr, 3 Gyr, 4 Gyr, and present day. Based on linear growth of continental crust , no recycling. Effective melt fraction F is (a) 0.004 or (b) 0.008.

Destroying Heterogeneity

Because diffusion rates in the solid mantle are so low (Hofmann and Hart, 1978), a subreservoir, once created, is never completely remixed. Its volume is reduced by fluxes out of the reservoir and participation in partial melting; each subreservoir contributes material to any flux in proportion to its relative volume. The subreservoir, however, never diffuses away. The effect of mechanical stirring is to change the topology of the subreservoir, increasing its length scale drastically in one direction while decreasing it in another. Because this long length scale is, in general, much greater than any sampling scale of interest, the relevant length scale of the subreservoir is the short one, which we will label l_h. Denoting the initial length scale as l_o , we can parameterize the relevant length scale of the subreservoir as

$$l_h(t) = l_o e^{-(t-t_o)/\tau_s}$$

where t_o is the time at which the subreservoir was created, and τ_s is the stirring time scale discussed earlier. We glean τ_s from numerical calculations (Kellogg and O 'Connell, 2001) and assign reasonable estimates to l_o.

Sampling the Depleted Mantle

The length scale l_h becomes important when we investigate the effects of sampling on the observed heterogeneity. We model sampling as follows. First, we break up each subreservoir into n subsubreservoirs, where $n = v/l^3_h$ and v is the volume of the subreservoir. Second, assuming that these subsubreservoirs are scattered randomly throughout the reservoir, we can do some simple statistics based on the idea that we take a box of length scale l_s which moves about the reservoir at random. A subreservoir which lies within the box contributes to the sampled composition in proportion to its volume and chemical concentrations. No bias is currently built in to model preferential sampling of enriched/primitive material over depleted material. Results of sampling the distribution of Figure 2 are shown in Figure 3.

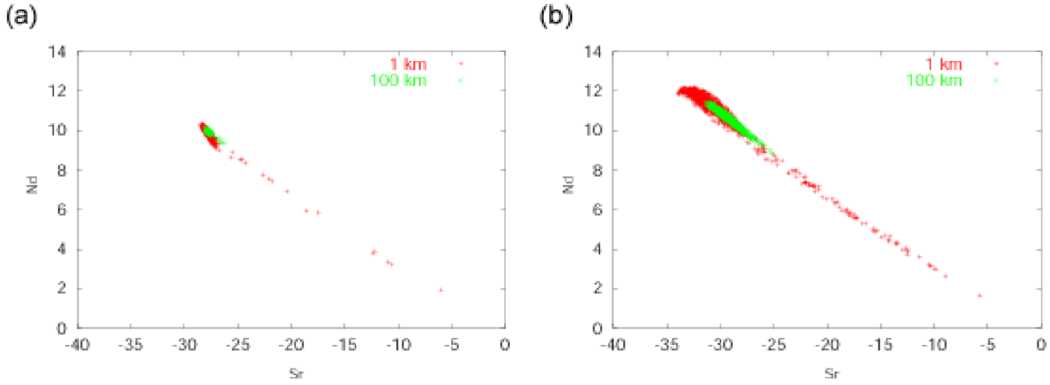


Figure 3 Expected observations today, given a linear growth of the continental crust ,1 and 100 km sampling scales, and melt fraction F (a) 0.004 or (b) 0.008.

Conclusions

We are able to reproduce the near-linear trend in Sr-Nd isotope space, dubbed the "mantle array". Other calculations involving continental crustal recycling (not shown) show an EMI-like component as well. However, more complexity, such as a heterogeneous continental crust or recycled oceanic crust, is needed to reproduce EMII and HIMU. We are currently working to implement these changes.

References

Allegre, C.J.and E.Lewin, Isotopic systems and stirring times of the Earth's mantle, Earth Planet. Sci. Lett., 136, 629 –646, 1995.

Hofmann, A.W.and S.R. Hart, An assessment of local and regional isotopic equilibrium in the mantle, Earth Planet. Sci. Lett., 38, 44 –62, 1978.

Jacobsen, S.B.and G.J. Wasserburg, The mean age of mantle and crustal reservoirs, J. Geophys. Res., 84,7411 –7427, 1979.

Jacobsen, S.B.and G.J. Wasserburg, A two-reservoir recycling model for mantle-crust evolution, Proc. Natl. Acad. Sci. USA., 77,6298 –6302, 1980.

Kellogg, J.B.and R.J. O 'Connell, The effects of plates and layered viscosity on stirring in three dimensional convection, in prep., 2001.

Zindler, A.and S. Hart, Chemical geodynamics, Ann. Rev. Earth Planet. Sci., 14,493 –571, 1986.

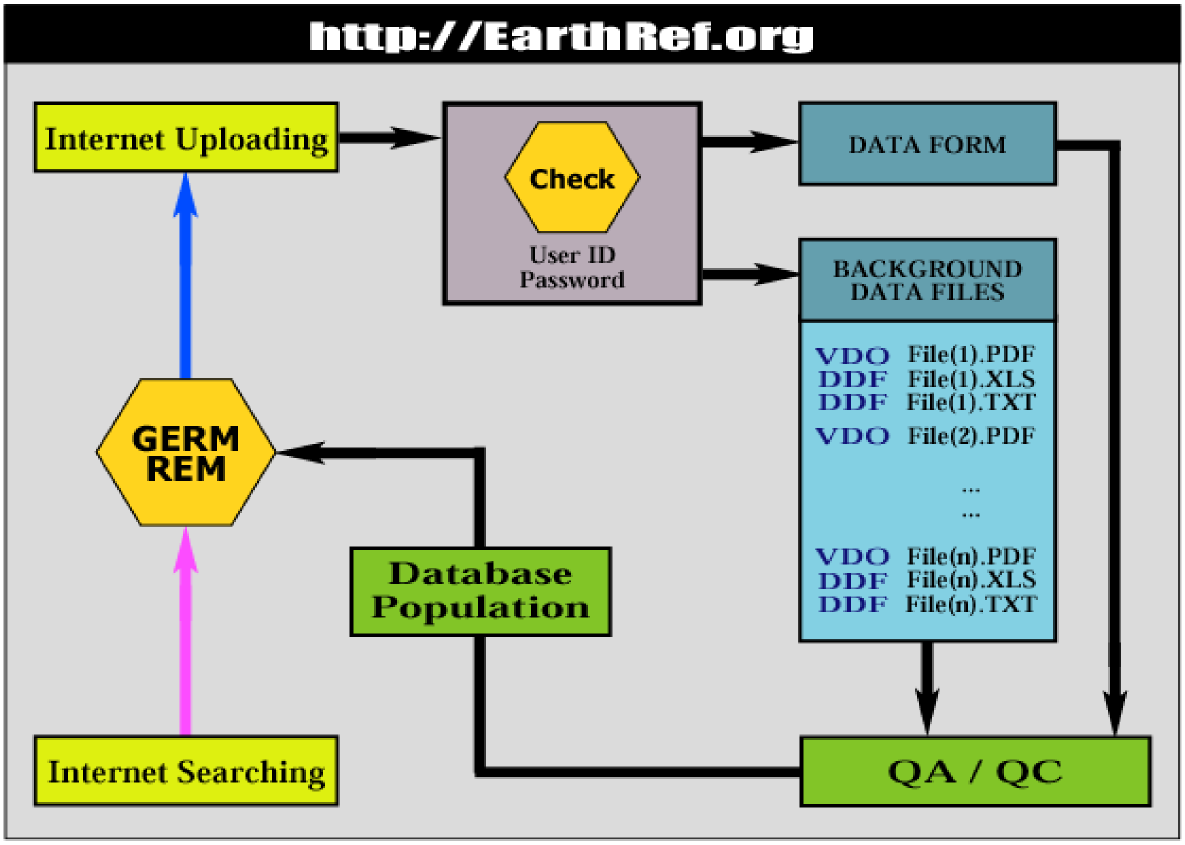
EarthRef.org Database Development

Koppers, AAP; Staudigel, H; Helly, J

The exponentially increasing number and quality of geochemical and geophysical data has led to major advances in our understanding of the Earth, but it also has lead to a similarly exponentially increasing need for meaningful data archiving and digital access to these data. The latter process has been extremely slow, in particular, in geochemistry. As a result, it has been slowing down the development of global geochemical and geophysical models such as GERM and REM. In fact, to date there is no global geochemical model that attempts to optimize constraints from all types of geochemical data. For these reasons it is important to establish databases that are comprehensive and available to the whole Earth science community through online connections.

The Scripps center for Physical and Chemical Earth References (PACER) was established to help create such global models by electronically making available a wide range of Earth science data. As part of these efforts PACER supports GERM and REM and maintains multiple online databases under the http://earthref.org umbrella web site. This web site has been build on top of a relational geochemical database that allows for the archiving and electronic access to a great variety of data types and formats, permitting data queries using a wide range of metadata. These online databases are designed in Oracle 8.0.5 and they are maintained at the San Diego Supercomputer Center. They are directly available via http://earthref.org/databases.htm.

Geochemical data may be found in the published literature in the form of data points in diagrams, immersed within the text of a paper, in printed data tables or as electronic data sets. EarthRef.org archives these data both as arbitrary digital objects (**ADO**) and as digital data files (**DDF**) before digesting them into the relational databases using easy-to-use data forms (Figure 1). The **ADO**s can include any digital object, in our case, typically PDF files of scanned images of diagrams, text passages or data tables. These visual digital objects (**VDO**) are then "digitized" and transferred into **DDF**s and will be made available as Microsoft Excel and tab-delimited text files. Each data point is subsequently entered into the EarthRef.org relational databases using easy-to-use data forms. Both the **ADO**s and **DDF**s serve as "original" records and "background" data files that also may be used to check for potential digitization errors.



Up to this moment, EarthRef.org has been compiling resources used to construct the Geochemical Earth Reference Model (GERM), but it may well be expanded to any type of geochemical or Earth science data. To that extent we have started new relational databases including an online geological time scale (including background data) and databases on paleosecular variations in the intensity of the Earth's magnetic field through geological history (PMAG). The visitor to EarthRef.org will find the complete set of literature resources as used in GERM. However, large numbers of additional data are located in the EarthRef Digital Archive (ERDA) and can be found via http://earthref.org/databases/ERDA.htm. EarthRef.org is structured such that it is operated by a central organization (currently PACER) but it specifically allows for contributions from all members of the Earth science community.

Comparing Mantle Convection Models through Modeling of their Geochemical Evolution with the Terra Nova Toolbox (TnT2000)

Koppers, AAP; Phipps Morgan, J; Staudigel, H

The geochemical evolution of the Earth is mainly determined by the differentiation of the mantle due to partial melting at hotspots and mid-oceanic ridges, the formation of continental crust and island arcs, and recycling at subduction zones. Important second order differentiation processes may include metasomatism of the mantle, alteration of the oceanic crust and chemical erosion of the continental crust. In the past, geochemical modeling approaches tended to focus on a relatively small number of these processes. They also tended to be restrictive in their model boundary conditions and in the number of parameters (elements, isotope ratios) considered. This incomplete geochemical modeling has significantly limited our understanding of the Earth as a dynamic and geochemical system. We developed the Terra Nova Toolbox (TnT2000) with the goal of providing a flexible modeling environment for exploring both simple and sophisticated geochemical evolution scenarios including the wide range of chemical and physical processes that shape the Earth.

