Conference Volume

Lyon
May 20-22, 2003

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http://earthref.org/GERM/

GERM Workshop

Lyon, France
May 20-22, 2003

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Welcome to the Geochemical Earth Reference Model Workshop

The **Geochemical Earth Reference Model** (GERM) initiative was born in 1996, with its first workshop in Lyon. At the time we argued that we need a reference model of the Earth that combines all the best possible evidence towards a self-consistent, but complete geochemical reference model of the Earth. Ideally such a model includes a complete set of “reservoirs” that describe planet Earth with respect to the chemical composition of all reservoirs, the fluxes between them, and their evolution through time. The ideal geochemical Earth reference model is probably the unattainable “holy grail” of geochemistry but even a “straw-man” GERM is very useful, for the use as a working model that is continuously refined. The “holy grail” may remain elusive, but the GERM process is nevertheless important — the journey is becoming the primary goal.

The GERM journey allowed us to make much progress over the last seven years. This progress can be measured in terms of well-cited papers from GERM workshops or special sessions at Goldschmidt conferences and AGU meetings. Some most important advances were made in the improvement of the scientific infrastructure for geochemistry. This includes the establishment of the GERM website, the development of the now-thriving journal G-cubed, and significant advances towards improving the methods of data publication in geochemistry. We brought up the issue of the need for making sure that geochemical samples are archived, together with the data. Much of these advances were published in various reports, commentaries and articles that can be found on the GERM website.

The GERM journey has been and continues to be most productive. We have a great pre-workshop modeling course, an impressive lineup of keynote speakers and discussion leaders, and a set of important breakout sessions. Thank you for coming to Lyon and for joining us at GERM 2003 !!!

Hubert Staudigel and Francis Albarède

For the GERM Steering Committee, and
the Conveners and Science Advisory Committee of GERM 2003

Thank You

This workshop has been supported by the National Science Foundation, the Ministry of Research and CNRS-INSU. We also appreciate donations of the District of Lyon, Hewlett Packard, VG instruments, Elsevier Publishers, and Cambridge University Press. This workshop was organized with the untiring help of Patty Keizer and Agnes Ganivet. We thank both of them — this would not have been possible without them!

Table of Contents

Schedule for GERM Modeling Workshop

Date: **19 May 2003**
Location: **Multimedia Room E0014** (ground floor)

08:15 Coffee and setup with computers.

08:30 **Lou Derry** Basic concepts in reservoir modeling: residence time, response time, steady state and periodic forcing.

Exercise 1 with MATLAB — Introduction to graphics: plotting analytical solutions.

09:15 **Lou Derry** Multiple reservoirs: steady state solutions, non-steady state solutions, the eigenvalue problem, real problems and complex eigenvalues.

Exercise 2 with MATLAB — Solution of simultaneous equations, extraction of eigencomponents.

10:00 Coffee.

10:15 **Lou Derry** Numerical approximation using MATLAB: Introduction to the ODE solver.

Exercise 3 with MATLAB — numerical solution of coupled non-linear ODEs.

11:00 **Yves Godderis** Description of the global carbon cycle, continental silicate weathering and the climate: an useful but still poorly constrained negative feedback. How to calculate atmospheric P_{CO2} and climate through time: an example with a 0D model?

12:00 Lunch break.

01:00 **Yves Godderis** Can we trust global carbon cycle models? The importance of degassing forcing functions, the correlation between the global climate and atmospheric P_{CO2} and the strontium isotopic ratio of seawater. Can we improve global carbon cycle models? What is the lithological effect in carbon cycle models? What is the role of mountain uplift in physical erosion? Coupling geochemical models to climate models: from 0D to (almost) 3D. The use of isotopes in global carbon cycle models: basic concepts and evolution of isotope ratios in models.

02:30 Coffee.

02:45 **Bernard Bourdon** Introduction to U-series: decay equations, basic concepts and some analytical solutions for a closed system.

03:15 **Bernard Bourdon** Dating with U-series: dating with U-Th-Pa “simple” open-system models.

03:45 **Bernard Bourdon** Modeling two-phase flow systems: a guided tour including dynamic, equilibrium and double porosity melting models; transport of nuclides in aquifers; simple models for chemical weathering using U-series.

05:15 Ice Breaker and Posters (in the basement of the school).

Program Summary Workshop

May 20 in 2003	May 21 in 2003	May 22 in 2003
Location of all Plenary Sessions: Amphitheater A, 4th Floor of the School		
8:45 – 10:15	8:45 – 10:15	8:45 – 10:15
Welcoming Remarks Francis Albarede **Introduction to Breakout Sessions** Hubert Staudigel	**Subcontinental Lithosphere Structure** Rob van der Hilst **Subcontinental Lithosphere Composition** Graham Pearson	**Recycling and Mantle composition** Rick Carlson **Solid Earth Water-Cycling** Jacqueline Dixon **Discussion Leader** Jason Phipps-Morgan
Coffee Break 10:15 – 10:45		
10:45 – 12:45	10:45 – 12:45	10:45 – 12:45
Mass Balances at Subduction Zones John Ludden **Dehydration and Seismicity at Arcs** Geoff Abers **Discussion Leaders** Abers-Ludden	**Mantle Geochemistry** Claude Allegre **Mantle Structure and Dynamics** Paul Tackley **Discussion Leader** Yanick Ricard	**Rivers and Erosion** John Milliman Christian France-Lanord **Discussion Leader** Lou Derry
Lunch Break 12:45 – 13:45		
13:15 – 13:45	13:15 – 13:45	13:00 – 13:45
Meeting-room (ground floor)	Amphitheater A (4th floor)	Amphitheater A (4th floor)
CLOSED LUNCH MEETING **Editors' Round Table**	**OPEN LUNCH MEETING** **Editors' Round Table**	**OPEN LUNCH MEETING** **The future of PetDB, GeoRoc, NavDat and GERM** Rick Carlson, Anthony Koppers, Kerstin Lehnert, Hubert Staudigel

May 20 in 2003	May 21 in 2003	May 22 in 2003
13:45 – 15:30	13:45 – 15:30	13:45 – 14:45
Location of Breakout Sessions: See Detailed Program		**Mass Transfer within the Continental Crust** Mark Harrison **Discussion Leader** Francis Albarede
BREAK OUT SESSIONS **Editors' Round Table** Chair: Frank Podosek **GERM Handbook** Chair: Bill McDonough **River Databases** Chair: Lou Derry **GERM Website Review** Chair: Rick Carlson	**BREAK OUT SESSIONS** **Editors' Round Table** Chair: Frank Podosek **SAMPLES** Chair: Steve Goldstein **River Databases** Chair: Lou Derry	
		14:45 – 15:30
		WORKING GROUP DISCUSSION **Data Publication in Geochemistry** Frank Podosek
Coffee Break 15:30 – 16:00		
16:00 – 17:00	16:00 – 17:00	16:00 – 17:15
New Trends in Chemical Oceanography Ed Boyle **Discussion Leader** Francis Albarede	**BioGeochemical Cycles** Bill Schlesinger **Discussion Leader** Hubert Staudigel	**WORKING GROUP DISCUSSION** **GERM Handbook** Bill McDonough **GERM Website Review** Rick Carlson **SAMPLES** Steve Goldstein **River Database** Lou Derry
17:00 – 17:30	17:00 – 17:30	
Cyber Infrastructure in Geochemistry NSF/CNRS	**GERM Website Demo** Anthony Koppers	
18:00 Poster Sessions (in the basement of the School)	**18:00 Wine Tasting** **18:00 Poster Sessions** (in the basement of the School) **20:15 Conference Banquet**	**End of Conference**

Breakout Sessions

Five working groups will assemble in parallel breakout sessions on Tuesday and Wednesday (see below for detailed program). Session chairs will take on responsibilities of leading discussion segments, solving particular issues, and co-writing reports. Working groups will present their results and have an open discussion in the last plenary session and summarize their results in a final report, that may be used as "white papers" published on the GERM website and provided to NSF, or as conference reports in the Geochemical Newsletter or in EOS. Above all, however, we hope to advance all these issues in practice, in terms of proposals written, new working groups formed, new and updated editorial guidelines for data publication in geochemistry, or improving what GERM does for geochemistry.

We will address a very diverse set of issues that address key infrastructure problems in geochemistry, largely in parallel sessions, and there will be many participants who will have to make important contributions to more than one session. In this case, please get in touch with the breakout session chair, and express yourself, by e-mail before the meeting or during coffee breaks at the meeting in Lyon. You may be able to split your time between working groups and/or it may be useful if you would write a paragraph or two that expresses your concern or solution to a particular problem. The GERM organizers and the group chairs will make any effort to accommodate these concerns, but we rely on you to bring them to our attention.

A GERM Handbook of Geochemistry

Chair: Bill McDonough

Time:	May 20, 2003, 13:45-15:30
Location:	Amphitheater J (ground floor)

One of the major goals of GERM is to provide easy access to a great variety of chemical reference data, including the chemical composition and evolution of major geochemical reservoirs and fluxes between them. This session will discuss a book proposal that covers that need, in the form of a combined print- and world-wide-web resource. These discussions will include, in particular, the format and extent of the book as well as identifying individuals who will take on a major organizational role. A copy of a proposal for this "Handbook" will be included in the registration package.

SAMPLES: Sample Archive and Management PLanning for the Earth Sciences

Chair: Steve Goldstein

Time:	May 21, 2003, 13:45-15:30
Location:	Amphitheater I (ground floor)

Geochemistry critically depends on reliable preservation of data, but until recently attention has not been adequately paid to preservation of important terrestrial samples. This problem was addressed at GERM

2001. The recent NSF ISES-CI Workshop (Workshop on CyberInfrastructure for the Integrated Solid Earth Sciences) strongly recommended that, along with a scheme for data access and preservation, there must be a complementary policy on samples. Access to original samples is essential to make geochemistry a truly reproducible science. This breakout group will explore options and next steps towards insuring sample preservation and community access. A copy of an article on SAMPLES by Goldstein and Melson in the Geochemical News will be included in the registration package.

Editor's Round Table

Chair: Frank Podosek

Open Discussion Forum (all invited)

Time:	May 21, 2003, 13:15-14:15; May 22, 2003, 14:45-15:30
Location:	Amphitheater A (4th floor)

Closed Session (for Editors only)

Time:	May 20, 2003, 13:15-15:30; May 21, 2003, 14:15-15:30
Location:	Meeting-room of Department SVT (ground floor)

Publishers and geochemistry editors will discuss current practices of data publication and how data publication in the peer-reviewed literature could improve and how it should relate to community database activities. The purpose of this meeting is to give editors an opportunity to discuss editorial policy amongst themselves (closed session) and with the GERM community present at the meeting (open Discussion Forum on May 21 and 22). Special attention will be paid to improving editorial guidelines that assure scholarly publication of all data or materials that are relevant to a publication. Publishers, editors and the community will discuss copyright issues regarding data publication in electronic or paper publications. A commentary on data publication by the GERM Steering Committee and some key metadata are included in the registration package.

Geochemical Database for Rivers

Chair: Lou Derry and Bernhard Peucker-Ehrenbrink

Time:	May 20, 2003, 13:45-15:30; May 21, 2003, 13:45-15:30
Location:	Amphitheater K (ground floor)

Rivers are amongst the most deserving candidates for the development of a database in geochemistry. Currently there is no systematic global database effort that archives data on river chemistry and runoff, for dissolved or suspended load. Geochemical databases for rivers should be integrated with, or at least related, to data on geology, vegetation, rainfall and an elevation model of the river basin. The GERM river database committee will define the scope, data and metadata formats for such a database, and discuss options for the development of such databases. There will be handouts at the meeting

GERM Website Review

Chair: Rick Carlson

Time: May 20, 2003, 13:45-15:30
Location: Meeting-room of Laboratory of Earth Sciences (ground floor)

The GERM website has developed from a static set of data tables to a relational database-driven, dynamic website that aims at satisfying a wide range of needs in geochemistry. The Website Review committee is charged with the mandate to evaluate the GERM website from an independent perspective and to solicit community criticism of the GERM website to guide future developments carried out by EarthRef.org.

Update on the GERM Website and Database

Anthony Koppers, Hubert Staudigel, John Helly, Stephen Hamilton, Alex Beilin and Jake Perez

The new GERM website and database was presented and introduced during the GERM2001 meeting in La Jolla, California (Koppers, GERM 2001 Workshop; http://earthref.org/cgi-bin/erda.cgi?n=26). Since GERM2001 we introduced many new features to the GERM website and its host EarthRef.org. In this update, we will give a short overview of these enhancements, the new data that were incorporated over the last two years and what we are working on currently. This update serves as an introduction of the GERM website to the geochemical community and the GERM website review committee, in particular.

GERM in EarthRef.org

The GERM website resides under http://earthref.org an umbrella website that is designed as a common host for any Earth sciences reference data. The EarthRef.org databases and websites are residing at the San Diego Supercomputing Center where we can make use of their Oracle 9.1.0 database license and an Apache 2.0.39 Unix web server running on a Sun Enterprise 450 with 4 Gigabytes of RAM and four 400 MHz CPU's. Over the coming weeks the EarthRef.org website will transfer to an even more powerful setup with double the amount of (faster) CPU's and available RAM memory.

EarthRef.org maintains several databases that are specific for GERM such as the Reservoir database and the Partition Coefficient database. EarthRef.org also hosts databases that share common resources with other Earth science databases at this site, such as MagIC. These common resources include a Reference database and an Address Book database that can be readily integrated with any disciplinary database, to archive papers or to provide the name/contact addresses of analysts and sample curators.

The GERM website under EarthRef.org is maintained by Anthony Koppers (SIO) in collaboration with Hubert Staudigel (SIO), John Helly (San Diego Supercomputer center), and Henry Shaw (LLNL, DOE). Our current staff includes one software programmer (Stephen Hamilton) who is maintaining the website and develops the CGI web-interfaces for the databases. We also have an assistant (Jake Perez) working on the training and supervision of undergraduates in the scanning and digitization that we perform for each paper in the EarthRef Reference database (see below). All of the above support the GERM website activities part-time. The GERM website is directly available through the http://earthref.org/GERM/ link; databases are directly available through the http://earthref.org/databases/ link.

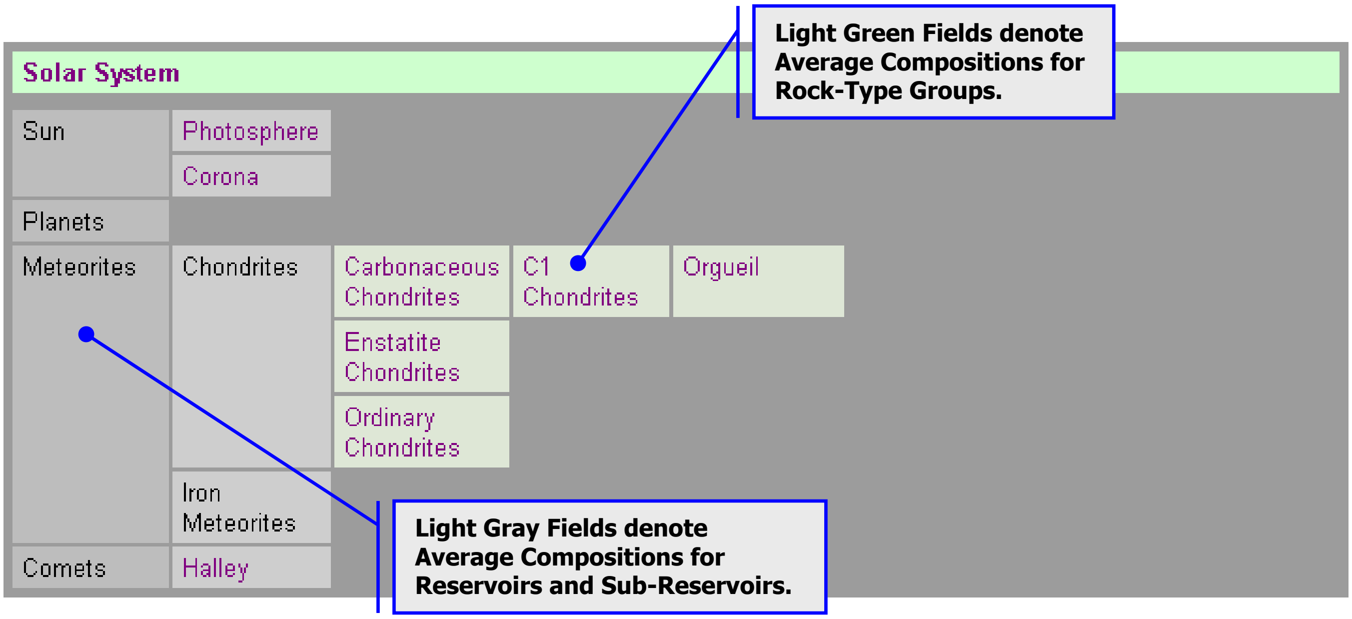
Feedback and Review

The main purpose of the GERM website is to provide an Information Technology (IT) infrastructure to geochemistry that helps with access to data and modeling tools. Such an infrastructure cannot be build top-down, it is dependent on feedback by users and the community at large. For these reasons, a review committee has been established to evaluate the current GERM website and database. The main charge of this committee is to review the functionality of current website and database and to advise us on how we could better meet the needs of the geochemical community. This review committee will be chaired by Rick Carlson (DTM, Carnegie Institute) and during the GERM2003 meeting in Lyon will convene for the first time in two break-out sessions. Rick Carlson and his committee will be happy to receive comments and suggestions from anybody outside this committee, but the GERM-EarthRef.org team will be happy to hear from you directly, in particular, if you have a problem that needs immediate attention.