TnT2000 accommodates the complete array of elements (*n*=92) and their natural-occurring isotopes (*n*=287) in a modular design that allows for different algorithms to define partial melting, alteration, metasomatism, mixing, entrainment and recycling. Reservoirs and their intrinsic properties can be defined to approximate a range of global reservoir geometries, ranging from whole mantle convection to two-layer mantle convection to complex box models scenarios. Chemical differentiation by batch, fractional or dynamic partial melting, metasomatism and water-rock exchange are simply described with partition coefficients. Different rock phase assemblages can be defined for each type of reservoir and its sub-reservoirs. Parent-daughter isotope abundances are constantly updated for radioactive decay. Mantle differentiation and overturn rates can be prescribed through Earth's history by choosing steady-state, linear, or exponential models as proxies for mantle convection and differentiation rates.

In most model calculations we assumed the squared-exponential heat loss model (Phipps Morgan, 1998; Phipps Morgan & Morgan, 1999) varying the current mantle overturn rate between 9.5 Myr (Phipps Morgan & Morgan, 1999) and 5.7 Myr (Kellogg & Wasserburg, 1990). The squared-exponential heat loss model seems to be the best proxy for the rate of chemical differentiation, as it assumes that Earth's mantle has been most efficiently cooled by the subduction of the oceanic plates (Phipps Morgan, 1998). Note that with this heat loss model the initial mantle convection and differentiation rates are up to 26 times the current rates. As a result, between 15-25% of the entire mantle is processed during the first 50 Myr of Earth evolution, whereas only ~0.5% of the mantle is differentiated during the most recent 50 Myr time period. This confines the most dynamic phase of Earth's differentiation to the Archean. The sharp decrease in the differentiation rate is even more exaggerated if the heat loss model is 'corrected' for the fraction of heat producing elements K-U-Th stored in the continents, where their energy does not contribute to mantle heating and convection. Secular cooling and the heat produced by the crystallization of the inner core are not (yet) taken into account, although these processes would further exaggerate early heat loss.

Here we will compare three different geochemical differentiation models for the Earth: (1) the classical two-layered mantle model, (2) the 'plum-pudding' whole mantle convection model, and (3) the dense deep layer model of Kellogg et al. (1999). In these comparisons we will, in particular, study the evolution of the primitive mantle components for their volumes, the amount of continental crust that is being recycled and how well these different models can reproduce the $^{87}Sr/^{86}Sr$ – $^{143}Nd/^{144}Nd$ mantle array and trace-element abundances.

TnT2000 provides a graphical user interface for the MATLAB 6.0 environment, including graphical tools that can be used to monitor the fractionation patterns for different Earth reservoirs. A basic toolbox has been established to explore simple geochemical scenarios for the Earth's evolution, as they are discussed above, based on commonly used geochemical parameters. However, the modular nature of TnT2000 allows for its expansion towards substantially more sophisticated Earth evolution models, to the incorporation of more complete melting models, to the calculation of more realistic element partitioning behavior, and to more complete data sets. TnT2000 will be made available at http://earthref.org/tools/tnt.htm.

References

Kellogg, L.H. & Wasserburg, G.J. (1990, Earth and Planetary Science Letters 99:276-289)
Kellogg, L.H., Hager, B.H. & van der Hilst, R.D. (1999, Science 283:1,881-1,884)
Phipps Morgan, J. (1998, Chemical Geology 145:431-445)
Phipps Morgan, J. & Morgan, W.J. (1999, Earth and Planetary Science Letters 170:215-239)

Chemical Diversity of Abyssal Volcanic Glass Erupted Along Sea-floor Spreading Centers: A 25 Year Update

Melson, W G.

We have continued to expand the coverage of our major and minor element analysis data base of deep-sea volcanic glasses since it was first made available in 1976 (references can be found via the web site http://www.nmnh.si.edu/minsci/research/glass/index.htm). The glass data set was initiated to understand and model the processes that produce magmas along spreading centers, processes that produce about 75% of the annual budget of the 26 to 34 km 3 of Earth's volcanic rocks (Crisp, 1984). Here we present a bit of bookkeeping about the newly available data set. Analyses of glasses (1) avoid the problems of compositions modified by halmyrolysis, and (2) can be done rapidly and accurately by the electron microprobe. The methodology used here emerged out of the need for analyses of the abundant glass spheres and glass fragments in the first lunar samples (Apollo 11, 1969). The natural quenching of melt against cold sea water that produces pillow rinds beautifully preserves the composition of the eruptive liquid, and such pillow rinds are abundant in dredge, drill core, and submersibly obtained samples. The standards and analytical setups have remained the same during all the analyses. It thus remains unequalled in precision, size, and coverage, and is by far the most frequently cited of its kind in the literature. We recognize small differences in our values from some of the other laboratories. These derive from different analytical setups and sometimes of standards. The major and minor elements determine the physical properties of the spreading center magmas. In particular, the viscosity, density, and liquidus and solidus temperatures can be calculated from these data.

The 1976 database contained 590 individual glass analyses. The new one includes 9035 analyses with far greater geographic coverage and compositional range. The individual analysis file (the IAF) and the magma batch file (MBF) are available. The MBF averages all analyses in a single dredge, contiguous samples in a drill core or from a submesrsibly recognized unit that have compositions within analytical precision (see above web site for precision). These we believe represent individual eruptions.

Segments of the mid-ocean ridge system with good coverage in our file include: the Galapagos Spreading Center (847 analyses), 9° to 12° N on the EPR (1038 analyses), the Juan de Fuca Ridge (490 analyses), the FAMOUS area (503 analyses), and the Reykjanes Ridge (593 analyses).

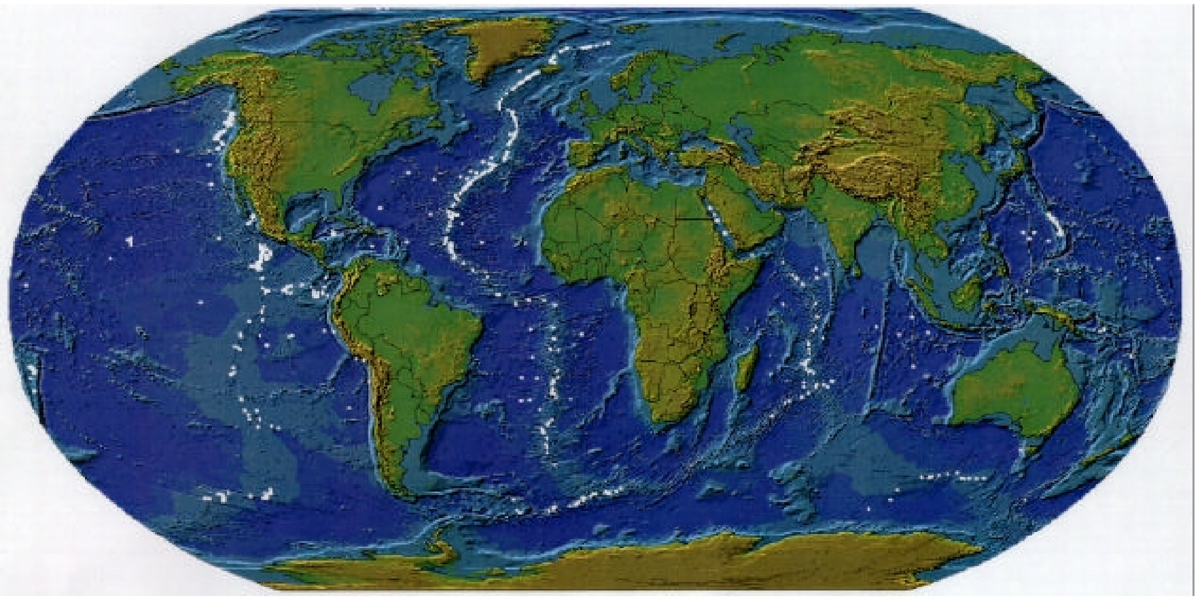
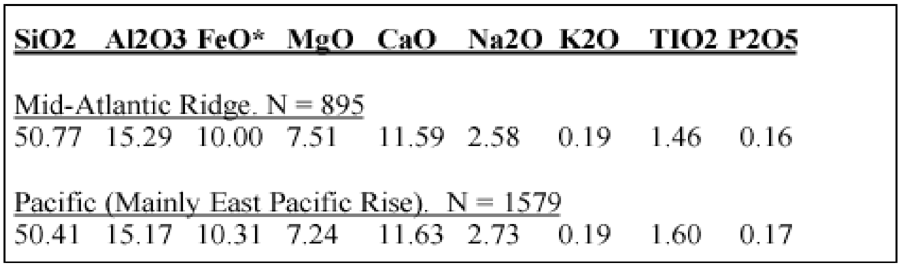


Figure 1 Smithsonian Abyssal Volcanic Glass Sample Locations.

New averages for the major spreading centers the East Pacific Rise and Mid-Atlantic Ridge are remarkably similar. The slightly higher FeO* and TiO_2 contents of Pacific samples, recognized in 1976, persists but is diminished. SiO_2 contents <45 and >55 and of FeO*>15 have been screened out, deleting about 64 (4.05% of the 1643 Pacific samples), and 5 (0.56% of the 900 Atlantic samples). Most of the screened out Pacific samples are the FETI-basalt and acidic glasses from the Galapagos spreading center.



SiO2	Al2O3	FeO*	MgO	CaO	Na2O	K2O	TIO2	P2O5
Mid-Atlantic Ridge. N = 895								
50.77	15.29	10.00	7.51	11.59	2.58	0.19	1.46	0.16
Pacific (Mainly East Pacific Rise). N = 1579								
50.41	15.17	10.31	7.24	11.63	2.73	0.19	1.60	0.17

Samples from the Caribbean (34) and Indian Oceans (124) are still too few to give meaningful averages. The MgO 10% barrier remains. Glasses with 10% or more of MgO have yet to be analyzed in our lab. The samples are at the U.S. National Museum of Natural History. The work could not have been done without the generous donations of samples from many individuals, listed in the data set.

Complementary He/Ne and He/Ar ratios in OIB and MORB: Further Evidence for the Recent Residual Derivation of the MORB Source through OIB Melting

Phipps Morgan, J

Two opposing misconceptions frequently surface in discussions on the isotope chemistry of rare gases in the mantle. One is that the source of ocean island basalts (OIB) is significantly more degassed than the source of mid-ocean ridge basalts (MORB). The other is that the MORB source is much more highly degassed and more radiogenic than the OIB source. Recent compilations of the ratios of rare gas abundances in OIB and MORB suggest that both views are wrong, that the OIB source is more gas rich than the MORB source, but that the MORB source is not highly degassed and dominated by in situ radiogenic ingrowth of ^{4}He, ^{21}Ne, and ^{40}Ar. This new evidence lend further support to two-stage melting hypothesis for the formation of the MORB asthenospheric source, in which the MORB source is the leftover to OIB-melt extraction from upwelling mantle plumes (Phipps Morgan & Morgan,1998).