Database Versioning and Statistics

Using “live” databases bears the risk that queries become non-reproducible after a period of sustained database growth. A query performed in March 2003 will be different from the same query in December 2007. EarthRef.org has started to version its databases since the beginning of 2003. Each database update carries an unique version number like “ER.2003.05” (at the time of the workshop) that will be upgraded once every month. Our monthly updates can be tracked via the http://earthref.org/cgi-bin/ers-s0-statistics.cgi webpage. This version number is also incorporated in the basic metadata structure of the underlying databases, so that future queries also can be based on version number, in order to accurately reproduce the state of the EarthRef.org databases at any specific point in time. It is important, therefore, that citations to the GERM databases include this version number.

EarthRef.org version “ER.2003.04” includes 34,022 data files (equaling 8.3 Gigabytes in total file sizes) that are available for viewing and/or downloading (see http://earthref.org/cgi-bin/ers-s0-statistics.cgi for current information). The GERM Reservoir Database (GERMRD) now contains 6,608 compositional estimates for 93 different reservoirs, and the KD database contains 5,798 partition coefficients from 189 citations. In total the EarthRef.org Reference database (ERR) contains 1,097 publications for which each abstract, table, technical note and appendix has been scanned and digitized. These scans and digitized files can be viewed online and subsequently downloaded to the users hard disk.



Solar System

Sun	Photosphere			
	Corona			
Planets				
Meteorites	Chondrites	Carbonaceous Chondrites	C1 Chondrites	Orgueil
		Enstatite Chondrites		
		Ordinary Chondrites		
	Iron Meteorites			
Comets	Halley			

Light Green Fields denote Average Compositions for Rock-Type Groups.

Light Gray Fields denote Average Compositions for Reservoirs and Sub-Reservoirs.

Figure 1. Snapshot of data model applied in the current GERM Reservoir Database (GERMRD). This part of the GERMRD data model contains two different data categories, that are (1) average compositions for the reservoirs and their sub-reservoirs describing the solar system, and (2) averages for different groups of Chondrites based on their rock-type. Items in dark purple are direct links into the GERMRD database; whereas for items in black no data are available yet.

Data Model for the GERM Reservoir Database

Since GERM 2001 the data model that underlies the GERM Reservoir Database (GERMRD) has been advanced to allow for a more flexible, but also a more accurate, population of this database. In the initial GERMRD setup the Earth was divided by reservoir and their sub-reservoirs. However, this simple data model ignored that many geochemical compilations organize their data by tectonic unit, geography, geological time or rock-type. This information is important for the understanding of a particular estimate of a reservoir composition. For example, Gao et al. (1998) summarize the "Chemical composition of the continental crust as revealed by studies in East China" (GCA 62: 1,959-1,975: 1998) but in the original GERMRD database this study could only be labeled as an estimate for the continental crust, without the reader being able to see that this estimate refers strictly speaking to a "regional" estimate in East China only. This regional estimate by Gao et al. is, therefore, fundamentally different from estimates of the "bulk" continental crust by Rudnick & Fountain (1995) or Taylor & McLennan (1995) and should be labeled according to geography ***and*** reservoir instead. The upgraded GERMRD data model reflects these differences. More specifically, the new model maintains the following hierarchal structure containing six different categories:

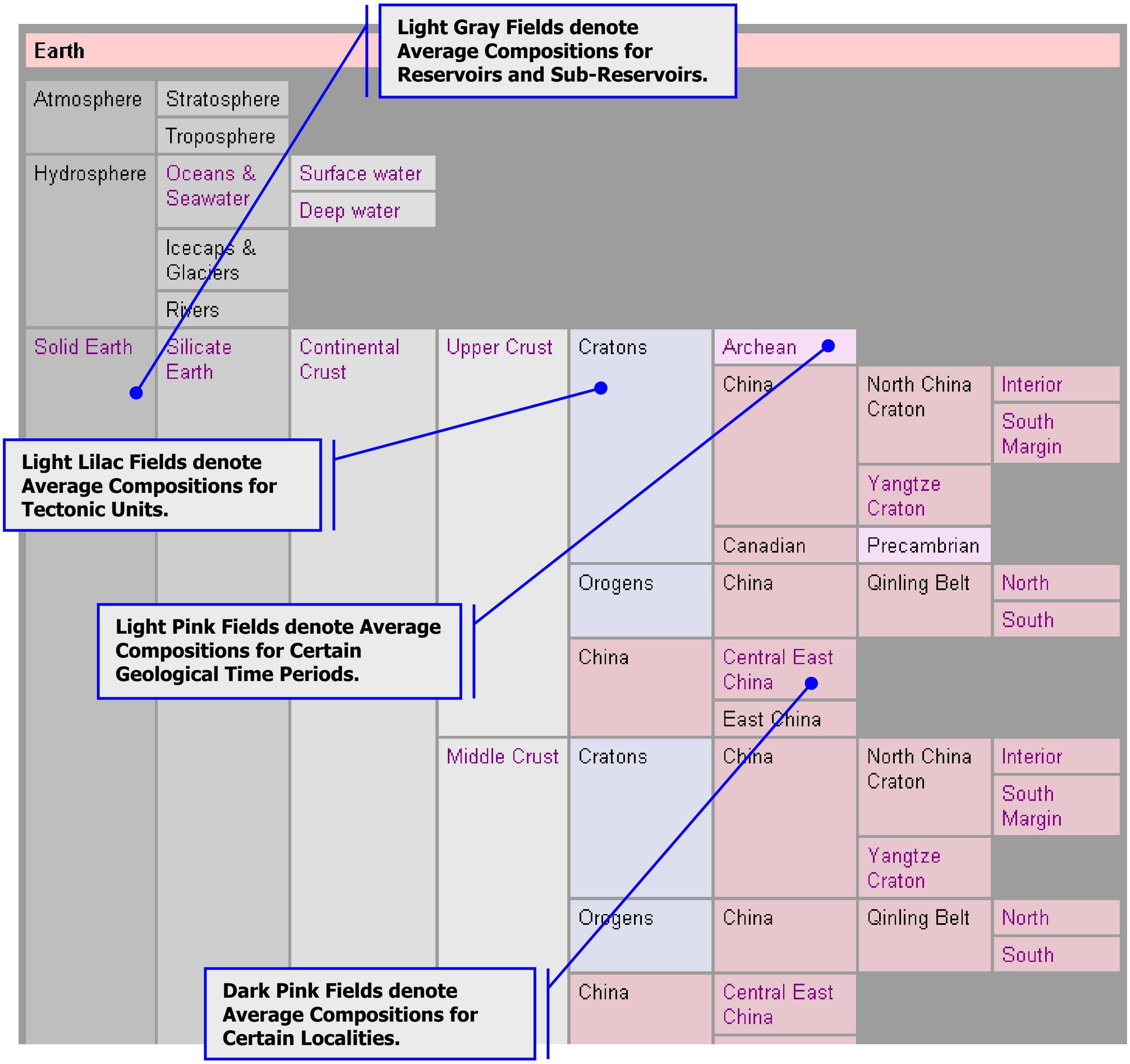
1. **Reservoirs**
2. **Tectonic Units**
3. **Age Units**
4. **Geography**
5. **Rock Type**
6. **Individual Samples**

If any or all of the above categories are used in describing a certain reservoir, we strictly adhere to the order as shown above. This order is maintained even when some categories are not relevant and need to be skipped. As can be seen in Figure 1 and 2 each category can be subdivided further as needed. This data model also allows for multiple boxes for "pelites" for example, where an estimate exists for pelites in the "Archean" continental crust in East China, but also for "Post-Archean" crust in the same region. The databases will always have the ability to alternatively link both estimates for pelites under the same rock-type group or in any other data model, based on tectonic setting or geography, for example. A key advantage of this data model is that it allows for tracing averages back to their original data and sources, which allows an user to actually work with the data rather than blindly accepting averages.

In the ideal world, each node in this hierarchal data model should have estimates for its compositions. These estimates should at least include the following data for each parameter:

1. **Average**
2. **Median**
3. **SD**
4. **Low range**
5. **High range**
6. **N**

However, this can only be the case when basing these estimates on a normally distributed (and slightly skewed) population of measurements. In case of more complex model calculations, these parameters are commonly based on data correlations and may be more difficult (if not impossible) to parameterize. For these cases we should expand this list with a group of cross-correlation and other appropriate statistical parameters to better describe each compositional estimate of the reservoirs and their uncertainties.



Light Gray Fields denote Average Compositions for Reservoirs and Sub-Reservoirs.

Light Lilac Fields denote Average Compositions for Tectonic Units.

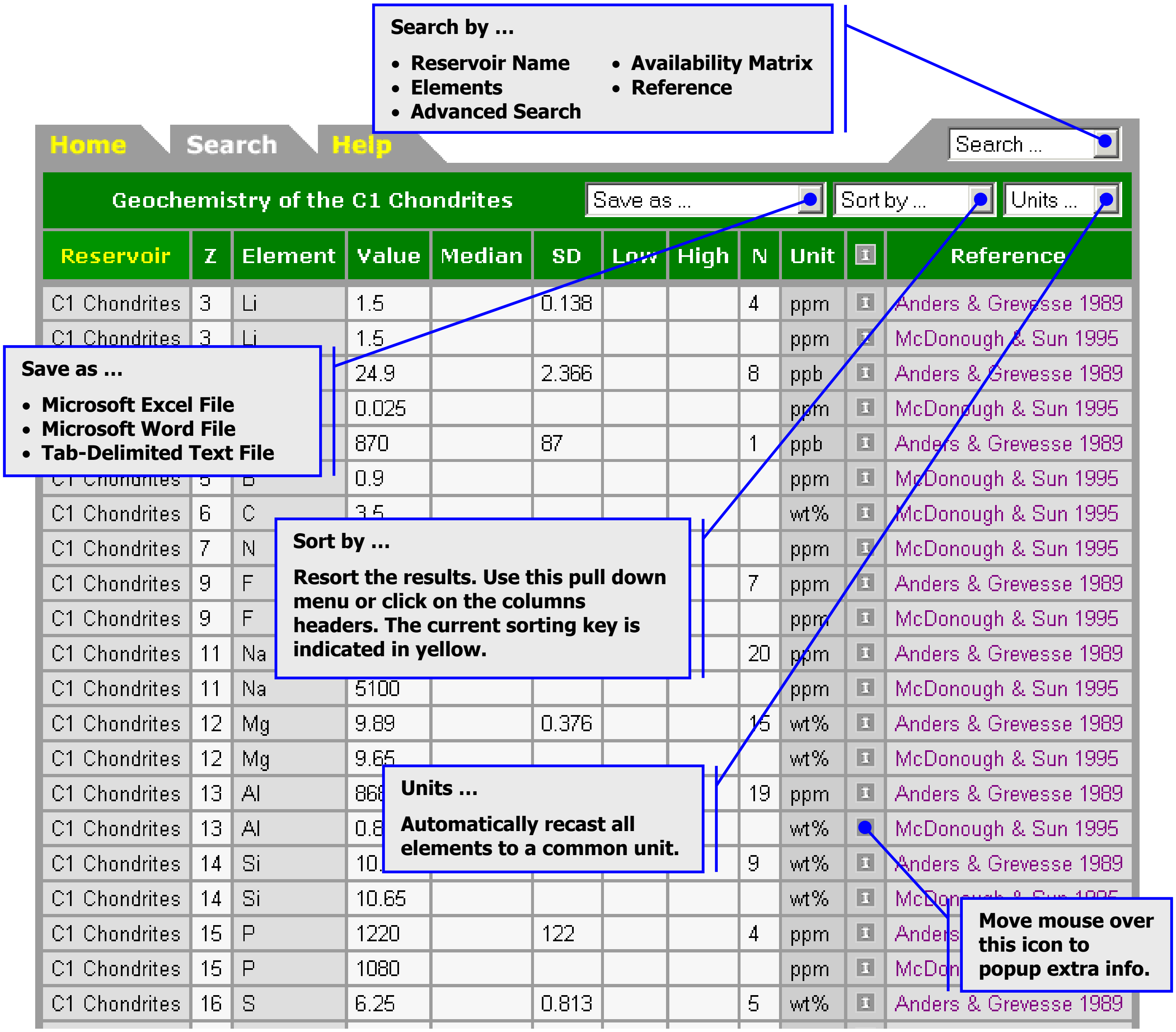
Light Pink Fields denote Average Compositions for Certain Geological Time Periods.

Dark Pink Fields denote Average Compositions for Certain Localities.

Figure 2. Snapshot of data model applied in the current GERM Reservoir Database (GERMRD). This part of the GERMRD data model contains four different data categories, that are (1) average compositions for the reservoirs and their sub-reservoirs that describe part of the solid Earth, (2) average compositions for different tectonic units, (3) for different geological time periods, and (4) for different localities. This model can (and should) be expanded further by adding different rock-types for each of these sub-divisions, as shown in the example of Figure 1. Items in dark purple are direct links into the GERMRD database; whereas for items in black no data are available yet.

Working with the GERM Reservoir Database

The GERMRD 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 the availability of data. Now there is also an “advanced” search option where the user can



Search by ...

- **Reservoir Name**
- **Elements**
- **Advanced Search**
- **Availability Matrix**
- **Reference**

Save as ...

- **Microsoft Excel File**
- **Microsoft Word File**
- **Tab-Delimited Text File**

Sort by ...

Resort the results. Use this pull down menu or click on the columns headers. The current sorting key is indicated in yellow.

Units ...

Automatically recast all elements to a common unit.

Move mouse over this icon to popup extra info.

Reservoir	Z	Element	Value	Median	SD	Low	High	N	Unit	ℹ	Reference
C1 Chondrites	3	Li	1.5		0.138			4	ppm	ℹ	Anders & Grevesse 1989
C1 Chondrites	3	Li	1.5						ppm	ℹ	McDonough & Sun 1995
			24.9		2.366			8	ppb	ℹ	Anders & Grevesse 1989
			0.025						ppm	ℹ	McDonough & Sun 1995
			870		87			1	ppb	ℹ	Anders & Grevesse 1989
			0.9						ppm	ℹ	McDonough & Sun 1995
C1 Chondrites	6	C	3.5						wt%	ℹ	McDonough & Sun 1995
C1 Chondrites	7	N							ppm	ℹ	McDonough & Sun 1995
C1 Chondrites	9	F						7	ppm	ℹ	Anders & Grevesse 1989
C1 Chondrites	9	F							ppm	ℹ	McDonough & Sun 1995
C1 Chondrites	11	Na						20	ppm	ℹ	Anders & Grevesse 1989
C1 Chondrites	11	Na	5100						ppm	ℹ	McDonough & Sun 1995
C1 Chondrites	12	Mg	9.89		0.376			15	wt%	ℹ	Anders & Grevesse 1989
C1 Chondrites	12	Mg	9.65						wt%	ℹ	McDonough & Sun 1995
C1 Chondrites	13	Al	86					19	ppm	ℹ	Anders & Grevesse 1989
C1 Chondrites	13	Al	0.8						wt%	●	McDonough & Sun 1995
C1 Chondrites	14	Si	10.					9	wt%	ℹ	Anders & Grevesse 1989
C1 Chondrites	14	Si	10.65						wt%	ℹ	McDon
C1 Chondrites	15	P	1220		122			4	ppm	ℹ	Anders
C1 Chondrites	15	P	1080						ppm	ℹ	McDon
C1 Chondrites	16	S	6.25		0.813			5	wt%	ℹ	Anders & Grevesse 1989

Figure 3. Results page for the GERM Reservoir Database (GERMRD). For each element the GERMRD results page contains an average (Value), median, standard deviation (SD), value range (Low and High) and the number of data points included in the abundance estimation (N). In case no information is available for these data points their respective fields will remain empty. By clicking on the citations the user will be linked to the EarthRef.org Reference database (ERR) as shown in Figure 4. Note that the “home” tab will guide the user to the home page of the GERMRD database, the “search” tab will bring the user back to the initial search form and the “help” tab will provide context sensitive help and examples (still under construction).

combine these searches and use Boolean expressions to make the searches more specific. Options have been added that allow the user to save each search in Microsoft Excel, Microsoft Word or tab-delimited ASCII text files. Other options include custom "sorting" of the search results and "recasting" of these data according to a common unit (e.g. ppm, ppt, wt% or wt%ox). Popup menus appear when additional information is available for a certain abundance estimate. An example of typical search results for C1-chondrites is shown in Figure 3.

Working with the KD's Database

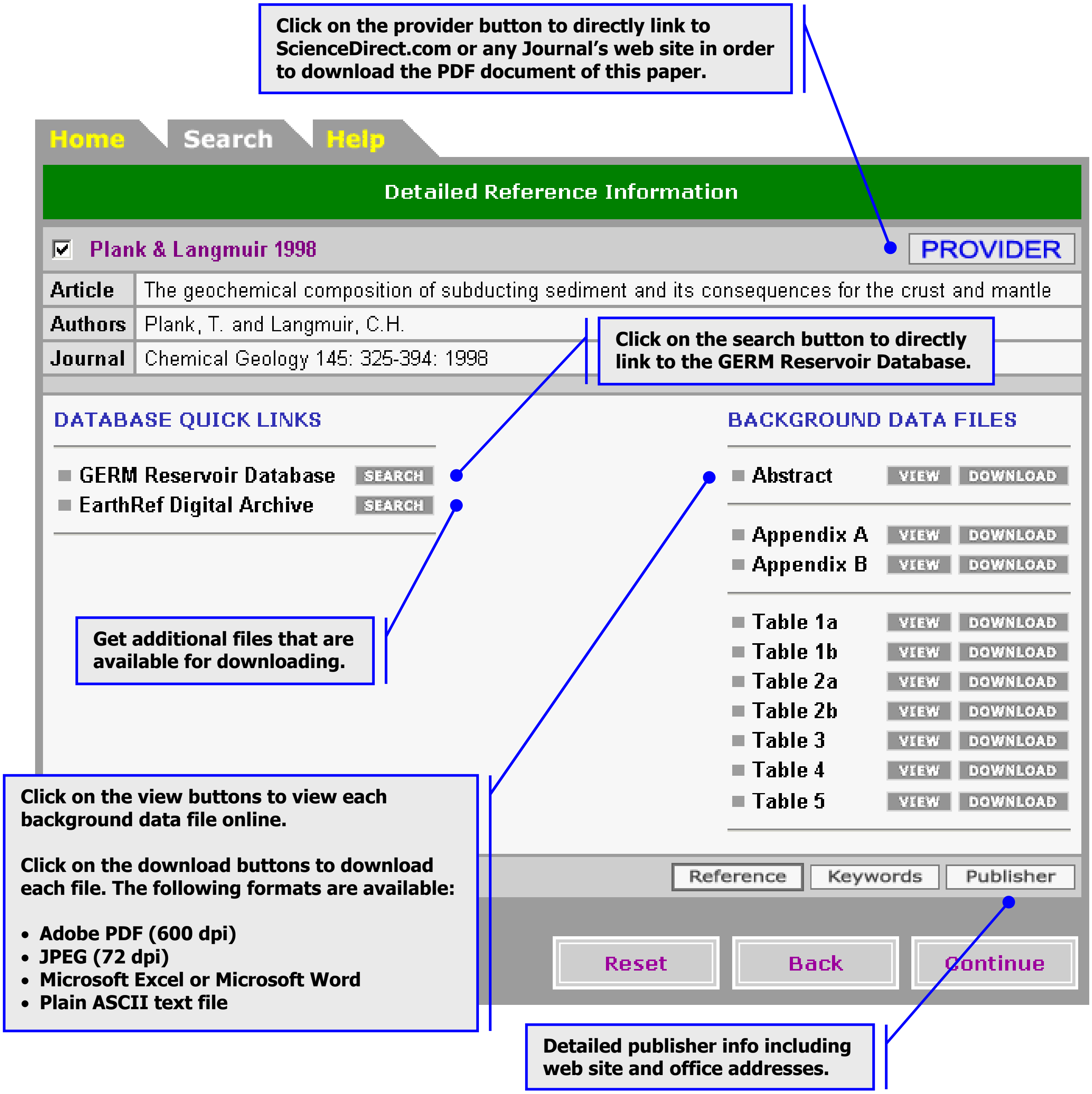
The KD's Database contains partition coefficient data for all types of rocks and minerals and for every element. All KD values can be searched for using combinations of rock name and mineral, element and reference and it includes experimental and empirical data. This database has similar user functions and options as the GERMRD database has (see above). This database has been developed by EarthRef.org while Roger Nielsen (Oregon State University) has compiled the contents and maintains the scientific responsibility for this database.

Digital Archives

The EarthRef Digital Archive (ERDA) has been built to hold any digital object including diagrams, data tables, animations, software, field guides, white papers, geological maps, videos, etc. This is a powerful instrument since ERDA allows both peer-reviewed and non-peer-reviewed data submissions. The major goal of this electronic archive is to offer a simple means of access to any type of digital file with a direct relevance to initiatives like GERM, and any other application in research and teaching.

ERDA supports GERM in several ways. Key functions include the archival of electronic data files that may include high resolution images of photographs from a paper, support data used in the calculation of compositional averages, computer programs or spreadsheet calculations, or any other file that was used in the preparation of a publication but that could ***not*** be published because of space restrictions. All these files can be uploaded into the ERDA database and linked to the original publication. Several download and upload features in ERDA give direct access to this rich source of geo-information.

New file contributions can be interactively uploaded via online forms (use "your contribution" under the http://earthref.org/databases/ERDA/ database page) together with all their metadata. We have built and tested such an upload scheme for the ERDA database, where the scientist can simply browse on their own local hard disk to select the file that needs to be uploaded. After logging in, the user gets the option to reload one of his/her previous contributions and use this one as a pre-filled template for their new contribution. This avoids annoying re-entry of similar metadata. There is also the possibility to interrupt the current upload and to continue at a later stage. The contributor will be asked for a minimum set of required metadata, while having the choice to add additional metadata including geography, geological time, project name, an URL, copyright information and a citation. When entering a citation, ERDA automatically searches the current EarthRef Reference database for this citation, displaying a list with the closest matches from which the contributor can choose the correct publication. If there is no match, an online form prompts for new bibliographic information. In the final wizard step, the scientist can browse on their own local hard disk to select the file for uploading. The contributor will be sent a confirmation email with an URL that directly links to the data contribution.



☑ Plank & Langmuir 1998

Article The geochemical composition of subducting sediment and its consequences for the crust and mantle

Authors Plank, T. and Langmuir, C.H.

Journal Chemical Geology 145: 325-394: 1998

Click on the provider button to directly link to ScienceDirect.com or any Journal's web site in order to download the PDF document of this paper.

Click on the search button to directly link to the GERM Reservoir Database.

Get additional files that are available for downloading.

Click on the view buttons to view each background data file online.

Click on the download buttons to download each file. The following formats are available:

- **Adobe PDF (600 dpi)**
- **JPEG (72 dpi)**
- **Microsoft Excel or Microsoft Word**
- **Plain ASCII text file**

Detailed publisher info including web site and office addresses.

Figure 4. Detailed reference information of a paper residing in the EarthRef.org Reference database (ERR). This table first of all displays the bibliography of the paper and allows the user to directly link to any online provider to download the PDF of this document (if available in this format). The same link also can be made by clicking on the "publisher" button that gives the user addresses and web links to the publisher of the paper. Quick links show up on this page whenever this paper has been included in any of the EarthRef.org databases (in this case links exist to the GERMRD and ERDA databases). For each paper in the ERR background data files are available in several formats ready for viewing and downloading. Note that for display purposes not all data tables are shown in this diagram; in the life database this paper carries many more (i.e. 24) data tables.

Reference Database

The Reference Database (ERR) is a key component of the EarthRef.org database. This database holds 1,097 publications that are cited throughout GERM and EarthRef.org and that can used to find a direct path into each individual database by following the "Quick Links" (Figure 4). For each publication the ERR database provides "scanned" excerpts of the abstracts, data tables, technical notes and appendices. These excerpts are "digitized" using Optical Character Recognition (OCR) resulting in Microsoft Word documents for text fragments and Microsoft Excel documents for data tables. In addition, the scans are made available as high resolution PDF documents or JPEG images. Scanning and digitization follows a strict protocol as documented in the EarthRef.org Data Population Protocol (ERDPP) that is available on request. This protocol can be used directly by research groups outside SIO to contribute new contents to the ERR database. In some cases the ERR database does archive PDF files of entire papers or colored diagrams. This is possible in the case of GERM-related articles in G-cubed that has a copyright policy that allows free access to these papers (see G-cubed copyright policy) via EarthRef.org.

Address Book

EarthRef.org maintains an Address Book database that contains contact information for all EarthRef.org contributors, the authors of GERM-archived papers, sample archivers and analysts as listed in metadata compilations, and any other Earth scientist who wants to have his/her address listed. This address book currently contains over 800 addresses of Earth scientists and it is used to provide address information for any contributor listed on EarthRef.org, and as a basis for mailing lists, such as the GERM list. Scientists who wish to add themselves to this list or who need to make an address change can do so via online data forms on the EarthRef.org website. Please use the http://earthref.org/cgi-bin/erml-c0-register.cgi link to register. The user will receive a confirmation email with their userid-password and an URL that directly links back to their current address information in this database. They should also use this URL in order to update their address information, if needed. The address book allows anybody to retrieve addresses from the http://earthref.org/databases/ERML/ webpage that also contains an advanced search option and a link if you forgot your password.

Future GERM Database Enhancements

Over the last year we have build the software engine for automatic keyword retrieval from all available Microsoft Word and Excel files in the ERR database. This software is able to pull out relevant keywords and label them as a general keyword, parameter, material, sample number, technique, continent, country, region, timescale name, age range or lat-lon range. This complex mechanism of "metadata harvesting" is automated in the sense that all keywords are being stored in a Microsoft Access database that acts as a keyword library to search against for other publications. Over the coming year we will integrate this software in the ERR database, which will enable "google-type" free-text searches. The goal is to allow the user of the EarthRef.org website to search for any publications that, for example, report Sr and Nd isotopes for alkali basalts in the Pacific.

Poster Abstracts

Listing in alphabetical order

Seismic Constraints on Slab Fluxes of Volatiles to Arcs and Deep Mantle

Abers, G A

Present constraints on volatile fluxes into trenches and out of arc volcanoes have wide uncertainties, with estimates of the relative arc flux ranging from 10% to 100%. To better constrain this process, seismic signals that sample the top of downgoing slabs are used to measure its fine-scale velocity structure, and from that infer H_2O content beneath and past arcs. A variety of seismic signals reveal structure at a variety of scales, and increasingly show evidence for layers a few kilometers thick at the tops of slabs. Typically the layers show seismically slow P and S velocities, as revealed by body-wave dispersion or mode-converted P-to-S signals. The layer velocities vary with location and depth, from 4 to 20% slower than surrounding mantle. In most cases, the layer appears to be 2-8 km thick, with some exceptions. Several explanations have been proposed for these layers, including persistence of metastable gabbro into the eclogite stability field, hydrated oceanic crust or crustal layers, a serpentinized mantle within the downgoing plate, a talc- and serpentine-rich altered zone above the slab, or localized abundance of free fluid. For all but the first case, a common relation exists between H_2O content and seismic velocities, at pressures above 2.5 GPa, such that each 2% reduction in velocity corresponds to 1 wt% H_2O. The velocities directly constrain the H_2O content, and show that up to 5 wt % H_2O may be present in a layer atop many slabs in a several km thick layer up to 150 km deep. Globally, little evidence has been found for low-velocity layers at depths greater than 150-200 km, but slabs at these depths are also less well sampled; observations permit layers up to 1-4% slower at these depths. Beneath some arcs, the predicted H_2O concentrations probably exceed that at the trench, and suggest an additional process enriches H_2O content. Steeper slab dips correspond with apparently higher H_2O concentrations, a correlation which could be explained if steep dips promote up-dip H_2O migration from deeper dehydration reactions. Such flow would increase H_2O locally beyond that delivered from the trench. While this such a process would limit the ability to determine overall fluid fluxes from seismic velocities, it does suggest that the slab serves as a significant two-way conduit for fluids.

Contribution to Chlorine Cycle: a Cl Stable Isotope Approach on Mantle–Ocean Exchanges

Bonifacie, M; Jendrzejewski, N; Pineau, F; Agrinier, P

The study of volatile geochemical cycles and the quantification of fluxes involved in Mantle-Exosphere exchanges are important in order to understand Earth's Geodynamic and passed evolution. Chlorine is of primary importance, because it's one of the main volatile component on Earth, but also one of the dominant anion in many geological fluids. Chlorine has two stable isotopes ^{37}Cl and ^{35}Cl and their abundance ratio is expressed as $\delta^{37}Cl$ in per-mil deviation relative to SMOC (Standard Mean Ocean Chloride, $\delta^{37}Cl = 0$ ‰). The stable isotope composition of chlorine can be used to trace its geochemical cycle during exchanges between Earth's reservoirs (e.g. via degassing, subduction or alteration). $\delta^{37}Cl$ values could also be a powerful tool to clarify the origin of high Cl contents of some fresh MORB glasses which have been explained by : i) assimilation of hydrothermally altered wall rocks, brine or seawater in the magma chamber (Mickael and Cornell, 98) ii) source heterogeneity. Chlorine cycle and isotopic fractionation factors during exchange processes between Earth's reservoirs or phases are still poorly known. Furthermore, the scarcity of data for solid samples (rocks or minerals) reflects the analytical difficulty to extract chlorine from silicate structure.

Analytical Development

To extract Chlorine from silicate samples, three different methods are commonly used : alkali fusion, HF-acid decomposition and pyrohydrolysis. Each method have been investigated for chlorine extraction followed by δ^{37}Cl determinations on IRMS or TIMS. We have adopted the method of pyrohydrolysis (for lowest blanks of analyses method) followed by isotope-ratio mass spectrometric measurements (IRMS) on CH_3Cl gas. Because of the small natural variation range of Cl isotopes, we have endeavor to optimize the analytical precision and accuracy. Mean extraction yields are 100 ± 3 %, this quantitative extraction is mandatory to avoid analytical fractionation. δ^{37}Cl values on duplicate extractions show reproducibility better than 0.2 ‰ and the blanks represent less than 5 % of the sample size. Our technique represents the most quantitative and precise method of chlorine extraction for δ^{37}Cl determination on solids published to date.

Oceanic crust samples

The oceanic crust plays a key role in chemical exchanges between surface and internal reservoirs of the Earth. After it's formation at ridge axis, seawater-rock interaction (both at high or low temperatures) is the main process which changes its chemical composition. To characterize chlorine behavior during the oceanic crust alteration, we have analyzed fresh MORB glasses (from SWIR and EPR), altered basalts from leg 504B site (EPR), serpentinized peridotites (from SWIR and MAR) and an altered gabbro from the Hess Deep site (EPR). Cl concentrations are between 200 and 2200 ppm.

All oceanic crust samples (n=14) show negative δ^{37}Cl values (from –1.6 to 0 ‰) which can be interpreted as a depletion in ^{37}Cl or an enrichment in ^{35}Cl relative to seawater (δ^{37}Cl =0 ‰). Furthermore, the small range of variation of δ^{37}Cl values described by the samples studied contrasts with the large range measured in previous works :-3 to +11 ‰ (Magenheim et al., 94 and 95; and Stewart et al., 97 and 98); see Fig 1. This contrast can be due to differences in the nature of samples analyzed or analytical discrepancies.