The first view has Don Anderson as perhaps its strongest proponent. This view results from the observation that erupted OIB almost always have much lower concentrations of He than do MORB. At first glance, this observation appears to contradict the conventional supposition that, because plumes such as Iceland often have much lower ratios of radiogenic to non-radiogenic rare gases (e.g. high ^{3}He/^{4}He), they must come from a more gas-rich source with lower U+Th/^{3}He and K/^{36}Ar ratios than the MORB source. The usual explanation for this is that OIB are more extensively degassed than MORB prior to eruption, which leads to their relatively low rare-gas abundances. Anderson's proposed solution to this paradox is that the OIB source is in fact an ancient residuum that is depleted in rare gases, but even more depleted in U, Th, and K, so that it has extremely low ^{4}He/^{3}He, ^{21}Ne/^{22}Ne and ^{40}Ar/^{36}Ar coupled with extremely low He, Ne, and Ar abundances.

The Iceland Plume-Ridge interaction provides an excellent means to monitor the He-abundance of upwelling plume material in a way that is insensitive to magma degassing processes. This on-ridge plume is known to have a pronounced effect on contaminating the He-isotope signature of MORB erupted along its adjacent spreading centers (Kurz et al.,1985). The Iceland plume actually has a larger and longer along-axis ^{3}He/^{4}He perturbation on the Reykjanes Ridge than it does on ^{87}Sr/^{86}Sr isotopes along this ridge (e.g., Schilling, 1986). If interpreted in terms of binary mixing between Iceland plume and MORB asthenosphere material, the fact that there is a stronger He perturbation than Sr perturbation along the Reykjanes Ridge suggests that $(\mathrm{He/Sr})_{\mathrm{plume}} > (\mathrm{He/Sr})_{\mathrm{MORB}}$. Since it is well agreed that the plume source is enriched in Sr and other incompatible elements relative to the MORB source, one is forced to conclude that at least the upwelling Iceland plume material has higher He abundances than the asthenosphere beneath the adjacent Reykjanes (and Kolbeinsey) ridges. The observation of plume-influenced ^{3}He/^{4}He along the Reykjanes Ridge is incompatible with the Andersenian inference that He-abundances in plumes are <100-fold lower than in MORB source material — if this were the case then contamination of the Reykjanes Ridge source by Iceland plume material would have no observable effect on He.

The opposing idea that the MORB source is much more highly degassed and radiogenic than the OIB source has been a cornerstone of all layered-mantle models for the evolution of the MORB source (e.g., Kellogg & Wasserburg, 1990; O'Nions & Tolstikhin, 1994; Porcelli & Wasserburg, 1995).

However, recent compilations of radiogenic and nonradiogenic noble gas isotopes in Ocean Island Basalts and Mid-Ocean Ridge Basalts suggest that this, too, is a misconception. Three recent syntheses of ratios of rare-gas abundances in OIB and MORB (Matsuda and Marty, 1996; Patterson & Honda, 1999; Ozima & Igarashi, 2000) present the same startling implication. While average He/Ne and He/Ar isotope ratios cluster around predicted mantle abundance ratios, in OIB He is systematically reduced relative to Ne and Ar, while in MORB, He is systematically concentrated relative to Ne and Ar (Ozima & Igarashi, 2000; Patterson & Honda, 1999). This holds for both radiogenic (^{4}He/^{21}Ne, ^{4}He/^{40}Ar) and nonradiogenic (^{3}He/^{22}Ne, ^{3}He, ^{36}Ar) isotope ratios, which correlate linearly on log-log ratio plots. A linear correlation implies a recent separation of the OIB and MORB sources. If the sources had separated a billion or more years ago, then the linear correlation between radiogenic and non-radiogenic isotope ratios would have been destroyed by subsequent radiogenic ingrowth that would evolve radiogenic isotope ratios back towards their mantle production values. (Since ^{4}He and ^{21}Ne are produced by the same U and Th decay processes, their production ratio is insensitive to chemical differentiation, and since K and U/Th have similar fractionation during melting processes, mantle ^{4}He/^{40}Ar production ratio is thought to mostly reflect the average age of the source material, varying between ~2 for a closed 4.5Ga system, and ~6 for present-day mantle production).

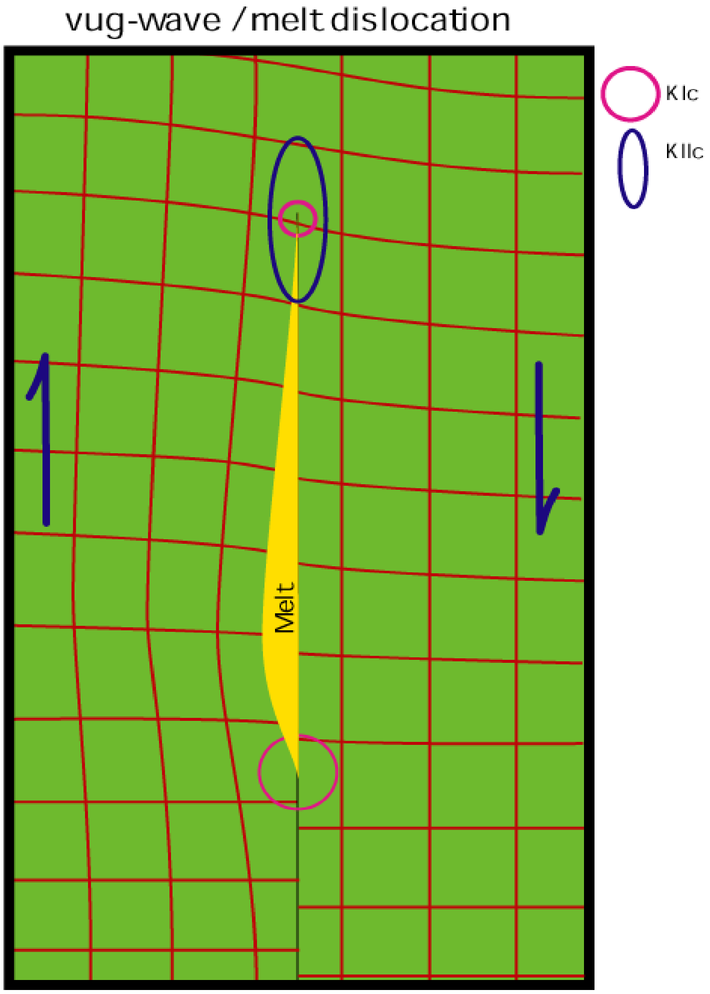
The complementary He/Ne and He/Ar abundances between MORB and OIB can be explained if the MORB source is a residue from OIB melting. However, it must be a relatively recent, gas-rich residue. For example, MORB typically has He/Ne>10 times the bulk mantle values. In the above radiogenic ingrowth models, in 1 Ga of ingrowth the MORB source would generate 36x ^{4}He for each ^{4}He received from the miniscule plume upwelling that supplies the ^{3}He to the MORB Reservoir. Radiogenic ingrowth would therefore produce 360x ^{21}Ne for each ^{21}Ne received from plume upwelling, which would destroy any linear ^{4}He/^{21}Ne correlation produced by preferential He-retention during OIB melt-extraction. For the upper-mantle MORB- source ratios of U+T/He used in the above layered-mantle evolution models, this separation must have occurred less than ~3-5 Ma ago, which is clearly incompatible with a ~1Ga residence time of a depleted MORB source.

In contrast, in the two-stage melting hypothesis for the formation of the MORB asthenospheric source, since the MORB source is the leftovers to OIB-melt extraction, preferential He-transfer from the OIB to MORB sources simply reflects preferential He-retention during OIB melt-extraction. This process would also lead to complementary He/Ne and He/Ar ratios in OIB and MORB that bracket mean mantle values for both radiogenic and non-radiogenic noble gas isotope ratios. Furthermore, if the MORB-asthenosphere was continually replenished by ~90% degassed upwelling plumes and recycled through spreading centers in ~300 Ma (Phipps Morgan &Morgan,1998), then there would be insufficient time for the MORB source to evolve towards radiogenic production values for He/Ne and He/Ar.

Melt migration in a deforming mantle: Implications of migrating non-dilatent 'melt-dislocations' for rapid magma transport and for the rheology of the asthenosphere

Phipps Morgan, J; Holtzman, B

We investigate a simple physical model for melt migration through a deforming mantle. Previous studies have mostly concentrated on melt migration through a static mantle, focussing on the role of melt buoyancy in driving tensile crack propagation. However, mantle deformation can provide a significant driving force for melt migration if the propagation of melt-filled ’dislocation’ significantly reduces the local strain-energy of the deforming mantle. The driving energy releases favoring the propagation of such a melt-dislocation or melt-filled ’vug-wave ’are the strain energy reduction within the surrounding deforming mantle and the gravitational energy release associated with buoyant melt ascent. Propagation-resisting energy ’sinks’ include the strain-energy rates associated with crack growth, closing the rear of the crack, and the viscous dissipation from migrating melt. We are currently exploring a fracture-mechanics development of this physics that assumes local adiabaticity.



Shear-cracks can fill as long as the crack-wall is ’overpressured’ relative to lithostatic. In a melting region, the volume increase upon melting will generate such an overpressure, whose magnitude will be governed by how easily the melt migrates away from where it is generated. (This overpressure would be huge if melt could not migrate, it would be the size of the product of the bulk compressibility (~50-100 GPa) and the volume increase due to partial melt (~0.01-0.10), or ~1-10 GPa.)

We initially explore these dynamics in a particularly simple form: their 2-D non-dilatent (or ’shear-crack’) limit. To analyze this we have developed a simple analytical theory that assumes idealized crack geometry. We are also exploring this physics by developing a 2-D numerical treatment of less-idealized crack geometries; and by furthermore trying to create a laboratory demonstration of this effect in gelatin.

Results from the analytical fracture-based theory suggest that shear cracks greater than 3 meters in length will spontaneously start to migrate in a mantle with 1 MPa deviatoric stress (Rubin, 1998) and a 3 MPa-m 1/2 fracture toughness (Atkinson, 1987). This is a much smaller lengthscale for crack initiation than that needed for tensile crack growth (70 m, Rubin, 1998), therefore we suggest that it may in fact be the dominant initial melt transport mechanism from the melting region. These melt-dislocations propagate rapidly, a ~10 m-long melt-dislocation would take only 1000 yr to traverse 100 km — thus this mode of melt migration may be a viable transport mechanism to rapidly transport small distinct batches of melt up to higher magma reservoirs. Furthermore, since a melt-dislocation involves a non-porous 'dike-like' mode of magma transport, this process can effectively transport xenoliths towards the surface.

An intriguing theoretical aspect of this work is that the viscous dissipation associated with moving the melt within the crack appears to be exactly equal to the strain energy rate needed to close the crack rear, so that these two effects are the dominant terms limiting the migration speed of a melt-dislocation.

An intriguing rheological aspect of this work is that the resulting melt+mantle aggregate viscosity will be highly anisotropic and extremely weak in shear-deformation parallel to the direction of melt propagation. For a 1%-melt-filled asthenosphere straining at a rate of 10^{-14} s^{-1}, this treatment predicts a σ^3 strainrate dependence with an effective viscosity of 1.3×10^{18} Pa-s. Furthermore, this mechanism for melt-migration will also tend to focus melt along the planes of maximum shear, which point towards a spreading ridge axis and towards the center of a symmetrically upwelling plume. In short, this appears to be a very interesting potential asthenosphere deformation and melt-transport mechanism!

Re-Os Isotope Systematics and PGE-Budgets of Continental and Oceanic Crust.

Peucker-Ehrenbrink, B

Eroding Continental Crust [collaborator B.-m. Jahn, Univ. Rennes, France]

Loess has been used extensively as a proxy for the chemical composition of eroding continental crust. Due to the siderophile and chalcophile nature of platinum group elements (PGE) and their affinity for trace mineral phases it is not (a priori) clear if sedimentary deposits such as loess are valid proxies for the PGE budget of the eroding continental crust. We have tested the applicability of this concept for PGE and the Re-Os isotope systematics.

Sixteen loess samples from China, Argentina, Central Europe and Spitzbergen, spanning a wide range in Sr-Nd isotope space, yield average $^{187}Os/^{188}Os$ of 1.05±0.23 (1σ). This value is similar to present-day seawater (1.06) and slightly less radiogenic than previous estimates for the eroding continental crust (1.20-1.32, Esser and Turekian, 1993). Average $^{187}Re/^{188}Os$ of 45.4 and $^{190}Pt/^{188}Os$ of 0.0195 are lower than previous estimates as well (Schmidt et al., 1997). Rhenium depletion ages appear to be affected by in situ weathering, as Re-Os data for three paleosols from the Chinese loess plateau yield significantly younger model ages (0.55-1.9 Ga) than intercalated loess deposits (2.09-2.84 Ga). As paleosols are characterized by significantly higher Re concentrations (181-617 pg/g) than loess (89-169 pg/g), this discrepancy is most likely caused by preferential mobility of Re (scavenging onto organic matter) relative to Os.

Pyrolite-normalized PGE pattern show striking regional differences. For instance, loess from Spitzbergen is characterized by Os/Ir of 4.5 and the highest ^{187}Re/^{188}Os (~200) of all analyzed loess samples. This pattern is typical of organic-rich sediments and can be linked to extensive outcrops of organic-rich sediments in Spitzbergen. Chinese loess, isotopically similar to average loess, shows highly fractionated PGE pattern with Os (31 pg/g) and Ir (25 pg/g) concentrations typical of UCC (Wedepohl, 1995; Schmitz et al., 1997). The slightly supra-chondritic Os/Ir of average loess most likely is characteristic of continental crust in general, as radiogenic ingrowth of ^{187}Os from Re-decay as well as preferential mobility of Os relative to Ir in subduction zones will increase the Os/Ir of continental crust with time. Average Ru (407 pg/g), Pt (390 pg/g), Pd (653 pg/g) and Re (237 pg/g) concentrations in Chinese loess are intermediate compared to previous estimates of UCC (Wedepohl, 1995; Schmitz et al., 1997). It thus appears as if PGE concentrations and ^{187}Os/^{188}Os of loess can be used as a proxy for average eroding continental crust.

Altered Oceanic Crust [collaborators W. Bach, S.R. Hart and J. Blusztajn, WHOI]

New Re-Os(PGE)-S isotope data for 50 samples from DSDP Hole 504B, covering 2 km of ocean crust, complement existing data for the upper 500 m of the lower crust recovered from ODP Hole 735B (Blusztajn et al., 2000). Os concentrations in 504B basalts vary from 0.4 to 275 pg/g (average: 25 pg/g), Re concentrations range from 0.16 to 15.9 ng/g (average: 3.3 ng/g), ^{187}Os/^{188}Os vary between 0.14 to 4.07 (weighted average: 0.27), whereas ^{187}Re/^{188}Os vary from 20 to ~30,000 (weighted average: 465). There are no discernible downhole trends in Os concentration or isotopic composition. However, Re concentrations are clearly higher in the sheeted dike complex, suggesting that Re enrichment may be related to greenschist-facies alteration. Neither Re nor Os exhibit significant correlations with S abundance or S isotope ratios, but Re enrichment appears to be confined to rocks with positive δ^{34}S values. The presently available data do not allow us to discern the host phases of Re in the rocks. Although S-rich samples (>1 wt.%) are generally high in Re (>9 ng/g), two of the most Re-rich samples have background S concentrations (around 0.1 wt./%). An interesting observation is that Re and U do not appear to be strongly coupled. U is enriched in rocks from the volcanic series and the transition zone, while Re is highest in rocks from the sheeted dike complex. This result may imply that along the flow path of downwelling seawater in a hydrothermal convection cell, U is removed at lower temperatures, or at faster rates, than Re. Rhenium-osmium isochron relationships require addition of radiogenic Os in the early stages of alteration, particularly to samples with low (<10 pg/g) Os concentrations.

Median PGE concentrations show a stepped pattern (pyrolite normalized) with low Os and Ir concentrations (<0.01 pyrolite), intermediate Ru concentrations (~0.02 pyrolite) and elevated Pt and Pd concentrations (~0.1 pyrolite). Significant fractionation between Os and Ir in duplicates of the same samples indicate that both elements are not necessarily hosted by the same phases.

Average values for Os (25 pg/g), Re (3.3 ng/g), ^{187}Os/^{188}Os (0.27) and ^{187}Re/^{188}Os (465) in DSDP 504B basalts are higher than weighted averages for the top 500 m drilled at ODP 735B: Os = 9 pg/g, Re = 0.42 ng/g, ^{187}Os/^{188}Os = 0.20 and ^{187}Re/^{188}Os = 115 (Blusztajn et al., 2000). We use the available data from both cores to estimate the average composition of relatively young (<15 Ma), altered upper (and middle) oceanic crust at: Os = 20 pg/g, Re = 1.3 ng/g, ^{187}Os/^{188}Os = 0.23 and ^{187}Re/^{188}Os = 425.

^{187}Re/^{188} Os - ^{190}Pt/^{188} Os Systematics of Crustal Reservoirs [collaborator G. Ravizza, WHOI]

Our data (Peucker-Ehrenbrink & Ravizza, 2001) show that near-surface reservoirs are characterized variations in ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os that are large compared to inferred differences between a chondritic lower mantle and the outer core (Walker et al., 1995). Black shales are characterized by extremely high ^{187}Re/^{188}Os (~1000), but low ^{190}Pt/^{188}Os (0.005). Upon weathering they loose a labile fraction that with ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os identical to seawater. Average eroding continental crust has elevated ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os, leading to coupled ingrowth in ^{187}Os/^{188}Os and ^{186}Os/^{188}Os. In contrast, metalliferous sediments, particularly marine Mn-nodules, have very high ^{190}Pt/^{188}Os (up to ~0.3), but low ^{187}Re/^{188}Os (~0.03). Over time such samples develop radiogenic ^{186}Os/^{188}Os that are not coupled to radiogenic ^{187}Os/^{188}Os. The large fractionation of ^{187}Re/^{188}Os and ^{190}Pt/^{188}Os in near-surface environments should be taken into account when interpreting ^{186}Os/^{188}Os - ^{187}Os/^{188}Os data for mantle-derived rocks.

References

Blusztajn, J., Hart, S.R., Ravizza, G., and Dick, H. J. B., 2000. Platinum-group elements and Osisotopic characteristics of the lower oceanic crust. Chem. Geol. 168, 113-122.

Esser, B.K. and Turekian, K.K., 1993. The osmium isotopic composition of the continental crust. Geochim. Cosmochim. Acta 57, 3093-3104.

Peucker-Ehrenbrink, B. and Ravizza, G., 2001. The marine Os isotope record. Terra Nova (invited review - in press).

Schmidt, G., Palme, H. and Kratz, K.-L., 1997. Highly siderophile elements (Re, Os, Ir, Ru, Pd, Au) in impact melts from three European craters (Sääksjärvi, Mien, and Dellen): Clues to the nature of the impacting bodies. Geochim. Cosmochim. Acta 61 (14), 2977-2987.

Walker, R. J., Morgan, J.W., and Horan, M.F., 1995. Osmium-187 enrichment in some plumes: Evidence for core-mantle interaction? Science 269, 819-822.

Wedepohl, K. H. The composition of the continental crust. Geochim. Cosmochim. Acta 59 (7), 1217-1232.

Input to the Mariana-Izu subduction factory (Leg 185 ODP): siderophile and chalcophile trace elements behaviour during seafloor weathering

Rouxel, O; Ludden, J

During Leg 185 (April-June 1999) two deep-water sites were drilled, one seaward of the Mariana Trench (Hole 801C) and one seaward of the Izu-Bonin Trench (Site 1149). Both of theses sites are located along the same flow line in Mesozoic Pacific oceanic crust, from about 170 to 130 Ma, and provide an unparalleled opportunity to study the geochemical and physical nature of old Pacific oceanic crust. The primary objectives of this leg were to investigate sediment subduction along this arc-trench system and to characterize the chemical fluxes during alteration of the oceanic crust. Here, we present the analyses of chalcophile and siderophile elements such as As, Se, Te, Ge, Sn, Cu, Zn in altered basalt and associated veins and interpillow material. The purpose of this work is the study of the mobility and net fluxes of metals and metalloids during low temperature interaction of seawater with oceanic basalt by analyzing variably altered basalts and alteration product as well as fresh samples and composites samples following the approach of Staudigel et al., 1996.

In site 801 alteration of the volcanic section is related to several discrete zones associated with ocherous Si-Fe-hydrothermal deposits and thick massive flows, with zones of remarkably unaltered basalts which contain fresh glass. The alteration pattern of the 500m of Jurassic crust at site 801 contrasts to simple downhole decreases in the extent of alteration observed at other sites drilled by ODP. The lithological sequence consists dominantly of aphyric basalt in the form of pillows, sheet flows, thick massive flows and breccias.

The alteration patterns of the basement core recovered at Site 1149 are similar to those of other shallow basement cores and old oceanic crust (e.g. Hole 765D, Argo Abyssal Plain Gillis et al., 1992) resulting from low temperature oxidative interaction between seawater and fractured oceanic crust. In general, the alteration is more intense at Site 1149 than at Site 801 and is associated with complex, multicolored alteration halos parallel to fractures. Halos at site 1149 represent 20% to 60% of total core in volume, as opposed to ~2% at site 801. Veining is also more intense at site 1149 with 35 veins/m compared to 25 veins/m at 801. The highly fractured zones (e.g. breccia, hyaloclastites, veins network and hydrothermal deposits) provided important controls on the fluid pathways and alteration.