Our results on fresh MORBs: δ^{37}Cl = –1.4 ‰ and – 0.6 ‰ are in the lower range already published (– 3 to +11 ‰, e.g. Magenheim et al., 95; Stewart, 2000). However, our δ^{37}Cl range of altered samples: δ^{37}Cl = –1.6 to –0.2 ‰ (basalts, serpentinized peridotites and gabbro) is outside the range observed by Magenheim et al., 95 for this type of samples (+0.4 to+7.5 ‰ in amphibole-rich rocks and smectite veins) despite the fact that in both study amphibole-rich rocks from the same site (i.e. leg 504B) have been analyzed. On this site, our δ^{37}Cl results are very homogeneous (–1.3 to – 1.0 ‰ ; n=3) and conflict with the large positive range (+1.7 to 3.4 ‰ ; n=3) observed by Magenheim et al. (1995). This difference could be explained by an analytical fractionation occurring during Cl extraction by the type of pyrohydrolysis used by Willmore et al., 2001 (who use the same method than Magenheim and Stewart). The calculation of Cl extraction yields in Willmore et al., 2001, shows two clear correlations between the measured δ^{37}Cl and recalculated extraction yields (between 25 and 75%). This suggests that the δ^{37}Cl values measured in those study might be dependent on extraction yields.

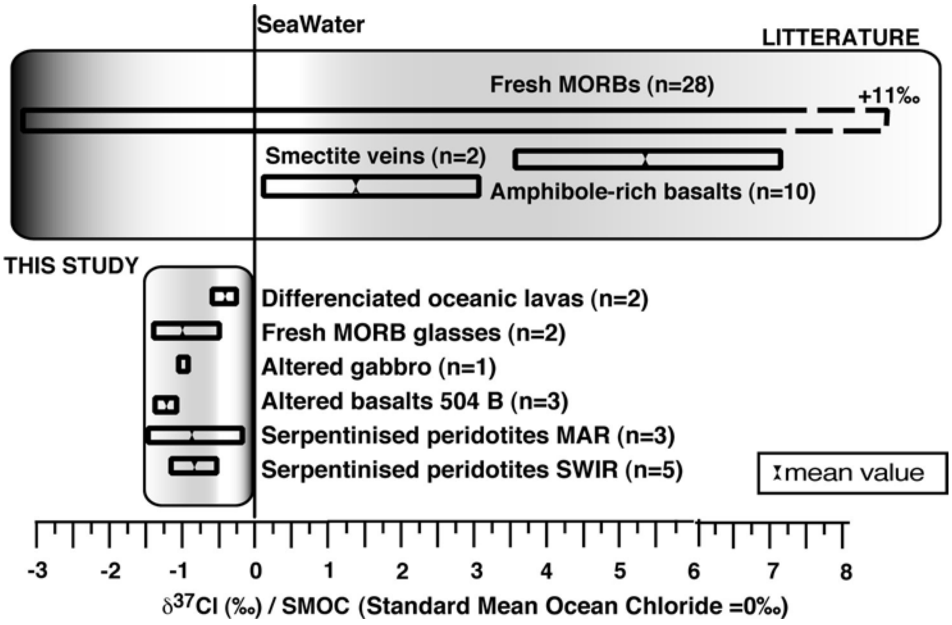


Figure 1. δ^{37}Cl variations of oceanic crust samples analyzed in this study compared to literature (Magenheim et al., 94 and 95; and Stewart et al., 97, 98 and 2000). n represents the number of samples analyzed, and X the mean δ^{37}Cl value for each kind of rocks.

In our study, the serpentinized peridotites analyzed (n=8) have δ^{37}Cl values from –1.6 to –0.2 ‰, and show no correlation with sample localization. During Cl analyses, we have underlined the existence of (at least) two different mineralogical sites for chlorine and most probably two different carrier phases. One type of Cl seems to be in the silicate network and only available by pyrohydrolysis whilst another is readily soluble in neutral water. In our samples, these different types of Cl seem to be in various proportions. Rucklidge et al. ,72 described the existence of such a soluble phase with a proposed formula of $Fe_2(OH)_3Cl$. On-going experiments (electron probe analysis, colorimetry, etc) will give additional constraints on the localization of Cl in those samples and identify the composition of the carrier phase. According to preliminary experiments, the soluble chlorine seems to keep stable in serpentinized peridotite at BP-HT conditions representative of the start of the amphibolite facies.

Conclusions

Our preliminary results on various derived mantle rocks (both fresh and altered) are systematically negative. The Cl cycle, largely based on δ^{37}Cl preliminary values should be taken with caution and revisited. Additional data from various types of samples and locations should be compiled to better constrain e.g. water-rock interactions, chlorine phases stability, devolatilization.

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Oceanic Geochemical Tracers: What's New since GEOSECS

Boyle, E

The last global ocean geochemical survey was GEOSECS in the 1970's; major programs since then have focused on other issues such as carbon fluxes and transient tracers. But in the time since GEOSECS major advances in geochemical instrumentation (dominated by plasma mass spectrometry) and reliable sea-going clean sampling devices have made it possible to measure ocean geochemical properties that GEOSECS could only dream of. We now have the capability to learn much more about ocean trace metal chemistry - including anthropogenic metals such as lead and natural metals such as biologically-limiting iron - and we can also make more practical and accurate measurements on natural radionuclides such as Th-230, Pa-231, and Be-10. Trace metal stable isotope ratio measurements are arriving as another tool in the geochemical arsenal. Many of these properties have paleoceanographic applications in calcareous fossils, ferromanganese crusts, and marine sediments. These advances are featured in a new international ocean geochemistry program ("GEOTRACERS", aka "GEOSECS II").

Reservoirs or Recycling?

Carlson, R W

Formation of Earth's continental crust has left a clear chemical and isotopic imprint on the mantle. Simple 3-box (crust, depleted mantle, undepleted mantle) mass balance models show that between 20% and 60% of the mantle, depending primarily on the value of average crustal composition chosen, must have been largely depleted of highly incompatible elements by continent formation (JACOBSEN and WASSERBURG, 1979; O'NIONS et al., 1979; ALLÈGRE et al., 1983). These models predict the presence of significant volumes of undepleted mantle; a prediction that is becoming increasingly unpalatable in view of geophysical evidence for whole mantle convection (VAN DER HILST et al., 1991) and the lack of geochemical evidence for primitive mantle as a component for any terrestrial volcanism. Even the source of high ^{3}He/^{4}He appears to have Sr and Nd isotopic compositions indicative of a depleted "reservoir" (HART et al., 1992). In addition, use of more LIL-rich estimates of bulk-continent composition (GAO et al., 1998) and less depleted estimates of the average composition of the depleted mantle (SU, 2002) allow the whole mantle to have been depleted by continent extraction (Figure 1).

Another option to consider is that the entire mantle has cycled through an ocean ridge system at some time in Earth history and consequently ALL the mantle has been partially melted to segregate into basalt and depleted peridotite. This assumption leads to a different 3-box mass balance model: 1) continental crust (and its mantle lithosphere), 2) all the basaltic oceanic crust formed over Earth history, and 3) the complementary depleted peridotite. Using an evolved average continent composition (GAO et al., 1998) and for "reservoir" 2, the global average MORB composition compiled from the PetDB database (SU, 2002) with a volume equal to 4.56 Ga of oceanic crust production assuming a constant rate equal to the modern rate, the calculated depleted mantle reservoir would have a major element composition nearly equal to that of the BSE with a slightly high (2.3%) Ca/Al ratio, a Th/U of 2.7 and, assuming a mean age of the basalt reservoir of 1.8 Ga, Sr Os and Pb isotopic compositions lying at the most depleted end of the MORB array. Corresponding 1.8 Ga basalt would plot close to the HIMU endmember in Pb (Figure

2). The MORB to HIMU isotopic array followed by many OIB could be produced by basalt:depleted-mantle proportions of 5:95 (MORB end) to 60:40 (HIMU end). Sr, Nd, Os and Pb isotopic compositions of FOZO fall at the composition expected for mantle that has only suffered the consequence of continent removal, not the additional depletion associated with oceanic crust production. In this model, FOZO reflects the average composition of the whole mantle. Adding recycled continental components then can produce the 2 EM end members. Whether this "completely processed" mantle model can be reconciled with He and Ar data remains to be seen, but it offers the alternative explanation that the heterogeneity of mantle-derived magmas primarily reflects variable proportions of recycled basalt to depleted peridotite in the magma source rather than mixing between distinct, geographically-isolated, reservoirs.

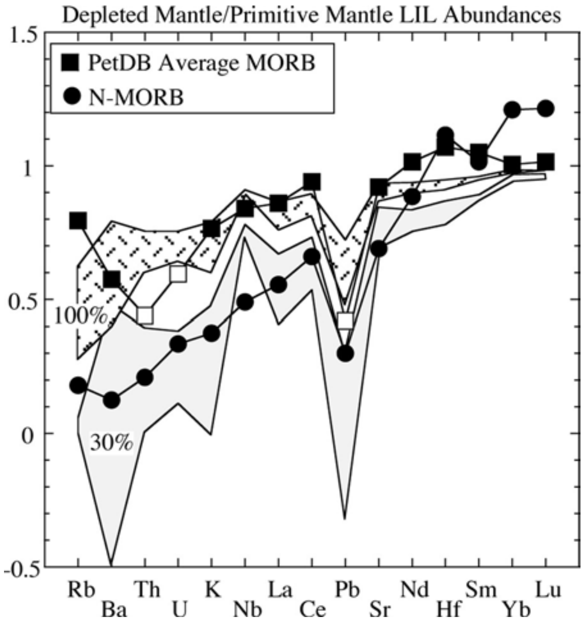

Figure 1. Trace element mass balance for continent extraction from the mantle. The stippled region is for crustal extraction from only 30% of the mantle, the patterned field involves 100% of the mantle. The width of these fields reflect the range in estimates of average continent composition (WEAVER and TARNEY, 1984; TAYLOR and MCLENNAN, 1985). Data plotted on this figure include the composition calculated for the sources of N-MORB (SUN and MCDONOUGH, 1989) and average oceanic crust (SU, 2002) assuming these oceanic basalts are the result of 15% partial melting of peridotite with no garnet present.

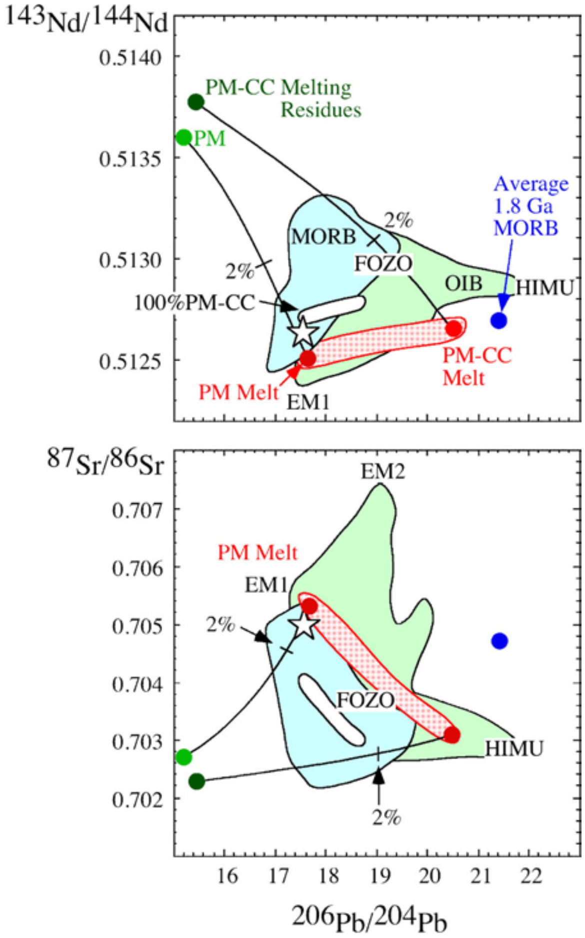

Figure 2. Sr-Nd-Pb isotopic range observed for oceanic basalts in comparison to the end member compositions discussed in the text. Plotted are the isotopic composition of 1.8 Ga ocean ridge melt and residue pairs, and the mixing lines between them from both primitive mantle (PM) and primitive mantle minus continental crust (PM-CC) starting compositions. The stippled red field reflects the range in composition of basalts derived from sources with various amounts of continental crust removed. The open field is the range of isotopic compositions expected for mantle residual from continent formation assuming the continents are balanced by the whole mantle.

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MagIC: The Magnetics Information Consortium and EarthRef.org

Constable, C; Koppers, A A P; Tauxe, L; Staudigel, H; Helly, J

EarthRef.org has compiled resources used to construct Earth Reference Models such as for geochemistry (GERM) and geophysics (REM). This approach can readily be expanded to any type of Earth science data and as a result we have started an online database for paleomagnetism (PMAG) under http://earthref.org/databases/PMAG/. This database stores all measurements and their derived properties for studies on paleomagnetic directions (inclination, declination) and intensities. Ultimately, this database will allow researchers to study on the internet and download important data sets that, for example, display the paleo-secular variations in the intensity of the Earth's magnetic field over geological time.

This paleomagnetic database is part of the Magnetics Information Consortium (MagIC) that is hosted by the EarthRef.org website and database. The MagIC consortium will establish a multi-user facility under this umbrella website that will accomplish two major goals. The first is to establish and maintain state-of-the-art relational databases that will form a digital archive for rock and paleomagnetic data. The second is to provide an Information Technology (IT) infrastructure and web portal for these and other research-oriented digital databases run by the international magnetics' community. As its name implies, MagIC will not be restricted to paleomagnetic or rock magnetic data, although the scope of material to be archived will initially focus on these kinds of information. In the longer term we anticipate that MagIC will effectively act as a kind of digital library for the full range of magnetic data collected in magnetic and electromagnetic research. As an example, the MagIC database will have direct links into the CHRONOS node on the Earth science cyber-infrastructure, where data with relevance of magneto-stratigraphy will be used in the construction of a dynamic timescale.

The PMAG database is completely integrated in the EarthRef.org relational database structure and thus benefits significantly from already-existing common database components, such as the EarthRef Reference Database (ERR) and Address Book (ERAB). The ERR allows researchers to find complete sets of literature resources as used in either GERM, REM or PMAG. The ERAB contains the addresses for all contributors to the EarthRef.org databases, but also for all the rock collectors, archivers and analysts appearing in these databases. Integration with both components will ensure direct traceability to the original sources of the PMAG data and metadata.

A prototype of the PMAG relational database is now operational within the existing EarthRef.org framework under http://earthref.org/databases/PMAG/. As will be shown in our presentation, the PMAG design focuses around the general workflow that results in the determination of typical paleo-magnetic analyses. This ensures that individual data points can be traced between the actual analysis and the specimen, sample, site, locality and expedition it belongs to. These relations guarantee traceability of the data by distinguishing between original and derived data, where the actual (raw) measurements are performed on the specimen level, and data on the sample level and higher are then derived products in the database. These relations may also serve to recalculate site means when new data becomes available for that locality.

The PMAG data records are extensively described in terms of metadata. These metadata are used when scientists search through this online database in order to view and download their needed data. They minimally include method descriptions for field sampling, laboratory techniques and statistical analyses. They also include selection criteria used during the interpretation of the data and, most importantly, critical information about the site location (latitude, longitude, elevation), geography (continent, country, region), geological setting (lithospheric plate or block, tectonic setting), geological age (age range, timescale name, stratigraphic position) and materials (rock type, classification, alteration state).

Data contribution to the PMAG database is most critical in achieving an useful research tool. We have developed data and metadata templates that can be used to provide all data during the publication process in a standardized format. Software tools are provided to facilitate an easy population of these templates. These tools allow for the import/export of data files in a delimited text format, and they provide functionality to validate data and to check their internal coherence in the template. During and after publication these standardized PMAG templates will be stored in the ERR database. From that moment on they can be searched for and downloaded from the EarthRef.org website. Finally, the contents of these template files will be automatically read out and parsed into the online relational PMAG database.

For more information on the development of MagIC data and metadata standards, template files and software tools, please visit the http://earthref.org/metadata/MAGIC/ website.

Temporal Evolution of Water in the Mantle

Dixon, J

A major uncertainty in the earth's water cycle is the effect of subduction and recycling of hydrated lithosphere on deep mantle water concentrations. There is general agreement that the earth accreted "wet" and that post-accretion influx of water to Earth from comets is limited to <~20% [1]. A minimum value of ~1000 ppm H_2O in the primitive mantle can be estimated by adding exosphere water (ocean, atmosphere, and crust) to the depleted mantle, assuming that this water comes from degassing of half the mantle and that the depleted mantle has ~100 ppm H_2O. Lower values of primitive mantle water (330 ppm for the Pacific and 430 ppm for the north Atlantic [2 & 3] are obtained by calculating the value required to produce a smooth depletion trend for highly incompatible elements in MORB. A similar phenomenon noted for Pb has been interpreted as preferential partitioning of Pb into the exosphere during subduction [e.g., 4]. I propose the same is true for water. Water concentrations in various mantle end-member components support this hypothesis. Mantle plumes enriched in recycled lithosphere (EM1, EM2, LOMU, and HIMU; $H_2O/Ce \leq 100$) have lower ratios of water to similarly incompatible elements than plumes dominated by the common plume component (FOZO; H_2O /Ce=210 to 300) [5]. High H_2O /Ce in FOZO plumes cannot be derived from recycled lithosphere; therefore, a significant amount of water must be juvenile, left over from planetary accretion. A model for mantle water evolution will be presented in which FOZO is composed dominantly of slightly-depleted, primitive, peridotitic mantle metasomatized by a small amount (1-3%) of a small extent melt (2-6%) of a HIMU component. Thus, dehydration during subduction effectively partitions water into the exosphere (mantle wedge, crust, ocean, atmosphere) resulting in time-integrated depletion of water relative to other incompatible elements in recycled lithosphere and accompanying continental-derived materials and, ultimately, the mantle.

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Seasonal to Millennial Gradients of Mercury in the San Francisco Bay Estuary

Flegal, A R; Conaway, C H; Luengen, A C; Flanders, J R

Relatively high levels [concentrations] of mercury in some of the sediments and biota in the San Francisco Bay estuary have been attributed both to historic inputs from cinnabar and gold mining within its drainage basin and to more recent inputs from other anthropogenic activities. The relative contribution of these diverse fluxes are now being resolved through a suite of complementary studies. They have also indicated that, in addition to those historic and contemporary fluxes of industrial mercury within the region, the estuary is now receiving measurable and potentially substantial fluxes of industrial mercury from the trans-Pacific advection of atmospheric emissions of fossil fuel combustion products in Asia.

Anthropogenic inputs of mercury to the estuary are evidenced by pronounced concentration gradients in both its southern and northern reaches. Inputs to the former are primarily attributed to historic and ongoing fluxes of mercury from the adjacent New Almaden quicksilver mining district (Thomas et al., 2002), that was the largest producer of mercury in North America with a total mercury yield of 37 million kg between 1845 and 1975 (Cargill et al., 1980). Inputs to the latter are primarily attributed to the fluvial transport of mercury contaminated sediments from the Sierra Nevada and Pacific Coast mountain ranges, where an estimated 5.8 million kg of mercury was used to extract gold during the preceding one and one half centuries (Conaway et al., 2003b).

The magnitudes of those historic perturbations are shown in sediment fluxes to the estuary, and are revealed by sediment core mercury concentration profiles in both the northern and southern reaches of the estuary. Hornberger et al. (1999) previously determined that the natural baseline concentration of mercury in sediments in the northern reach of 60 ng/g had been elevated to as high as 1000 ng/g by the deposition of mercury contaminated sediments from gold mining activities in the Sierras; and Conaway et al., (2003a) has recently determined that the natural baseline concentration of mercury in sediments in the southern reach of 70 ng/g had been elevated to as high as 1000 ng/g by the deposition of mercury contaminated sediments from mercury mining activities in the New Almaden mining district. It is notable that those baseline values are comparable to the average (10–100 ng/g) crustal abundance of mercury (Adriano 2001), considering the relatively large and extensive amounts of cinnabar deposits within the estuary's drainage basin.

The spatial distributions of mercury in surface sediments and waters also reflect, in part, those historic depositions (Conaway et al., 2003b). Those gradients in much more fluid [aquatic?] matrices are, of course, much more complex (Conaway et al., 2003c). It is remarkable that those mercury concentrations are similar to those of other large, urbanized estuaries that do not have comparable historic records of contamination and are primarily contaminated with recent industrial mercury inputs.

Moreover, contemporary fluxes of mercury to the estuary appear to be impacted by industrial emissions beyond the system's drainage basin. Recent analyses of mercury concentrations in precipitation within that region and in the adjacent coastal system indicate that much of the mercury is derived from the trans-Pacific transport of industrial aerosols from China (Steding and Flegal, 2002). These may include both mercury and oxidants that reduce elemental mercury to reactive species. The importance of the latter is further indicated by the relatively higher (2x) concentrations of mercury in precipitation within the estuarine system, where atmospheric fluxes of industrial mercury are considered to be relatively small.

In summary, these initial analyses of mercury concentrations and speciation in the San Francisco Bay estuary attest to the element's complex biogeochemical cycling. Several ongoing studies are in progress to further resolve some of the principal factors influencing that cycle.

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Variability of the Chemical Composition of Brahmaputra and Ganga Sediments

France-Lanord, C; Galy, A; Singh, S K

Riverine fluxes are of primary importance to understand geochemical cycling at the earth surface. Dissolved fluxes directly document the weathering reactions which control the input of element to the ocean. On the other hand, river sediment also document weathering reactions and are important to monitor the transfer of organic carbon and adsorbed elements to the ocean. Modern dissolved fluxes are relatively well known due to extensive measurements of international organizations for water quality and to efforts of the scientific community to trace the source of dissolved elements. In contrast, physical erosion is much less constrained. Fluxes of sediments are based on more or less reliable data on suspended load fluxes and little is know about the chemical and mineralogical composition of the sediments. This due to the fact that such fluxes are very difficult to monitor on large rivers and that large unknown remain on bedload transport (e.g. Callede et al., 2000, Galy and France-Lanord, 2001). Regarding the chemical composition of sediments, the problem is related to the complexity of the system. Unlike dissolved species which are essentially constant within a river section, suspended sediments are highly variable with depth due to mineral sorting during transport. Following the shape, size and density of minerals, the upper suspended loads have higher proportion of clay and micas than in deeper water and in bedload, which are enriched in quartz and coarser minerals. While this general figure appears simple, assessing the average chemical composition of the suspended load is far to be trivial due to this diversity. As a consequence, most data available, which correspond to sampling in the upper meter of water, are not representative of the real material transported in rivers.

We present a detailed sampling of the Brahmaputra and Ganga sediments to document the chemical composition of suspended and bed sediments. This includes sampling at various depths within the water column and dredged bedload sediments. Most samples were taken in summer 2000, 01 and 02 during the high flow period of the monsoon. The Ganga has been over ca. 1000 km of its course from Benares to Bangladesh. Combined with available data on stream flow by acoustic Doppler current profilers (ADCP) those data are used to calculate an average suspended sediment composition. For the Ganga and Brahmaputra, Al_2O_3/SiO_2 ratio evolve from 0.25-0.35 at the surface down to 0.15-0.27 at 10 m depth mainly as a response to the progressive increase of quartz. To the reverse, Fe_2O_3/SiO_2 ratios decrease from 0.08-0.10 at the surface to 0.05-0.08 at depth as a response to the progressive depletion in clays and micas. In the bedload, these ratios are much more extreme: Al_2O_3/SiO_2 = 0.10-0.18 and Fe_2O_3/SiO_2 0.02-0.05. Grain size distribution also evolves in parallel from an unimodal distribution around 20 μm at the surface to a bimodal distribution with a second mode around 200 μm at depth. Elements like Na, which is controlled by plagioclase, and Ca controlled by carbonates do no not show any systematic evolution with depth. Along the Ganga course, the suspended sediments are more progressively depleted in SiO_2 likely as a response to the deposition of quartz rich sediments in the floodplain. The data show that in Bangladesh, the Ganga suspended sediments are clearly enriched in Al and Fe relative to the average Himalayan sources. Using a simple geochemical mass balance and assuming steady state erosion of the Himalayan basins, these data imply that the fluxes of bedload transport and floodplain sequestration do represent 50 to 80 % of the suspended load fluxes.

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River Geochemistry and Hydrodynamics: Examples from the Amazon Basin

Gaillardet, J; Dosseto, A; Métivier, F; Maurice-Bourgoin, L; Guyot, J L

The degradation of rocks by weathering and erosion processes form materials whose size range from dissolved substances to millimetric particles. Their mobility strongly depends on the water flow velocity. The use of rivers to compute weathering and erosion budgets relies on the implicit assumption that all materials formed during the interaction of surface waters and rocks are exported out of the drainage basin. If this is probably true on a long-term average, a single point sampling may introduce a chemical bias due to heterogeneities in flow hydrodynamics. So far, geochemical studies of rivers have only focused on the dissolved and suspended products. The bottom sands have received little attention as well as the variation of chemical composition with depth within the river. We have conducted a series of depth profiles along transects of the Amazon main stem, the Solimoes and Madeira rivers and in the headwaters of the Rio Beni. Suspended solids and sands were sampled and analyzed for major and trace elements. Absolute concentrations vary significantly as a function of depth. However, elements do not have a unique behavior. A general decrease (15-20%) of concentrations with depth is observed for elements such as Al, Th, metals, Conversely, elements such as Si, Ti, Na and the REE show increasing concentrations with increasing depth. Consistently, elemental ratios vary with depth. This is particularly visible for ratios such as Al/Si ratios or REE patterns. Mass oxide Al/Si ratios vary from 0.4 to 0.25 from surface to depth in the Amazon main stem at Obidos. REE patterns show significant variations with depth with increasing HREE enrichment with depth. A good inverse correlation between La/Yb and Zr concentrations is observed at all depth profiles.

These remarkable trends are observed in the different locations are have probably to do to with mineralogical sorting as a function of depth. Si variations are imposed by quartz abundances, while REE or Zr are controlled by heavy metals. Ultimately, these relations between the chemistry of suspended sediments and depth are related to the flow velocity.

These preliminary results for the biggest river of the Earth clearly indicate that any calculation of chemical mass budgets using rivers has to take into account the variability with depth and therefore river hydrodynamics. Recent data obtained on the Brahmaputra river system by France Lanord et al. (this workshop) confirm our observations on the Amazon.

CHRONOS Network for Earth System History and the Geochemical Cycles-through-Time Node

Grossman, E L; McArthur, J; Bowring, S; Cervato, C; Davydov, V; Flower, B; Hinnov, L; Huber, B; Keane, C; Koppers, A A P; Leckie, R M; Marshall, C; Ogg, J; Sikora, P; Wardlaw, B

The CHRONOS Concept

Deciphering Earth System history depends increasingly upon the analysis of voluminous and varied sets of time-calibrated data. The process of compiling certain Earth history data, or even learning of their existence, remains a time-consuming and error-prone enterprise because centralized repositories and web-based archives that contain geological and geochemical data are few, restricted in content, and not of standardized format. The goal of the CHRONOS project is to deliver a dynamic, interactive and time-calibrated framework for Earth System history as a network of comprehensive databases containing information related to biotic evolution and diversity, climate change, geochemical cycles, geodynamical processes, and other aspects of the Earth system. The CHRONOS system will consist of a 'central hub' coordinating a network of individual databases (nodes) all linked to the same temporal framework (Fig. 1). The databases will be interactive and referenced to a constantly updating timescale that forms the core control on the data presentation. Proposed nodes include Life-through-Time, Radiometric Ages, Climate-through-Time, Geochemical Cycles-through-Time, Core-to-Crust Dynamics through Time, Education and Outreach, and Standard Geologic Time Scale.

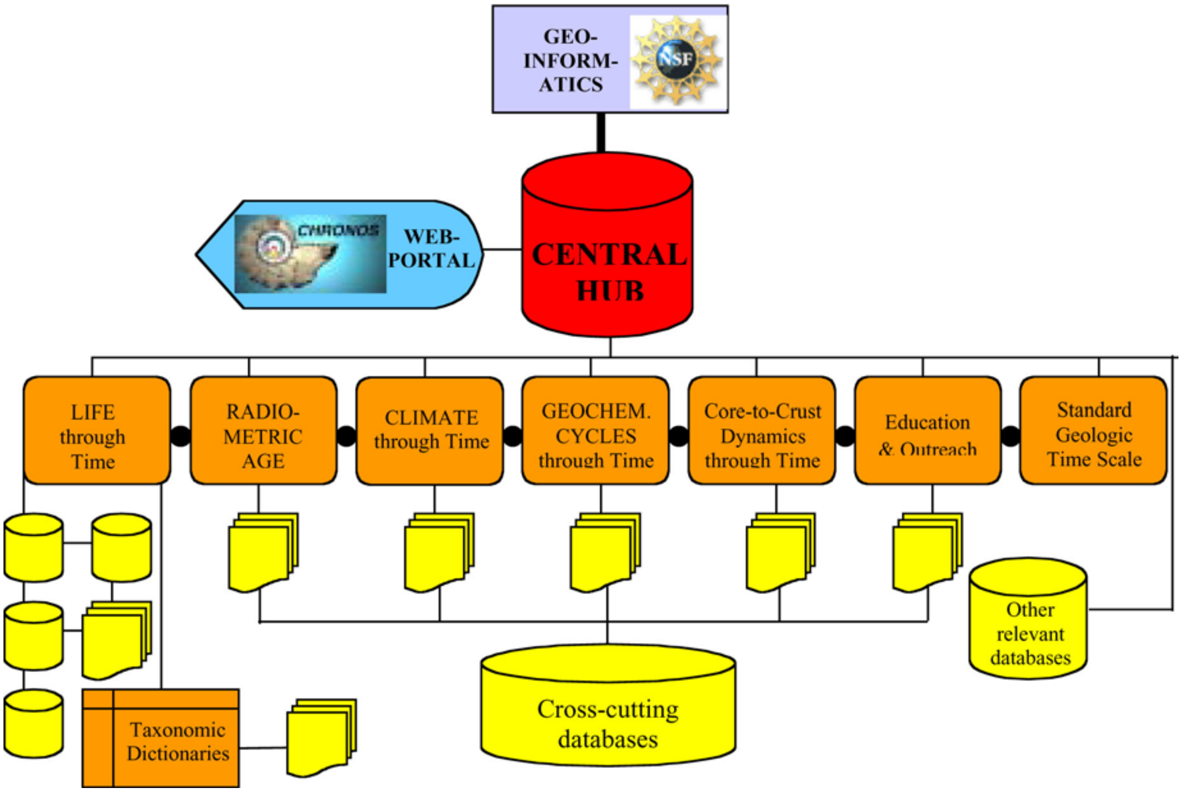

Figure 1. Basic structure of the CHRONOS system, and its envisioned role with the NSF geoinformatics network. Orange rectangles indicate thematic coordination task groups. Yellow cylinders and sheets represent databases and data sets, respectively.

CHRONOS will serve as a major portal for geological research and outreach, equipped with powerful, interactive analytical and visualization toolkits to enable Earth exploration. The wealth of existing Earth history data can be integrated with state-of-the-art information technologies and advanced correlation tools, with the goal of increasing the precision of global and regional geological time scales by an order of magnitude.

The CHRONOS IT System

The CHRONOS IT system will be a platform-independent open database network system that utilizes open software and standards. It will be composed of open and well-described interfaces to hosted and federated databases based on the web services model. This is an extremely flexible and open system that will be designed to inter-operate with Grid-based solutions such as OGSA (Open Grid Service Architecture) and other systems employed by GEON. It can be described in terms of five layers consisting of (from bottom up): (1) Database, (2) Translation/wrapper, (3) Interface registry, (4) Client, and (5) User and tools.

Implementation

The proposed CHRONOS project will carry out the following tasks over the next 6 years (2003-2009):

- Assemble a high-precision 'Standard Geological Time Scale' under the aegis of the International Commission on Stratigraphy;
- Progressively establish and interlink critical thematic database networks for fossil occurrences, radiometric ages, climate change, geochemical cycles, core-to-crust processes, and other components of Earth system history;
- Establish central CHRONOS portals to access and analyze major component data types for researchers and the general public;
- Develop advanced tools and visualization capabilities that investigators can apply to uploaded data; and
- Coordinate an outreach program with educational modules and informative demonstrations of the CHRONOS system.

The Geochemical Cycles through-Time node

The Geochemical Cycles through-Time (GCT) node of CHRONOS will be responsible for compiling the geochemical proxies linked to chronostratigraphy for interpreting global change and paleoclimate. These include the proven proxies of carbon, oxygen, sulfur, and strontium isotopes, and emerging proxies like boron, calcium, osmium, silicon, and iron isotopes. Furthermore, the GCT node will spearhead the repository of time-series data for element/calcium ratios in marine carbonates. The system will permit the integration of different proxy records for holistic interpretations, and enable evaluation of data schemes within a variety of stratigraphic and temporal schemes. Data will be catalogued with a comprehensive set of metadata permitting detailed evaluation of sample quality both in the fidelity of the data and in its spatial and temporal placement. As a start, metadata categories will include those discussed in Staudigel et al. (2002, Geochemistry, Geophysics, Geosystems). Additional information on sample quality will include overall specimen preservation, screening methods and ancillary data (e.g., trace-element data, petrographic and cathodoluminescent character), maximum burial depth, conodont alteration index, and sample size. Data compilation will be coordinated with GERM, enhancing the temporal component of that program. The two programs will share data and use standardized protocols so as to complement and not duplicate efforts.