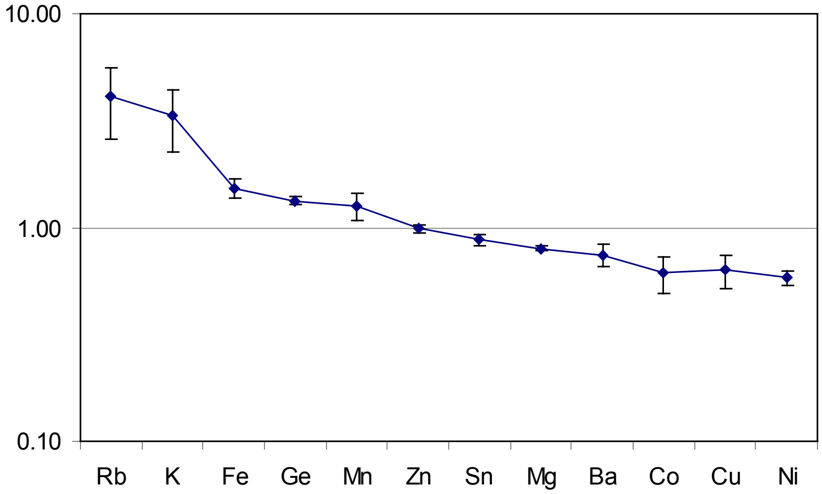


Figure 1: Enrichment factor of major and trace elements associated with the development of alteration halos.

Many siderophile and chalcophile elements behave as ordinary incompatible elements during magmatic processes in the absence of metal and sulfide phase. Furthermore, magmatic sulfide fractionation as well as subaerial magma degassing control significantly the behavior of the siderophile/chalcophile elements (see Yi et al., 2000). Another interesting feature of theses groups of elements is there relative solubility in hydrothermal fluids leading to the formation of massive sulfide deposits at various sizes at mid-ocean ridges (see Alt, 1995) or the transfer to subduction zone magmas (Noll et al., 1996). One poorly known part of the behavior of siderophile/chalcophile in the oceanic crust is the role of the pervasive low temperature alteration of the upper oceanic crust continuing off-axis for tens of million year.

To evaluate what elements are mobilized during the development of the alteration halos and to assess possible processes that cause the enrichment/depletion, we compared the compositions of the alteration halos and their adjacent fresh/least altered diabase (figure 1). Mg-depletion and K, Rb and to a lesser extent Fe enrichment reflect the alteration of the mesostasis to celadonite and Fe-oxyhydroxides. Low sulfur content (<100ppm), increase of FeIII/FeT ratio (up to 0.6) and depletion in metals Cu, Co and Ni are related to the breakdown of primary sulfides and olivine. However Sn and Zn are not significantly mobilized during alteration and are probably hosted by titanomagnetite. Surprisingly, Ge is significantly enriched in alteration halos and may result from scavenging from seawater by adsorption on ferrous iron precipitates. This Ge sink is consistent with Ge enrichment in iron and manganese-bearing oxides (Berstein, 1985). This low temperature Ge sink contrast therefore with the high temperature Ge flux in seawater (Mortlock et al. 1993). The magnitude of this sink may affect the oceanic Ge budget providing a reasonable candidate for the missing Ge sink in seawater (Mortlock et al., 1993).

Following the approach of Alt and Teagle, 1999, we calculated the C and S budget using the CO_2 and S contents of altered basalts, and the abundance of different alteration types, breccia and carbonate/sulfides veins. For sites 801 and 1149, the net sink of C in the oceanic crust have been evaluated at $1.9x10^{12}$ mol/an and $2.8x10^{12}$ mol/an respectively which is concordant with previous studies of old oceanic crust (>100Ma) at site 417 ($2.6x10^{12}$ mol/an) (Staudigel et al., 1996). Average S content of the upper oceanic crust determined at site 801 is about 420 ppm which is the same order of magnitude than for 504B (466 ppm, Alt 1995). S isotope data of secondary pyrite and marcasite in veins and in the groundmass are highly variable with $\delta^{34}S$ data ranging from magmatic values at 0‰ down to -45‰. S depletion and low $\delta^{34}S$ values in the upper oceanic crust have been attributed to partial oxidation of basaltic sulfides by seawater and isotopic fractionation between resultant aqueous sulfate and sulfide species (Andrews, 1979). However, the extreme isotopic variability of up to 20‰ within a single basalt sample and within a single sulfide grain and the apparent non correlation with the degree of alteration (and S content) and the isotope signature are consistent with an origin involving bacterial reduction of seawater sulfate (or oxidized magmatic sulfur). Microscopic examination of rocks from depths of 500m to 900m below the seafloor revealed that volcanic glass was being altered by invasive microbial channels and tubes (Fisk and leg 185 shipboard scientific party). Further analyses of sulfur isotopes data of glass-rich samples performed in conjunction with C and Se isotopes are in progress to provide geochemical evidence of microbial activity in the igneous oceanic crust.

A major component of ongoing research from Leg 185 is a coordinated shipboard sampling and analytical effort in order to develop a common set of samples leading to an unprecedented geochemical data set (major and trace elements, radiogenic and stables isotopes) for these two unique reference sites that represent the crustal input inventory to the Mariana and Izu-Bonin subduction factory.

Natural variations of Selenium, Copper and Antimony isotopes determined by MC-ICP-MS: application to seafloor hydrothermal systems.

Rouxel, O; Ludden, J; Carignan, J; Fouquet, Y

The recent development of new isotopic systems such as Fe, Cu, Zn considerably enlarge the potential for the study of biological and geological systems. Within the past 5 years, scientists have used multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for the precise isotope measurement of elements with high first ionisation potential. For elements such as Selenium (Se) and Fe which suffer the presence of argides molecular interferences, the development of hexapole collision cell allowing the removal of theses isobaric interferences is expect to provide new advance for the study of these elements. Se has six stable isotopes 74, 76, 77, 78, 80 and 82 with abundances of approximately 1, 9, 7.5, 23.5, 50 and 9%. Chemically similar to sulphur, Se occurs as +6, +4, 0 and -2 valences in a

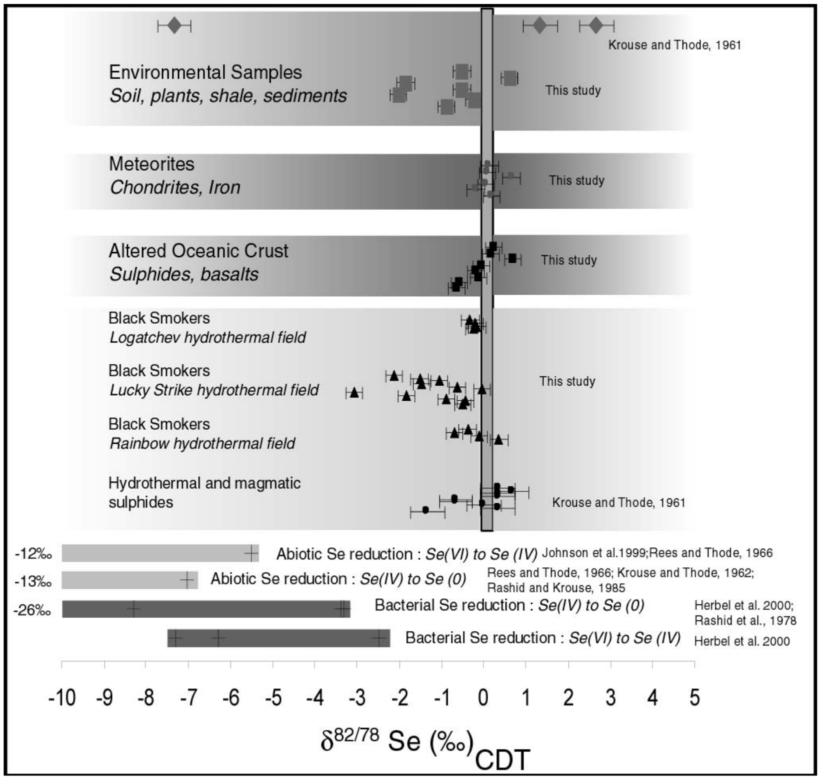


Figure 1 Summary of Se isotopes fractionation in natural samples and experimental studies (delta notation relative to the Canon Diablo Troilite CDT)

variety of organic compounds and geological settings. This makes the study of Se stable isotope ratios a potential indicator of geological and biological processes. Se isotopes were first determined in the early 60's (Krouse and Thode, 1962) using gas-source MS and recently by N-TIMS (Johnson et al., 1999) using the double spike technique. These previous results showed that the ^{82}Se/^{76}Se ratio vary by as much as 15‰ and indicate that reduction of soluble oxyanions is the dominant cause of Se isotope fractionation (Figure1). Natural variation of Sb isotope ratios is not documented. Despite the heavy mass of this element (2 isotopes at mass 123 and 121), redox changes of Sb(V) and Sb(III) species as well as biological activity and volatilization can produce significant isotope fractionation in natural systems. Some preliminary results of Cu isotopic compositions (Maréchal et al., 1999; Zhu et al., 2000) showed the existence of variations of up to several per mil amongst natural samples.

In this study, we report a technique for the isotopic analysis of Se and Sb using continuous flow hydride generation coupled to a micromass MC-ICP-MS after chemical purification. This new technique combine: (1) the classic and easy-to-operate gas source mass spectrometry technique with instrumental mass fractionation corrected using a "standard-sample bracketing" approach; (2) high sensitivity using gaseous hydride introduction in the plasma torch; (3) precise and accurate isotope ratios provided by the magnetic sector and multiple collector device MC-ICP-MS. The estimated external precision of the ^{82}Se/^{76}Se isotope ratio is 0.5‰ (2σ) whereas the precision of the ^{123}Sb/^{121}Sb isotope ratio is 0.06‰ (2σ). The data are reported relative to our internal standards. Cu isotopic ratios are reported relative to the measured ratio for NIST 976 Cu-isotope international standard. No chemical pretreatment was necessary for the analysis of Cu-sulphides as reported by Zhu et al.(2000). Based on replicate measurements of standards doped with different matrix composition as well as sample analysis duplicate, the external precision of the δ^{65}Cu data is 0.08‰ (2σ).

In this study we have used Se, Cu, Sb in conjunction with S isotopes to provide further insights on the geochemistry of these elements. Several hydrothermal fields were studied along the Mid Atlantic Ridge; in particular these include: (1) Lucky Strike located near the Azores Triple Junction; (2) Logatchev and Rainbow in an ultramafic hosted rock environment. At Lucky Strike, the setting of the hydrothermal field in a caldera system with abundant low-permeability layers of cemented breccia results in fluid cooling and mixing below the hydrothermal field. Based on vent structures, mineral abundance, and geochemistry, two types of hydrothermal deposits were identified. The δ^{34}S (between 1.5 and 4.5 ‰) and Se values (up to 2000 ppm) of Cu-rich sulphides suggest a high temperature undepleted hydrothermal fluid, whereas pyrite and marcasite generally have lower δ^{34}S values (down to -1.0‰) and low concentration of Se (<50ppm). Se-depletion and sulphur isotope fractionation result from the sub-seafloor precipitation during the progressive oxidation of the fluid. The overall isotopic variation for δ^{65}Cu for chalcopyrite is 1.2‰ with a mean of 0.03‰. For δ^{82}Se the values range from meteoritic and magmatic values (near -1.1‰) to values depleted in ^{82}Se of -5.5‰. For Se isotopes, the present results show consistent and distinct geochemical signatures for massive sulphides hosted hydrothermal deposits and Si-slab hosted active chimneys. Se isotopes are thus an important source indicator and imply the leaching and mixing of a fractionated Se source beneath hydrothermal chimneys with the hydrothermal fluid. Fluid cooling and oxidation in subsurface environment may provide suitable conditions for microbial activity which are recorded by Se isotopes.