Pending funding of the program, a workshop will be organized to discuss how to organize the database and display data to best fulfill the needs of the geochemistry community. In the meantime, the CHRONOS group and its GCM node are soliciting comments on what data and metadata to include in CHRONOS, and how best to integrate with GERM.

Testing and Application

The CHRONOS Consortium will study four critical time-slices of Earth history to test the expanding capabilities of the information-technology infrastructure and toolkits of the assembled CHRONOS system. The four time-slice studies will address longstanding scientific questions of societal relevance and interest (Cambrian life explosion; Permian-Triassic catastrophic extinctions; middle Cretaceous super-greenhouse world; middle Miocene climate transitions). Each involves different types and qualities of data and will improve and refine marine and continental data correlations at the global scale. The ultimate goal is for all geoscientists to be able to apply the CHRONOS system of integrated databases for deciphering the complex interactions of the Earth system through all of geologic time.

Carbon and Oxygen Isotopic Records of Late Paleozoic Oceans, Diagenetic Diversions, and Paleochemical Reference Samples

Grossman, E L; Yancey, T E

A key obstacle to producing a global record of isotopic variation in seawater and paleoclimate is distinguishing between the global signal and local environmental variability, interbasin environmental variability, and sample alteration. This is especially relevant to studies of the Paleozoic, though the issue is even central to Tertiary studies (e.g., Pearson et al., 2001). The well-studied Permo-Carboniferous provides some of the best examples of the power and pitfalls of Paleozoic paleochemical studies.

More than 2000 Permo-Carboniferous brachiopod shells and fine-grained carbonate samples have been analyzed by several research groups to provide fundamental understanding of Earth history (e.g., Popp et al., 1986; Bruckschen et al., 1999; Mii et al., 1999, 2001; Saltzman, 2002). Key discoveries include evidence for enhanced global burial of organic carbon in the Mid-Carboniferous (Popp et al., 1986) and its relation to Mid-Carboniferous glaciation (Bruckschen et al., 1999; Mii et al., 1999, 2001; Grossman et al., 2002). Superimposed on such global signals are important interbasin differences that reveal vital clues to ocean circulation patterns. For example, carbonates deposited on the European continent during the Pennsylvanian are enriched in ^{13}C relative to U.S. carbonates. Do such isotopic differences imply paleocirculation differences in eastern Panthalassan and western Paleotethyan oceans (e.g., upwelling versus downwelling), or isolation of the North American epicontinental sea (Holmden et al., 1998; Grossman et al., 2002; Saltzman, 2003). Answering such questions requires broader spatial coverage of fine-grained carbonate and brachiopod isotopic data, and application of coupled and uncoupled climate, ocean, ice-sheet, and biogeochemical models (e.g., Hyde et al., 1999; Hotinski et al., 2001; Huber et al., 2003).

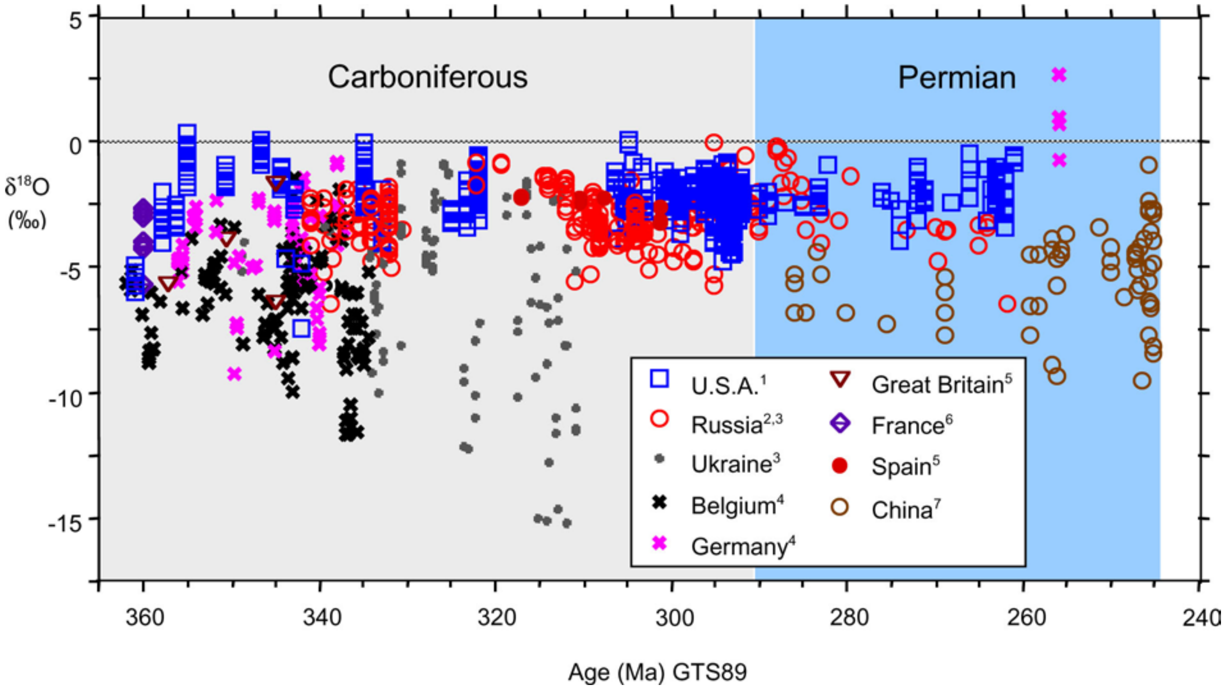

Figure 1. Oxygen isotope compositions of Permo-Carboniferous brachiopod shells from various countries. References: 1. Grossman et al., 1993, Mii et al., 1999, and Grossman et al., 2001; 2. Mii et al, 2001; 3. Bruckschen et al., 1999; 4. Bruckschen and Veizer, 1997; 5. Popp et al., 1986; 6. Brand and Legrand-Blain, 1993; 7. Veizer et al., 1999. Time scale is from Harland et al. (1990).

The greatest challenge to full description f the Paleozoic Earth system is to produce paleochemistry data free of diagenetic artifacts. Research groups disagree on the efficacy of different diagenetic screening approaches and obvious irregularities are commonplace in the isotopic record, especially in the δ^{18}O record. For example, δ^{18}O values for Carboniferous brachiopods from Belgium (–6.4 ± 2.1‰, N = 118; Bruckschen and Veizer, 1997) and the Ukraine (–5.9 ± 3.5‰, 102; Bruckschen et al., 1999) are low and highly variable, in contrast to values for specimens from the U.S. midcontinent (–2.2 ± 0.9‰, 737; Grossman et al., 1993; Mii et al., 1999) and Russian Platform (–3.0 ± 1.0‰, 293; Mii et al., 2001, Bruckschen et al., 2001) (Fig. 1). Do the low and variable δ^{18}O values for Belgian and Ukrainian specimens reflect a low-salinity habitat for brachiopods or undetected alteration of shells? Assuming a marine habitat for brachiopods, such low δ^{18}O values can only be explained by shell alteration or ocean temperatures greater than 50°C. The former is more likely.

One approach to better anchor paleochemical data is to establish reference samples, much as specimens are designated as type samples in taxonomic studies of organisms. Samples of unusual preservation, for example specimens from the Buckhorn Asphalt in Oklahoma (Brand, 1982) or late Pennsylvanian shales of North Central Texas (Grossman et al., 1991), could provide a baseline for the isotopic and trace-element chemistry of specific taxa. At the same time, we must explore new chemical and isotopic systems that are more sensitive to diagenesis than the diagenetic indicators currently in use. Perhaps boron or osmium chemistry has utility. A final goal should be standardized hierarchy of preservation tests that can be used to establish levels of confidence in the integrity of paleochemistry samples and data.

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Scalable Models of Data Sharing in Earth Sciences

Helly, J; Staudigel, H; Koppers, A A P

Many earth Science disciplines are currently experiencing the emergence of new ways of data publication and the establishment of an information technology infrastructure for data archiving and exchange. Building on efforts to standardize data and metadata publication in geochemistry (Staudigel et al., 2003) we are discussing options for data publication, archiving and exchange. All of these options have to be structured to meet some minimum requirements of scholarly publication, in particular reliability of archival, reproducibility and falsifiability. All data publication and archival methods should strive to produce data bases that are fully interoperable which requires an appropriate data and metadata interchange protocol. To accomplish the latter we propose a new Metadata Interchange Format (.mif) that can be used for more effective sharing of data and metadata across digital libraries, data archives and research projects. This is not a proposal for a particular set of metadata parameters but rather of a methodology that will enable them to be easily developed and interchanged between research organizations. Examples are provided for geochemical data as well as map images to illustrate the flexibility of the approach.

Temporal Variation of Hawaiian Plume Composition: Evidence from Hana Ridge (Submarine Haleakala Volcano), Hawaii

Johnson, K; Ren, Z Y; Takahashi, E

The mantle source generating the Hawaiian Islands is chemically heterogeneous from volcano to volcano as is well documented in numerous studies. Moreover, growing evidence suggests that the source also varies over time within a single volcano [Takahashi and Nakajima, 2002; Tanaka et al., 2002]. New data from the submarine shield stage of Haleakala volcano on Maui also suggest temporal variation of the Hawaiian plume source and contribute to new ideas on the structure, geometry, and composition of the plume itself.

Hana Ridge is the submarine portion of the east rift zone of Haleakala Volcano, Hawaii. At 140 km long, Hana Ridge is the longest submarine rift zone in the Hawaiian Island chain and has developed a complex morphology compared to other Hawaiian rift zones, such as Puna Ridge. The main ridge comprises three subparallel ridges related to distinct accretionary periods within the shield-building phase of Haleakala volcano. In order to investigate the variability of Hawaiian plume compositions over time and the geochemical evolution of Haleakala shield-building, we sampled several sections of Hana Ridge on six dives with ROV Kaiko and Shinkai 6500 submersible, both operated by JAMSTEC, in 2001 and 2002 [Johnson et al., 2002] (Figure 1).

All recovered rocks are tholeiitic basalts and more than half of them, those obtained in the deeper portions of the ridge, are picrites. This contrasts with the transitional to alkalic compositions from the subaerial shield stage of Haleakala (Honomanu stage) sparsely exposed in isolated outcrops [Chen et al., 1991]. Major and trace elements of the submarine Hana ridge rocks are similar to modern Kilauea and unlike subaerial Haleakala shield lavas. Each of the three subparallel ridges has a distinct trace element and rare earth element signature and their variations are geochemically self-consistent. This distinction carries over to radiogenic isotope compositions as well. The chemical variations defined by the sub-ridges plot within the general field for Kilauea lavas, but show consistent trends in trace element and isotope space from 2 strongly "Kilauea-like" to transitional with "Mauna Loa-like" compositions; all subaerial Honomanu shield lavas plot within the Mauna Loa trace element and isotope fields (Figure 2).

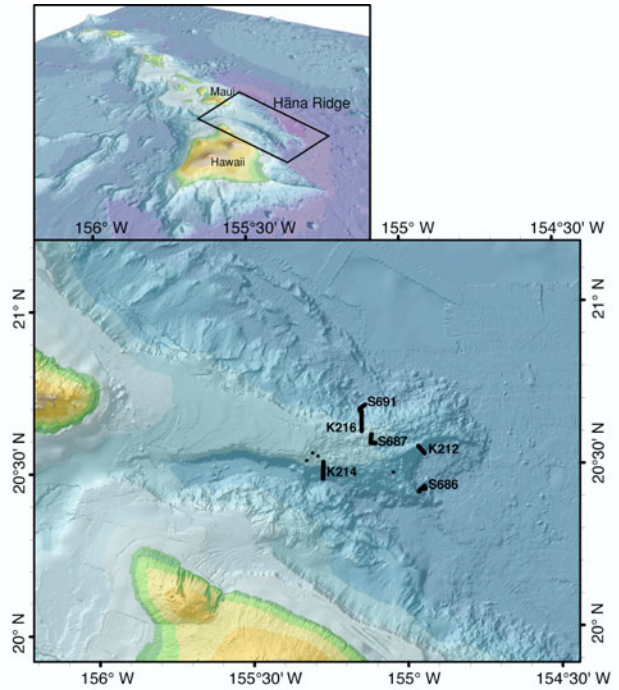

Figure 1. Perspective view of the Hawaiian Islands (top) showing the location and relative size of the Hana Ridge. Hana Ridge is shown (bottom) along with existing dredge sites (small dots; Moore et al., 1990) and JAMSTEC dive sites (Kxxx – ROV Kaiko, Sxxx – Shinkai 6500). Broad, smooth area uprift of sample sites is drowned coral reef.

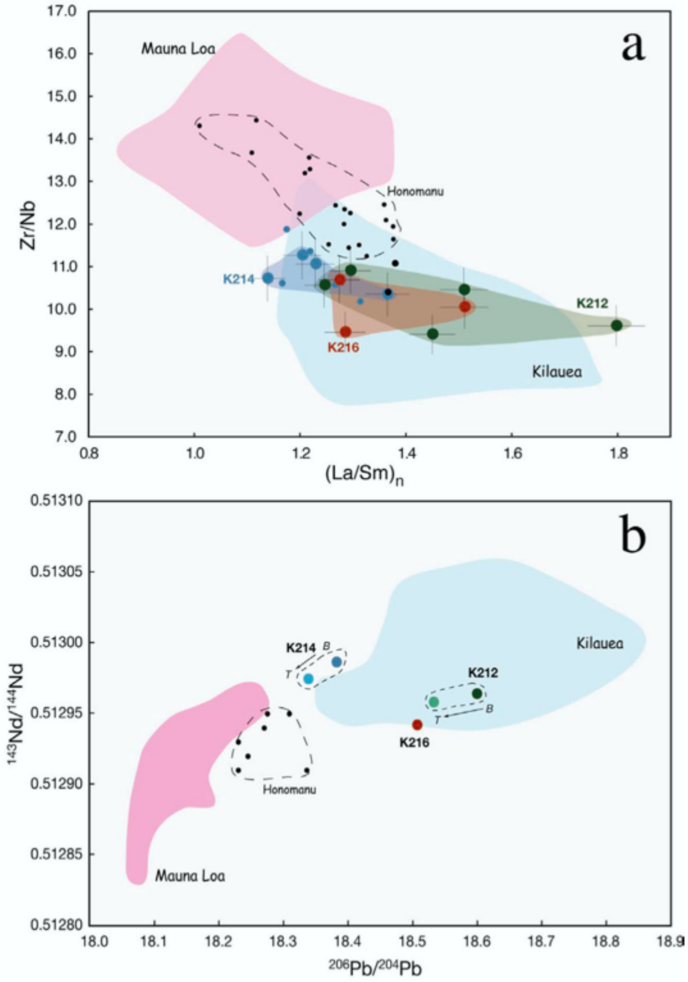

Figure 2. Variation diagrams for trace elements and isotopes in Hana Ridge samples analyzed to date [Johnson et al., 2002]. Fields for Kilauea and Mauna Loa are well separated in these plots. The Hana Ridge $(La/Sm)_n$-Zr/Nb (a) and Nd-Pb isotope (b) data plot within the field for Kilauea basalts, while the Honomanu data (subaerial Haleakala)extend strongly into the Mauna Loa field. The clustering and relative positions of data points are consistent in both plots. B an T indicate bottom and top of dive track.

Our results indicate that the mantle plume source for the Haleakala shield has changed over time from Kilauea-like compositions (high La/Sm, low Zr/Nb) in the submarine lavas to Mauna Loa-like compositions (lower La/Sm, higher Zr/Nb) in the subaerial Honomanu shield lavas. Moreover, the subparallel ridges comprising the greater Hana Ridge show a trend from higher to lower La/Sm and $^{206}Pb/^{204}Pb$ with location. We infer that Haleakala shield volcano originally had tholeiite magma compositions whose source material was similar to present-day Kilauea volcano and that the magma source became more Mauna Loa-like during growth of Haleakala volcano. Whether this temporal variation is consistent with that observed at Ko'olau volcano [Tanaka et al., 2002] awaits further analysis. It is hoped that the data from this study, coupled with work on other Hawaiian shields, can improve our understanding of the structure and melting processes of the Hawaiian plume.

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Geochemical Implications of Subduction of a Young, Sediment-Starved Slab

Keller, R

Young, sediment-starved oceanic lithosphere has been subducting into the South Shetland Trench (northern Antarctic Peninsula) for at least the past 30 million years. Sometime between 50 Ma and 25 Ma a dramatic change occurred in the isotopic characteristics of volcanism in the South Shetland Arc that may be tied to the unusual composition of the subducted slab. This may have important implications for the early chemical history of the Earth, when subduction of young lithosphere was common.

Until the Drake Passage opened between the Antarctic Peninsula and the southern tip of South America at about 30 Ma, the northern Antarctic Peninsula had much in common with the southern Andes. Arc volcanism on the South Shetland Islands can be traced back more than 120 m.y., although it appears to have waned or ceased after about 20 Ma. More recently, trench rollback caused rifting between the South Shetland Islands and the northern tip of the Antarctic Peninsula, creating the Bransfield Strait back-arc basin. Arc volcanism younger than 30 Ma is isotopically unlike the older arc volcanism, but is similar to some of the recent back-arc volcanism. This isotopic shift coincides with a change in the nature of the subducting slab. For at least the past 30 m.y. the subducting lithosphere has not been much older than 20-25 m.y. old at the trench. Also for the past 30 m.y., the opening of Drake Passage allowed the establishment of the Antarctic Circumpolar Current, which sweeps clean the oceanic plate and keeps sediment, with the exception of isolated pondings, from reaching the South Shetland Trench. The strong currents and lack of sediment also promote the growth of thick ferromanganese crusts.

The role of subducted ferromanganese crusts is evident in comparing the isotopic characteristics of pre- vs post-30 Ma volcanism. Isotopic data from the arc are extremely limited, but Sr-Nd-Pb isotopic compositions of volcanic rocks older than 30 Ma (prior to opening of Drake Passage and establishment of the Antarctic Circumpolar Current) can be modeled by mixing a depleted mantle source with a few percent sediment (short-dashed mixing line in figure). The youngest arc sample for which data are available (24 Ma) is isotopically similar to the Quaternary back-arc volcanism, but is very different from the earlier arc volcanism. This post-30 Ma volcanism (both arc and back arc) can not be modeled by mixing depleted mantle with a sediment component, unless that sediment component has a very high Pb

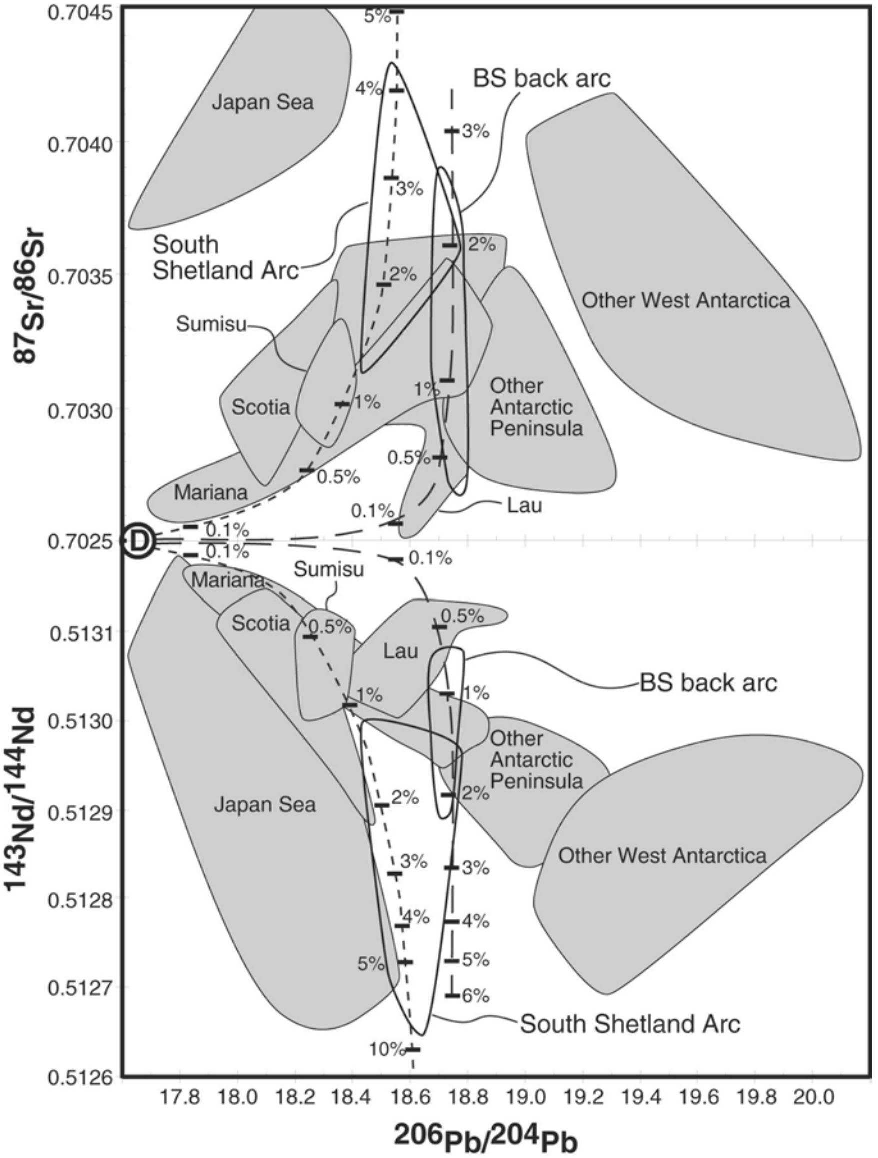

Figure 1. ^{206}Pb/^{204}Pb vs. ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd of South Shetland Island Arc and Bransfield Strait back arc volcanism (unfilled fields) compared to published data from other backarc basins and West Antarctica (filled fields). The short-dashed line is a calculated mixing line between a depleted mantle component (shown by large D) and South Atlantic sediment. This mixing line reproduces the isotopic characteristics of most of the older South Shetland Arc volcanism, however, it does not account for the isotopic characteristics of the post-30 Ma arc volcanism, nor any of the back-arc volcanism. The long-dashed line is a calculated mixing line between the depleted mantle component and a metalliferous sediment component with very high Pb concentration, high ^{87}Sr/^{86}Sr, low ^{143}Nd/^{144}Nd, and very low Sr/Pb and Nd/Pb. This mixing line successfully reproduces the isotopic characteristics of the post-30 Ma volcanism. Tick marks on the mixing lines are labeled with the percentages of the sediment components. Values used for the mixing calculations are: D (Sr = 20 ppm, ^{87}Sr/^{86}Sr = 0.7025, Nd = 1.1 ppm, ^{143}Nd/^{144}Nd = 0.5132, Pb = 0.043 ppm, and ^{206}Pb/^{204}Pb = 17.6), South Atlantic sediment (Sr = 173 ppm, ^{87}Sr/^{86}Sr = 0.7089, Nd = 9.4 ppm, ^{143}Nd/^{144}Nd = 0.5125, Pb = 13.4 ppm, and ^{206}Pb/^{204}Pb = 18.63), and metalliferous sediment (Pb = 200 ppm, ^{206}Pb/^{204}Pb = 18.75, 87Sr/86Sr = 0.709, ^{143}Nd/^{144}Nd = 0.5124, Sr/Pb = 1, and Nd/Pb = 0.1). Shaded fields are Japan Sea, Sumisu Rift, East Scotia Sea, Lau Basin, Mariana Trough, other locations on the Antarctic Peninsula (not subduction related), and other locations in West Antarctica.

concentration (long-dashed mixing line in figure). Metalliferous sediments are known to have high Pb concentrations, and are a likely mixing component given the tectonic history of the area. That this shift in isotopic signature of the volcanism coincided with a change to a young, sediment-starved subducting slab, suggests that times in Earth's history when subduction of young slabs was more common may have seen very different crust-mantle fluxes of Pb and other elements abundant in metalliferous sediments.

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Lau Basin: Hergt and Farley, 1994; Hergt and Hawkesworth, 1994; Volpe et al., 1988.
Mariana Trough: Hawkins et al., 1990; Stern et al., 1990; Volpe et al., 1990.
Other Antarctica: Hart et al., 1995; Hole, 1990; Hole et al., 1993; Rocholl et al., 1995.
Sediments: Ben Othman et al., 1989.
Sumisu Rift: Hochstaedter et al., 1990

Linking Cretaceous to Current Volcanism in the SW Pacific

Konter, J G; Koppers, A A P; Staudigel, H; Blichert-Toft, J

The isotopic variations in the islands in the Southern Pacific (SOPITA) can be tracked back in time by studying seamounts in the West Pacific Seamount Province (WPSP). Seamounts in the latter region are located on Cretaceous and Jurassic crust and may be related to younger island chains of SOPITA. Age progression, geochemistry and backtracking using absolute plate motions, make it possible to distinguish several different groups in this complicated region.

The WPSP can be divided into age groups of 120 – 100 Ma, 100 – 70 Ma and younger than 70 Ma (cf. Koppers, 1998; Koppers et al., 2003). Different chains that fall in a certain age group define parallel trends on the Pacific plate. These trends, however, can be difficult to discern, since younger trails are often superimposed on older ones. Therefore, additional (geochemical) data is needed to define a link between currently-active chains and older chains in the WPSP.

Backtracking of 100 - 70 Ma old seamount chains in the area (Magellan, Anewetak, Ralik and Ratak, see figure 1 for overview) based on absolute Pacific plate motion, places these seamounts close to the currently-active chains of Macdonald Seamount and the Cook (Rarotonga) and Austral (Rurutu) islands. Moreover, the pattern of the backtracked older (120-100 Ma) South Wake seamounts shows a wide scatter of locations instead of a single point. Their pattern resembles the currently-active Austral-Cook islands, suggesting a more complicated origin than a single melt source (i.e. hot spot). Possible causes for this type of distributed activity could be that this chain is a result of either a hot-line or closely-spaced conduits, both causing distributed melting. Either may explain the lack of age progression in these seamount chains. This type of distributed volcanism has been suggested to be due to plate tension, faulting, wetspots or self-propagating volcanoes instead of to a rising mantle plume. The discontinuity in volcanism is also reflected in several current chains not having clear trails back into the past (Samoa and Marquesas) and several older chains that suddenly ceased activity (Typhoon and Japanese Seamounts, and the Magellan, Anewetak and Ralik seamount trails) as described in Koppers et al. (2003).

The overall isotopic composition of the seamounts in the WPSP spans a similarly large range to that of the volcanic islands in the SOPITA region. However, each individual seamount trail seems to have distinct isotopic signatures. These compositional variations show similarities with islands and seamounts in the Southern Pacific. Most notably the Ratak chain, with the exception of Limalok seamount, has a similar isotopic composition to the Australs (Rurutu). The range in $^{143}Nd/^{144}Nd$ (0.512792 - 0.513186) of the Ratak chain overlaps but is slightly higher than 143Nd/144Nd (0.512629 – 0.512980) of the Austral-Cook islands. The $^{176}Hf/^{177}Hf$ (0.282910 - 0.283040) of the latter corresponds well to that of the South Wake chain (HIMU seamount and Golden Dragon respectively have $^{176}Hf/^{177}Hf$ of 0.282896 - 0.282920, and $^{143}Nd/^{144}Nd$ of 0.512866 - 0.512899). The isotopic ratios in the Ratak and Austral-Cook chains are not age-corrected and, therefore, likely to be closer in initial isotopic composition (Nd for S Wake from Koppers et al. (2003), others from GEOROC database, Hf this study). These similar compositions combined with the backtrack patterns of South Wake and Ratak plotting close to the Austral islands, argue for continuous magmatic activity in a SOPITA-like region over approximately 100-140 Ma.

The southern end of the Ratak chain, however, continues into the Gilbert Islands (Kiribati Islands). This chain of islands and seamounts is, therefore, expected to be both younger than 70 Ma and to be similar in isotopic composition to the Ratak chain. Initial results of geochemical and geochronological studies have shown that the ages of the Gilbert Islands and seamounts range from approximately 74 to 65 Ma, apparently showing a (moderately slow) age progression towards the south. Geochemically, these seamounts show similarity in $^{176}Hf/^{177}Hf$ with the South Wake chain. The total range is defined by Musina seamount in the north, which has $^{176}Hf/^{177}Hf$ of 0.282871 and Palutu in the south with 0.282948, while Ava has an anomalously low ratio of 0.282641. Pb isotopes will have to show conclusively, whether or not the South Wake – Ratak – Gilberts form a continuous chain. Noteworthy is that there seems to be a bend in the Gilberts chain around 3°S. In age this does not match the controversial bend in the Hawaiian - Emperor chain at 43 or 48 Ma. However, backtracking exercises still place its current activity in the SOPITA region, but this location would likely lie more towards the northeast (stage pole path in figure 1: used seamount: red square, backtracked position: circle). Moreover, this does not match geochemically, since the Pb isotopic compositions of the Society Islands are lower.

The Tokelau chain has a similar bend, again at a much older age than the Hawaiian – Emperor bend. This chain is located approximately 10° east of the Gilbert chain. It shows a similar age range (76 - 58 Ma) and a slightly higher $^{176}Hf/^{177}Hf$ signature at 0.282903 (Maitai) and 0.283050 (Polo). Backtracking using stage poles would place its current activity around Macdonald seamount, although its bend also suggests a more northeasterly location for current activity (figure 1, blue icons).

Therefore, although most volcanic activity in SOPITA seems to be discontinuous, a few links may be established between currently-active centers and older chains in the WPSP. However, due to the uncertainty of the tracks using stage poles, more geochemical data is necessary to be able to establish those links. Nevertheless, it remains clear that activity of SOPITA extends back for over 100 Ma.

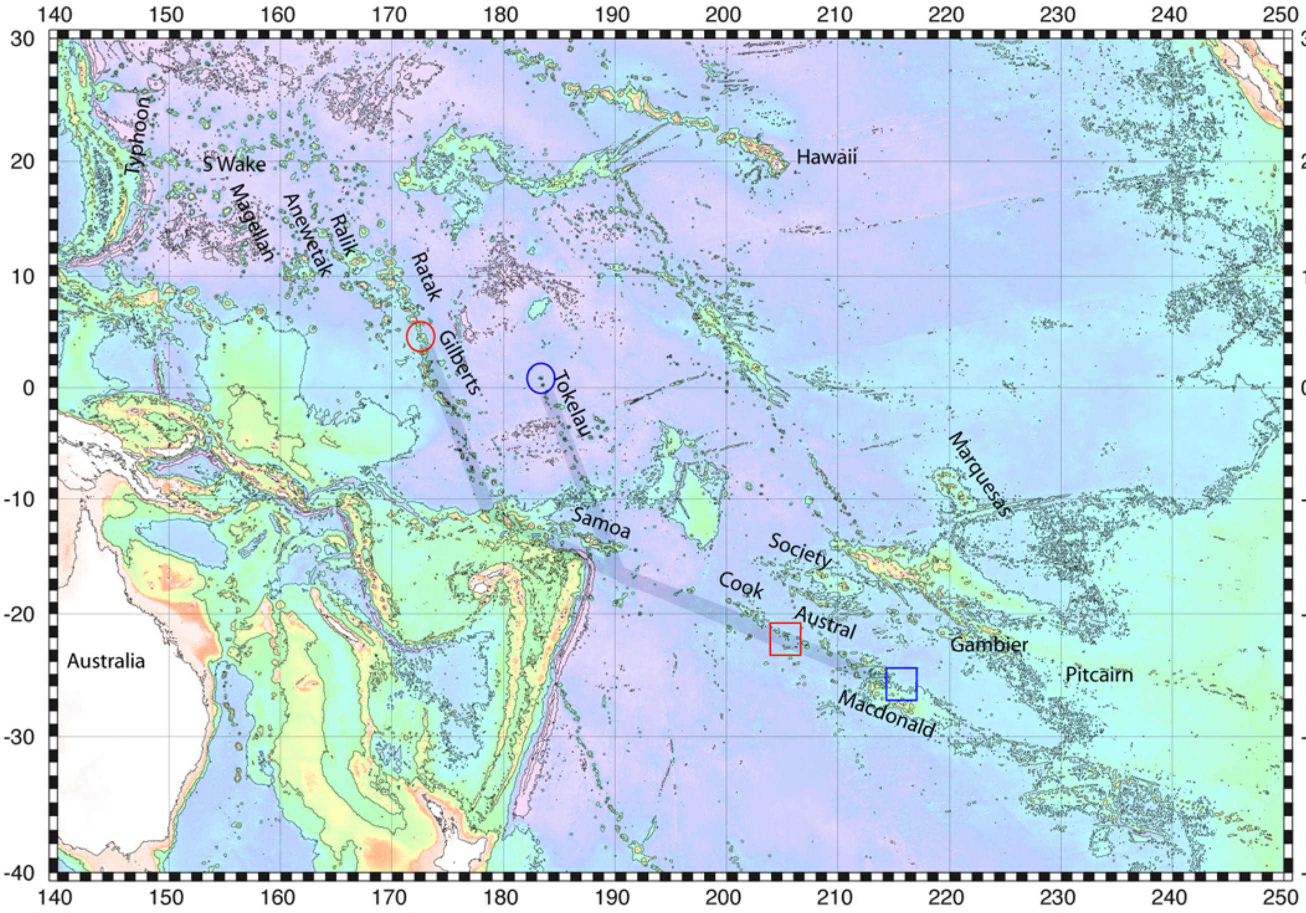

Figure 1. Map of the SW Pacific, showing the chains in SOPITA and WPSP. The red icons show the track of the Gilberts according to absolute Pacific plate motion, similarly blue for the Tokelaus. Circles represent the backtracked seamounts, squares the location of original volcanic activity.