The Logatchev and Rainbow hydrothermal deposits have a restricted range of δ^{34}S of 4.6 to 6.1‰ and 2.2 to 5.5‰ respectively. The sulphur isotope variations within and between chimneys are explained by the process of sulphate reduction in the near surface environment. Cu-isotope fractionation is large (up to 4.4‰) and the highest isotopic composition are found in active chimneys formed from high temperature undepleted fluid whereas negative values are recorded in inactive vents and massive sulphides. Isotopic fractionation occurring in the upflow zone and within the deposit itself may combine to produce such an isotopic signature.

Preliminary results on Sb isotopic compositions of hydrothermal zinc and iron sulphides show a variation of 0.8‰ which is 10 times higher than the analytical precision of 0.08‰. This demonstrates the existence of natural variations of the Sb isotopic composition, which can be analyzed at the ng level by MC-ICP-MS.

The natural variations of Se, Cu and Sb isotopes obtained in this study highlight the potential use of these elements as tracers in hydrothermal systems and probably also in other disciplines such as cosmochemistry and biogeochemistry.

Parametrization of trace element partitioning on the mantle solidus at pressures up to 3.4Gpa

Salters, V J M; Longhi, J E; Bizimis, M

We present new experimental partitioning data for a range of petrogenetically important elements up to pressures of 3.4 GPa which is an extension of our previous study (Salters and Longhi, 1999). The experiments are designed to mimic melting beneath mid-ocean ridges. The available data indicates that the partition coefficients are pressure, temperature and composition dependent. Therefore, if melt is extracted continuously during the adiabatic rise of mantle material, knowledge of partition behavior over the appropriate range of pressure, temperature and composition is required. For this purpose, we have parameterized the partitioning behavior of the REE, Hf, Zr, U and Th based on a simple thermodynamic model. This parameterization shows that although it cannot be used for retrieving thermodynamic constants yet, the parameterization does yield a description of the partitioning behavior, which is useful for modeling decompression melting.

Our parameterization shows that on the peridotite solidus the partitioning of trace elements is strongly dependent on the Ca and Al-content of the clinopyroxene. However, REE are always incompatible in cpx on the peridotite solidus at pressures up to 3.4 GPa. For garnet the data indicates that the heavy REE partition coefficients decrease with increasing pressure. One surprising result of the modeling of the partitioining is that for both cpx and garnet the substitution mechanism for the large tetravalent ions (U and Th) is different than for small ions (Hf and Zr). Our data indicates that Pb is more incompatible than Ce and in garnet Ce and Pb have similar partition coefficients. Therefore, in order to explain the near-constant Ce/Pb ratios in MORB and OIB a residual phase with high Pb partition coefficients is required. It is suggested that sulfides are the most likely phase that buffer the Pb content in the melt.

Figure 1 and 2 show the trace element fractionations as a results of melting during adiabatic melting. This is the first model that adjust partition coefficients in response to changes in P, T and X during melting. This more realistic model of trace element partitioining allows for a better estimation of degree and average depth of melting as well as the modeling of the major element variations in conjunction trace element fractionations.

Clinopyroxene on the peridotite solidus is unable to fractionate U from Th to large enough extend that it can ceate the ^{230}Th excess in MORB. Garnet can fractionate U from Th effectively and is required for MORB genesis (see figure 1). Previous studies showed that the coupled Sm/Nd and Lu/Hf fractionation in MORB require residual garnet. The new partitioning parameterization of the REE and Hf is agreement with these previous studies see figure 2. Furthermore, the parametrization for clinopyroxene from this study results in estimates of partition coefficients that are similar to estimates using the Wood and Blundy (1997) model.

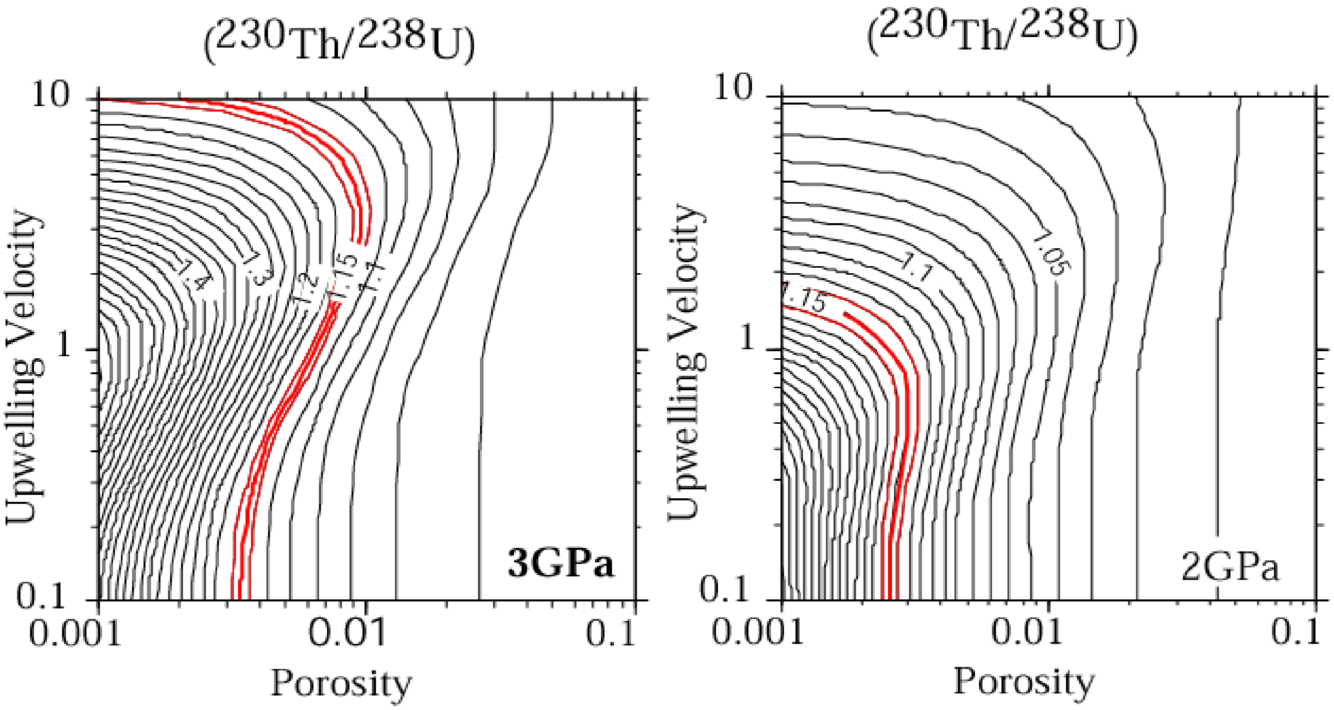


Figure 1 Contours of ^{230}Th-excesses for melts generated using the cpx and garnet parameterizations of this study for a range of upwelling velocities (0.1-1-cm/year) and a range of initial porosity (0.1%-10%). Melting model used is that of Spiegelman and Elliott (Spiegelman and Elliott, 1993), using the web-based program Usercalc (Spiegelman, 2000). Lines in red are the 15% ^{230}Th-excess, which is the average excess of MORB. When melting starts at 3 Gpa 15% excess can be created at porosities that are up to 1% and matrix upwelling velocities of between 2 and 7 cm/year. In contrast, if melting starts at 2GPa, i.e. no garnet present, 15% excess can only be created at porosities less than 0.3% and upwelling velocities of less than 2 cm/year.

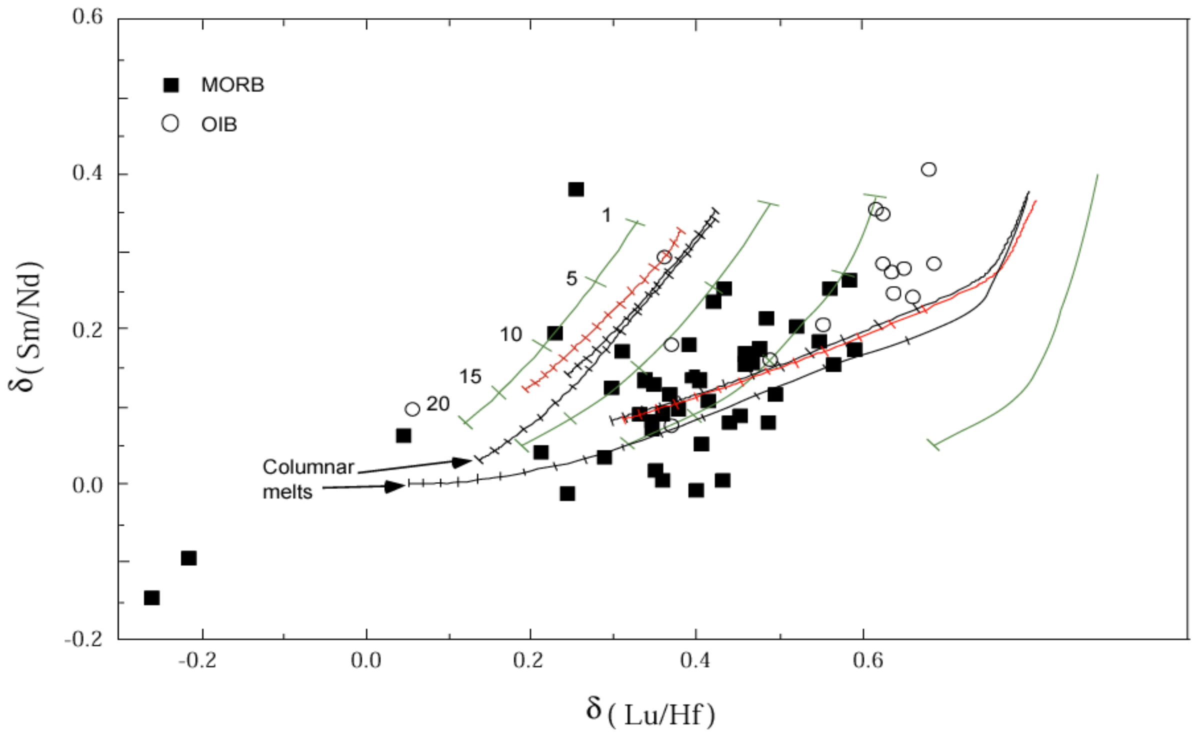


Figure 2 $\delta_{(Lu/Hf)}$ versus $\delta_{(Sm/Nd)}$ diagram with various melting curves for the different trace element parameterization. Melting curves are the aggregated melts from the complete melting regime. Except for where noted melting curves are for triangular melting regime. Green curves are old models (Salters and Hart, 1989), numbers at tick marks on left most green curve is extend of melting (in percent) for a peridotite unit that has undergone the largest degree of melting in the melting regime (i.e. ascended directly under a ridge). Black curves use the trace element parameterization presented in this study combined with the Longhi model for fractional melting at decreasing pressure. Tick marks are at 1% melt increments of the peridotite unit that has undergone the largest degree of melting in the melting regime. Red curves are the same as the black curves, but Wood and Blundy parameterization for cpx partitioning. The experimental database for both cpx partitioning models was the same.

GEOROC – the Online Geochemical Database: Now for Oceanic Islands, Island Arcs and Large Igneous Provinces

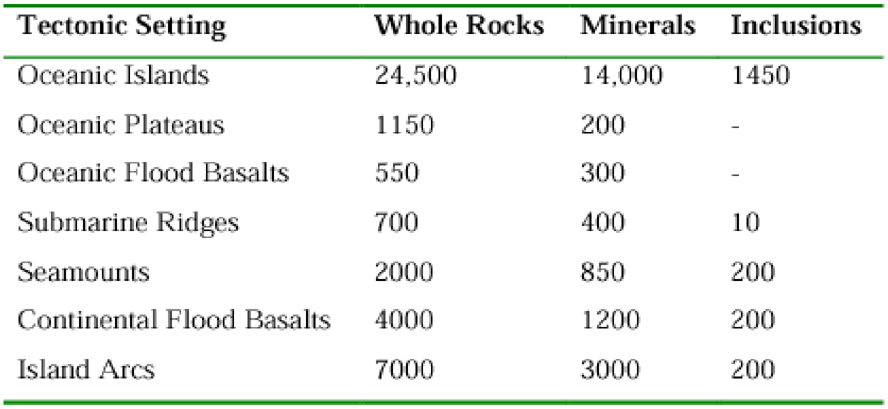
Särbas, B; Busch, U; Jäckel, P; Maissenbacher, P C; Nohl, U; Schäfer H

The estimation of the chemical and isotopic inventories of the Earth's reservoirs and of the chemical fluxes between them is one of the aims of GERM initiative. It requires the collection and evaluation of a large and rapidly growing volume of published analytical chemical data. The success of GERM thus depends on the availability of tools that provide these data in easily accessible form.

Such a tool is the geochemical database GEOROC of the Max-Planck-Institut für Chemie in Mainz. GEOROC is accessible over the Internet http://georoc.mpch-mainz.gwdg.de/. The database GEOROC contains published chemical analyses of whole rocks, volcanic glasses, minerals, and inclusions. The chemical data are combined with additional information comprising, for instance, geographical location, rock name, rock mode, grade and type of alteration, sampling technique, analytical method, location of method, analytical uncertainty, and reference source (Nohl et al., 1999; Sarbas et al., 1999).

Currently, GEOROC covers data on igneous-rock samples from oceanic islands, island arcs, and Large Igneous Provinces (Sarbas et al., 2000). Data on samples from mid-ocean ridges are compiled in the database PetDB, which uses an almost identical database structure (Lehnert et al., 1999). For samples from oceanic islands, almost all published analyses are included. Newly published papers are added as soon as published. Samples from Large Igneous Provinces are divided into the tectonic settings oceanic plateaus, oceanic flood basalts, submarine ridges, seamounts, and continental flood basalts (according to a classification of Coffin & Eldholm, 1994). At present, about 80% of the published analysis on oceanic LIP's and about 40% of the data on continental LIP's are included in GEOROC. Recently, data entry was extended to samples from island arcs. So far, analyses for the Aleutian, Kamchatka, Kurile, Honshu, Izu-Bonin-Mariana, Tonga, Kermadec, Lesser Antilles and South Sandwich arcs are available.

GEOROC includes the chemical analyses of about 40,000 whole rocks (including volcanic glasses), 20,000 minerals, and 2000 mineral and melt inclusions published in about 1700 papers (see Table 1). These analyses comprise about 800,000 single values.



Tectonic Setting	Whole Rocks	Minerals	Inclusions
Oceanic Islands	24,500	14,000	1450
Oceanic Plateaus	1150	200	-
Oceanic Flood Basalts	550	300	-
Submarine Ridges	700	400	10
Seamounts	2000	850	200
Continental Flood Basalts	4000	1200	200
Island Arcs	7000	3000	200

Table 1 Numbers of analyses currently available in GEOROC for samples from the different tectonic settings.

The GEOROC web interface uses Active Server Pages that combine HTML and server-side Visual Basic scripts to create and run dynamic web pages. It offers several possibilities of data selection: by bibliography (author name and/or publication year), by tectonic setting, by geography (geographic name or latitude and longitude), by chemistry, and by petrography (rock name or sample name). In further steps, the query can be refined by other criteria. Examples are the type of material (whole rock, volcanic glass, mineral, inclusion), the rock type (e.g., volcanic, plutonic), the rock name (e.g., basalt, rhyolite, granite), and the sample name.

The result of a query is shown as an HTML table. This table can be downloaded as a comma-separated text file and saved as an Excel spread sheet on the client machine. In addition to the GEOROC version available in the internet, a CD-ROM version of GEOROC is available now. It requires a PC with Windows 98, Me, 2000 or NT, Microsoft Access 2000, and Personal Webserver (Windows 98) or Internet Information Server (Windows Me, 2000, NT).

Essential for a scientifically sound usage of databases are complete chemical analyses and an unequivocal correlation of chemical data and metadata. These metadata provide important criteria for extracting and limiting chemical data, in order to meet specific requirements of data quality and other parameters. A large portion of published data reveals a serious deficit in this respect. Therefore, we provide a set of Excel input forms that include fields for all necessary data. These forms should be used by future authors as guideline for publications. They also can be used to provide input data for GEOROC.

References

Coffin, M. F., Eldholm, O.; Large Igneous Provinces: Crustal Structure, Dimensions, and External Consequences, Rev. Geophys. 32, 1-36 (1994)

Lehnert, K., Su, Y., Langmuir, C.H., Sarbas, B., Nohl, U.; A Global Geochemical Database Structure for Rocks, Geochemistry, Geophysics, Geosystems 1, No. 1999GC000026 (2000)

Nohl, U., Sarbas, B., Jochum, K. P., Hofmann, A. W.; GEOROC, the MPI Rock Database: Introduction of the Web Interface, EOS, Trans. AGU 80 (46), Fall Meeting Suppl., F1177 (1999)

Sarbas, B., Jochum, K. P., Nohl, U., Hofmann, A.W.; GEOROC, the MPI Geochemical Rock Database: A New Tool for Geochemists, EOS, Trans. AGU 80 (46), Fall Meeting Suppl., F1184 (1999).

Sarbas, B., Nohl, U., Busch, U., Schäfer, H.; LIP and IAV Data in GEOROC – the MPI Geochemical Database Expands to Samples from Large Igneous Provinces and Island Arcs, EOS, Trans. AGU 81(48) Fall Meeting Suppl. (2000) F1284.

Constraining Volcanic CO_2 Fluxes Using the CO_2 / ^{3}He Ratio in Submarine Lavas

Shaw, A M; Hilton, D R; Macpherson, C G; Sinton, J M.

Constraining the flux of CO_2 associated with magmatic activity is fundamental to understanding carbon cycling between the mantle and the hydrosphere-atmosphere system. One approach to this problem [Marty and Tolstikhin, *Chem. Geol.,* 1998] combines an assumed ^{3}He flux with a measured $CO_2/^3$He ratio in various media (basalt glasses, geothermal fluids etc.). In this case, the validity of any derived flux calculation is limited by the assumption that the measured $CO_2/^3$He ratio is representative of the underlying mantle source. The observation that the $CO_2/^3$He ratio was remarkably invariant ($\sim 2 \times 10^9$) in MORB worldwide [Marty and Tolstikhin, *Chem. Geol.,* 1998] suggested that this ratio was not fractionated upon degassing, implying similar solubilities for He and CO_2. However, more recent studies, e.g. of geothermal fluids from Loihi Seamount [Hilton et al., *Nature,* 1998], reveal that the $CO_2/^3$He ratio can be highly variable and that the solubilities of He and CO_2 are composition dependent. In this presentation, we have studied a diverse suite of well-characterized samples from the Manus Back-arc basin to examine factors which control this key $CO_2/^3$He parameter: 1) magma composition, 2) source mixing, and 3) the extent and mode of degassing.

CO_2, H_2O, He, Ar, and Ne analyses have been carried out on 14 tholeiitic glasses from the Manus basin. These lavas are distinguished petrologically on the basis of major and trace element chemistry and radiogenic isotopes as MORB type-1, MORB type-2, Back-arc basin basalt (BABB) and arc-type. Additionally ^{3}He/^{4}He ratios greater than MORB ($\sim 8R_A$) identify a plume component superimposed on all lava types [Macpherson et al., *Geology,* 1998]. We find that samples with the highest water contents (the BABB and the Arc-type lavas) are the most under-saturated with respect to CO_2 compared to the MORB type lavas. The $CO_2/^3$He ratio in the vesicle phase of the MORB-1 glasses is $\sim 3\text{-}7 \times 10^8$, lower than typical MORB. The MORB-2 and the BABB lavas have a slightly higher range ($\sim 2\text{-}20 \times 10^9$), while the arc type lavas have a significantly higher $CO_2/^3$He ratio.

To investigate the mode and degree of degassing and its affect on the $CO_2/^3He$, we have measured the $^4He/^{40}Ar^*$ ratio. It is anticipated that this ratio will increase with degassing due to the lower solubility of Ar in basaltic magma. Results indicate the following:

- degassing has altered the initial $CO_2/^3He$ ratio to lower values
- different petrologic types have undergone different degrees of degassing
- the higher temperature extraction steps (representing the gas dissolved in the matrix) show evidence of crustal contamination from a source having a $^4He/^{40}Ar^*$ ratio lower than its upper mantle production value (~ 2).

It is apparent that there is a petrologic control exerting an influence on the $CO_2/^3He$ ratio, in addition to a compositional control in terms of water content and that the initial ratio may be altered upon degassing to lower values. The Manus samples provide a unique opportunity to realistically examine the factors controlling the $CO_2/^3He$ ratio, which is an essential parameter used to quantify magmatic CO_2 fluxes.

3-D spherical mantle convection simulations of D": fluxes of segregated oceanic crust and depleted lithosphere at the base of the mantle

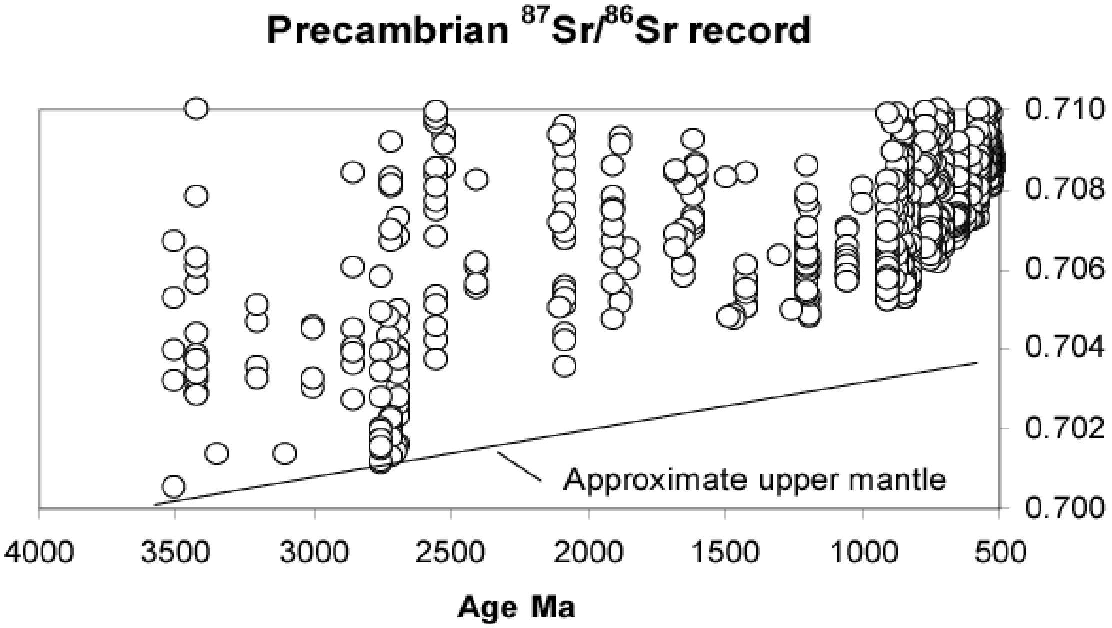
Stegman, D

We consider two models of differing radiogenic content: one of McDonough and Sun, 1995 with ~2.75 C1 abundances for the bulk silicate Earth and another of ~1.5 C1 abundances (Calderwood, 2000). Both models have uniform distribution of heat producing elements in the mantle, but have different partitioning between the amount of internal heating and bottom heating given a total heat flux similar to that of the Earth. The present day plate motions are used as a surface boundary condition. Plates are approximated as downwellings and we have attempted to provide these downwellings witha crude differentiation into a dense, eclogitic component and a lithospheric component. The downwelling reaches the core-mantle boundary while it is still cold, and due to the temperature-dependent viscosity, as it heats up the denser, eclogitic material will gravitationally settle while the lighter component will become more easily entrained by the overlying flow. This model is similar to that of Christensen and Hofmann, 1994, except that we are not tracking specific isotopic fractionation or evolution. We attempt to quantify the fluxes and residence time of such segregration of subducted oceanic crust.

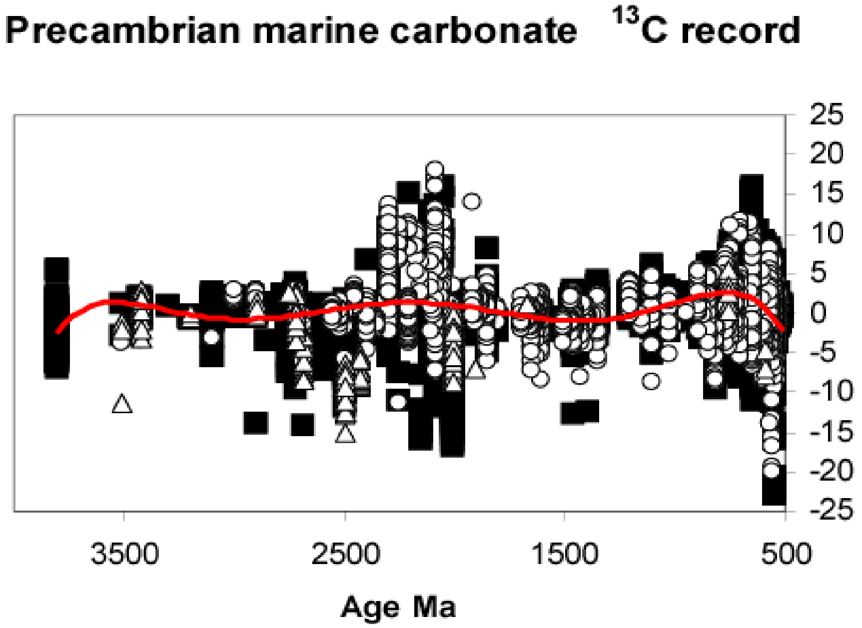
Precambrian seawater isotope record

Shields, G A; Veizer, J

A compilation is presented of marine carbonate Sr, C and O isotope data from the entire Precambrian as well as Lower Cambrian (4.0–0.53 Ga). These data were published by various authors in 114 research articles over the past forty years and represent approximately 1200 $^{87}Sr/^{86}Sr$ analyses and over 10,000 coupled $\delta^{13}C/\delta^{18}O$ analyses. An attempt has been made to assign all data to one of sixteen Precambrian subdivisions based on current age constraints. Where age constraints are too poor for this task, these data have been rejected for now. In addition, $\delta^{18}O$ data have been rejected that were mineral non-specific. Although some generalizations about the relative degree of sample preservation can be made, this was not a factor in data rejection. Only 3% of published data have been rejected.



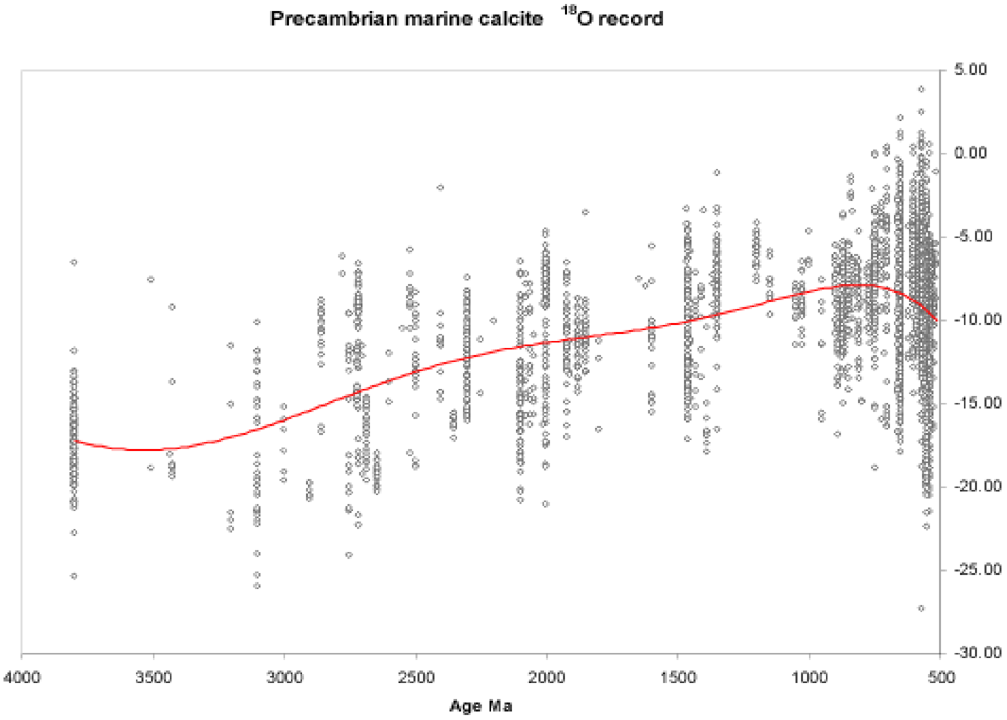
All $^{87}Sr/^{86}Sr$ data have been normalized to a NBS 987 standard value of 0.71025 and are shown plotted in Figure 1 below. No corrections have been carried out for ^{87}Rb decay because these lead to unjustifiable errors, and commonly considerable overcorrection. The reason for such errors lies in the inherent assumption of congruent leaching behavior between Rb and Sr over geologic time as well as during laboratory procedures, while any errors in the absolute ages of samples will also lead to significant errors in estimating initial $^{87}Sr/^{86}Sr$ ratios. The considerable data spread within and between sample populations implies that post-depositional alteration has significantly affected carbonate $^{87}Sr/^{86}Sr$, causing an increase in measured $^{87}Sr/^{86}Sr$ in most cases. Therefore, the lower part of the $^{87}Sr/^{86}Sr$ band is likely to represent a maximum constraint on contemporary seawater $^{87}Sr/^{86}Sr$. Although pre-Neoproterozoic isotope data are scarce and suffer from relatively poor age constraints, they reveal a marked switch from mantle-like $^{87}Sr/^{86}Sr$ before ca. 2.5 Ga to more radiogenic $^{87}Sr/^{86}Sr$ after ca. 2.5 Ga. This switch is consistent with a change from a “mantle”-buffered to a “river”-buffered global ocean around this time, and could be the result of the combination of 1) the exponentially decreasing heat flux from the mantle and 2) the concomitant growth of the continents (Veizer, 1989). The Neoproterozoic-Cambrian $^{87}Sr/^{86}Sr$ record is more complete and reveals a rise from 0.7052 to 0.7092 over 500 Ma, which can be used to support limited global stratigraphic correlation of marine successions (Jacobsen and Kaufman, 1999; Shields, 1999).



Precambrian marine carbonate ^{13}C record

The Precambrian $\delta^{13}C$ record is more complete by comparison but suffers from poor age constraints. $\delta^{13}C$ data shown in Figure 2 below have been divided according to their carbonate mineralogy into calcite (black squares), dolomite (open circles) and siderite/ankerite/rhodocrosite/magnesite groups (open triangles). Extremely negative $\delta^{13}C$ (<-5‰) is found throughout the Precambrian and generally derives from individual studies, suggesting that these samples have been influenced by diagenetic exchange with organically-derived carbon. However, anomalously high $\delta^{13}C$ (>+10‰) is associated with two intervals during the Proterozoic: the middle Paleoproterozoic (2.3–1.9 Ga) and the middle Neoproterozoic (0.8–0.6 Ga). It is unclear to which extent marine carbonate $\delta^{13}C$ for either period represents anomalously high seawater bicarbonate $\delta^{13}C$ or whether the oceans were less homogeneous with respect to $\delta^{13}C$ at these times due to, for instance, ocean stratification. Aside from these two episodes, marine carbonate $\delta^{13}C$ remained close to 0‰ during the Precambrian (cf. Schidlowski et al., 1975).

The Precambrian $\delta^{18}O$ record has also been divided according to carbonate mineralogy. Only the calcite $\delta^{18}O$ data are shown here in Figure 3. The wide range of data provides evidence for considerable diagenetic alteration, which has generally caused $\delta^{18}O$ to decrease. Mean $\delta^{18}O$ appears to have increased through the Precambrian in both calcites and dolomites. However, the considerable data dispersion and poor sampling coverage make this and other features of the $\delta^{18}O$ record difficult to interpret at present.



References

Jacobsen, S.B and Kaufman, A.J. (1999) The Sr, C and O isotopic evolution of Neoproterozoic seawater. Chemical Geology 161, 37-57.

Schidlowski, M., Eichmann, R. and Junge, C.E. (1975) Precambrian sedimentary carbonates: carbon and oxygen geochemistry and implications for the terrestrial oxygen budget. Precambrian Research 2, 1-69.

Shields, G.A. (1999) Towards a new calibration scheme for the Terminal Proterozoic. Eclogae Geologicae Helvetica 92, 221-233.

Veizer, J. (1989) Strontium isotopes in seawater through time. Annual Review Earth Planetary Science 17, 141-167.

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Maps