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The CHRONOS Radio-Isotopic Age Database under the EarthRef.org Umbrella Website

Koppers, A A P; Bowring, S; Renne, P; Staudigel, H; and the CHRONOS initiative

CHRONOS is an international network that sets out to assemble, integrate and distribute any chronological data relevant to the Earth's history. A dynamic timescale will be one of its most important products, where scientists (but also the general public) can easily find not just summary information, but all relevant data that were used to define the standard geological timescale. The CHRONOS timescale will be dynamic to allow for interactive searching in the underlying databases, and to see what effects new timescale data has on the overall timescale. It is also dynamic in the sense that it will allow users to drill down into the underlying data sources — all the way to the original scientific publications or the raw measurements, in case of radio-isotopic ages. The CHRONOS network will maintain a stable version of the timescale, which only will be updated and reviewed every 4 years.

The structure of the CHRONOS networking system will be composed of a central hub linking to a set of thematically coordinated databases. The central hub will function as a portal to all these databases and it will provide basic search, interrogation and visualization tools for the geological timescale. However, the thematic databases themselves will be highly-specialized with their own web interface and visualization tools. For example, the Radio-Isotopic Age Database (RAD) will be hosted under the http://earthref.org website, which forms another central hub in the Earth science cyber-infrastructure. Another analytical database for the Magnetics Information Consortium (MagIC) that archives paleopoles and magneto-stratigraphy data is already being developed and operational on EarthRef.org as a prototype database. Both the RAD and MagIC databases have an analytical nature and to allow other scientists to effectively use these resources, these databases will store all data including raw measurements, applied correction factors, and all their variously derived parameters. This is an important design feature, because it allows scientists to interrogate these databases to answer questions about data quality — which is one of the primary issues in the definition of the timescale, and scientific databases in general. This database setup also allows to recalibrate an entire suite of radio-isotopic ages towards new standard calibrations or using better-determined decay constants.

By integrating the RAD and MagIC databases in the relational database structure of EarthRef.org these CHRONOS-related initiatives will benefit significantly from already-existing database components, such as the EarthRef Reference Database (ERR) and Address Book (ERAB). The ERR allows researchers to find complete sets of literature resources. The ERAB contains the addresses for all contributors to the EarthRef.org databases, but also for all the rock collectors, archivers and analysts appearing in these databases. Integration with both components will ensure direct traceability to the original sources of the timescale data and metadata.

Earth sciences stand on the threshold of a new era in data publication. It is, therefore, that today determines how we will archive all our scientific data and models, to make them most efficiently usable in an internet-driven research environment. The geological timescale clearly offers one of the more perfect data models, in which we can archive all data relevant to the Earth's history. Geological time is amongst the most fundamental geological data types with major implications to research and education, and it is an important part of most Earth science databases including GERM, PETDB, GEOROC and NAVDAT.

Advanced Data Management in Igneous Geochemistry

Lehnert, K; Langmuir, C; Carlson, R; Walker, D; Glazner, A; Farmer, L; Grossman, J; Black, R; Sarbas, B; Nohl, U; Hofmann, A

Geochemical and isotopic datasets for igneous rocks represent major investments by both investigators and funding agencies. Until a few years ago, these data were available only in data tables in printed journals. Transfer of these data into electronic format was done by individual investigators in a piecemeal fashion, and usually stored on the investigators' personal computer, inaccessible to the broader community. Recognizing the need to move beyond this quaint tradition, the ocean sciences community identified the need for a complete and widely available electronic database of geochemical results (White & Michael 1991). As a result, the PetDB database effort was initiated. As of 2001, PetDB contains ALL published and many unpublished analyses of igneous rocks generated at mid-ocean ridges and of abyssal peridotites in a freely accessible web-based data repository. An analogous effort addressing on-land igneous rocks was taken up by the GEOROC group at the Max Planck Institut fuer Chemie. GEOROC currently contains complete analyses of within-plate ocean island volcanic rocks and a substantial collection of volcanic rock analyses from convergent margins and large igneous provinces in their web-accessible database. Recently, another database effort, NAVDAT (North American Volcanic Rock Database), was initiated focusing on Cenozoic igneous rocks from western North America. All three databases use a similar data schema (Lehnert et al. 2000), which will allow them to be cross-searchable once suitable cross-database query programs are constructed.

While the databases share many common elements, parts of the schema for each database are specific to the needs of the different data sets. For example, PetDB contains considerable information related to the cruise where the samples were collected. NAVDAT contains more detailed location information and a deeper chronological data table to allow for information such as stratigraphic classification and complicated geochronologic results (e.g. ages determined with different techniques on different minerals with different closure temperatures). Extending this utility to other sample types (water, sediments, etc.) is easily done since sample-based geochemical data share many similarities irrespective of the nature of the specimen being analyzed.

In order for the geochemical databases to be mutually compatible, and to allow future integration with other data types, especially geospatial data, and interoperability with related databases, standards for data reporting and adoption of existing standards such as FGDC are essential. GERM could serve as the main proponent of this data standardization effort with the eventual reward of desktop accessibility of geochemical data for all members of the geochemistry community. Efforts are already underway to suggest standards for electronic data publication (Staudigel et al. 2002). The most pressing needs can be identified in the common problems shared by PetDB, GEOROC and NAVDAT. These include:

- Lack of unique sample identifiers. These are essential to identification and compilation of all data for one sample from different sources (publications or laboratories).
- Lack of detailed sample location and age information. For example, geographical coordinates are a prerequisite to integration with geospatial data and for the use of mapping tools.
- Limited, if any, discussion of analytical precision and/or presentation of results for international rock standards, crucial for proper evaluation of data and correction of interlaboratory bias.

The objectives for current geochemical data management efforts are two-fold: (1) to archive legacy data, and (2) to develop systems that will ensure correct and comprehensive reporting for future data. No clear solution to the above listed problems can be suggested for archival data except for the time-consuming task to track down essential information from authors. For future data, all problems of missing or incomplete information could be eliminated by requiring that authors provide this information before a paper can be accepted for publication. A more rigorous enforcement of data policies from funding agencies requiring submission and sharing of data and metadata could provide additional ways to ensure complete reporting of sample information. The problem of unique sample identification could be addressed in the context of establishing community-wide accessible sample archives.

A number of other issues important to database standards for igneous rocks require further consideration. These include issues such as the normalization of major element data to 100% anhydrous, standards for reporting Fe data (FeO vs. Fe_2O_3), establishment of standard isotope fractionation correction values (e.g. for Nd and stable isotope studies) and standards for interlaboratory comparison.

Finally, perhaps the most serious criticism that has been raised about electronic databases in geochemistry is that it currently is difficult to achieve correct attribution to subsets of data in large databases contributed by individual investigators. We suggest the following, at least partial, solutions to this problem. First, contributors of data to community-run databases could be allowed to list in their CVs the nature of their contributions to databases, in much the same way they now include lists of publications. Secondly, since the data in the database can be keyed to its source, databases potentially could keep track of the number of times a given dataset is accessed. In essence, this record keeping could provide something analogous to a “citation index”, and hence some measure of the community contribution provided by an individual's dataset contributed to the database. In addition, GERM should discuss this problem with ISI (the company producing the Science Citation Index) to find appropriate mechanisms for analysts’ recognition in the SCI.

Establishing clear standards that could be adopted by all existing and future database efforts and that were enforced in journals or through funding agencies would be a major step forward in making data universally available and properly attributed, to the benefit of all. We suggest that a GERM subcommittee be formed to establish such standards in combination with those responsible for the databases so that future data can be easily and rapidly included.

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A reference site for inputs into the West Pacific subduction Factory

Ludden, J; Plank, T; Staudigel, H

We have created a database for fresh glass, altered oceanic crust and overlying sediments from a reference site in the Pigafetta Basin in the West Pacific Ocean. ODP Site 801 was cored and sampled as part of ODP Leg 185 (see www site): http://www-odp.tamu.edu/publications/185_IR/185TOC.HTM.

This site is in Mesozoic ocean crust on a flow line sea-wards of the Mariana Arc. A complementary site, 15° to the north, also cored by ODP Leg 185, is located in the Nedezhda Basin seaward of the Izu-Bonnin arc. These two sites have undergone a significantly different sedimentation history and the substantial difference in the sedimentary package being subducted at the two sites can explain much of the north-south variation in arc-lava geochemistry. This is particularly evident in mixing relationships for Pb-isotopes between ocean crust compositions and the local sediment column. Similar compositional trends related to the incoming sediment flux in terms of aeolian input, fish particles in pelagic sediments, hot-spot related volcaniclastics are reflected in the compositions of the arc lavas.

One of the main objectives of this project was to have a full data set on a well defined section of altered oceanic crust at Site 801 which has been cored to almost 500 meters and is in fast-spread ocean crust formed in an environment similar to the modern East Pacific Rise. The site has volcanic glass preserved throughout the section allowing definition of the primary geochemistry and petrology. Alteration mineralogy and characteristics were described in detail and include quantification of alteration types and vein distribution. Downhole logs were used to "fill the gaps" in the coring intervals and to quantify the amount of interflow material based primarily on U, Th and K-compositions derived from the logs

The geochemical database involves discrete downhole samples and, in particular, a suite of "composite" samples that were sampled onboard, crushed and then mixed by the Leg 185 team. The composites were split into two batches, one has been kept at the CRPG (Ludden), the other at Scripps (Staudigel). Based on the quantities of different lithologies estimated from the logs and the core-descriptions, the composites were constructed from different mixtures of massive and pillowed flow material and volcaniclastic layers (including sediments in the upper section). Of particular note is that the estimates for the volcaniclastic components of the different depth composites exceed 20% in all of the depth intervals in the normal-MORB section of Site 801. This amount is 2 to 3 times higher than determined in many previous estimates in different oceanic crust sections.

Leg 185 results bear directly on the problems of (1) the forcing functions in the subduction factory output in arcs and in recycled crust, and (2) global geochemical cycles in the continental/ocean crust and ocean system for major anionic species (e.g. species of C and B) and for trace-elements (e.g. Fe, K, Re, Se, etc.).

Exchange of volatile elements between the mantle and the Earth's surface through time

Marty, B

It has been long assumed that atmospheric gases originated from the terrestrial mantle, mainly through early catastrophic degassing, possibly linked to terrestrial differentiation (Allègre et al., 1983; Ozima, 1975), and later on through residual mantle degassing as exemplified by helium. Such views, mostly based on differences between the atmosphere and the mantle in the amount of radiogenic rare gas isotopes produced by long-lived decay (^{40}K-^{36}Ar, leading to ^{40}Ar/^{36}Ar = 295.5 in air, versus $\geq$ 40,000 in the upper mantle (Moreira et al., 1998)) and short lived decay (^{129}I-^{129}Xe, leading to ^{129}Xe/^{130}Xe = 6.50 in air, versus 8.2 in the upper mantle (Staudacher et al., 1989)). This view has dramatically changed with the discovery of a neon isotope composition in the mantle different from that of the atmosphere, the mantle presenting a close to solar signature (e.g. ^{20}Ne/^{22}Ne = 13.8) whereas the atmosphere is characterized by a lower ^{20}Ne/^{22}Ne ratio of 9.80 (Hiyagon et al., 1992; Honda et al., 1991; Marty, 1989; Sarda et al., 1988). Such difference would not preclude a mantle origin for atmospheric gases if the latter were isotopically fractionated through atmospheric processes after degassing. However, a careful examination of the ^{129}I-^{129}Xe short-lived decay ($T_{1/2}$ = 16 Ma) and ^{244}Pu-$^{131-136}$Xe short-lived fission ($T_{1/2}$ = 82 Ma; after correction for contribution of ^{238}U-$^{131-136}$Xe long-lived fission, $T_{1/2}$ = 4.46 Ga) revealed that mantle gases could not straightforwardly associated with atmospheric gases (Ozima et al., 1985), requiring two different sources of volatile elements for the Earth (Marty, 1989).

The terrestrial mantle contains indeed volatile elements that were never degassed to the Earth's surface nor recycled back into the mantle through plate subduction. The best evidence for this is the isotopic composition of helium measured in mantle-derived rocks and minerals and in volcanic and geothermal gases, which indicates the occurrence of ^{3}He trapped during Earth's accretion (Clarke et al., 1969; Mamyrin et al., 1969). Helium degassing is still active and its recycling is negligible because helium is lost from the terrestrial atmosphere and because, as a light rare gas, it can be hardly recycled back into the mantle.

The isotopic composition of atmospheric xenon, when radiogenic and fissiogenic contributions are discarded, is unique in that it is fractionated by ~3 ‰ per amu relative to solar, or Q, xenon. Such fractionation could be due either to a "pre-terrestrial" process like gravitational fractionation in planetesimals (Ozima and Nakasawa, 1980), in which case the mantle should have a Xe isotope composition similar to that of air, or could have been produced during early atmospheric processing (Hunten et al., 1987), so that the mantle could have preserved non-fractionated Xe. This problem is not yet fully settled, mainly because mantle-derived samples contain extremely small amounts of trapped Xe which are difficult to analyze with precision, and also prone to surface contamination during magmatic evolution, lava eruption, or laboratory processing. So far, all samples analyzed with sufficient analytical precision to address this problem present an air-like isotopic composition (Moreira et al., 1998; Staudacher et al., 1989), with the notable exception of Xe present in some of natural gases rich in CO_2 of mantle derivation, for which the high abundance of Xe allowed extremely precise analysis of Xe isotopes. These analyses have revealed that CO_2-well gas Xe contains a small (≤ 10 %) component of planetary-like (or solar-like) Xe (Caffee et al., 1988). This discovery suggests that the solid Earth contains non-atmospheric Xe which was diluted by atmospheric Xe recycled into the mantle through subduction processes.

The case of other volatile elements is contrasted. The carbon isotopic composition of the surface inventory (organic inorganic) is about $\delta^{13}C = -7$ ‰, not significantly different from the isotopic composition of mantle carbon (-5 ‰) given uncertainties in computing the global surface carbon isotope budget. This similarity has been taken as evidence that carbon is exchanged between the mantle and the surface through magma generation along divergent plate boundaries on one hand, and through subduction of sediments and altered oceanic crust on another hand, at rates that are sufficiently fast on a geological time scale to insure efficient stirring of the concerned reservoirs. In contrast, the D/H ratio of the mantle (δD down to -90 ‰ vs. SMOW in MORBs originating from the upper mantle, δD down to -125 ‰ in amphibole from the Hawaiian plume presumably tapping the deep mantle (Deloule et al., 1991)) is clearly different from that of ocean water, demonstrating that the mantle is not in isotope equilibrium with the surface inventory.

The nitrogen isotopic composition of mantle-derived rocks and minerals indicates large-scale heterogeneity. Eclogitic, peridotitic, and fibrous diamonds show a distribution of $\delta^{15}N$ values (relative to atmospheric N), with a strong mode around –5 ‰ (Boyd and Pillinger, 1994; Cartigny et al., 1997; Javoy et al., 1984). The $\delta^{15}N$ distribution may be due to mixing between a light nitrogen end-member that could represent the primordial signature of the silicate Earth (Javoy, 1997) and a heavy nitrogen component originally residing at the Earth's surface and progressively recycled into the mantle.

Alternatively, the distribution of $\delta^{15}N$ values in diamonds may also be due to isotope fractionation occurring during diamond growth (Boyd et al., 1988). The mantle source of fluid-forming diamonds acquired probably this specific light nitrogen isotope signature (-5 ‰) as far back the Archean. Basalts erupted on the seafloor under considerable hydrostatic pressure contain CO_2-rich inclusions representing quenched gas bubbles having concentrated magmatic volatiles before eruption and being preserved from surface-derived contamination. Nitrogen and argon extracted by crushing of Mid-Ocean Ridge Basalt (MORB) glasses are correlated, and permit the identification of a mantle source nitrogen end-member depleted in $\delta^{15}N$ by 3-5 parts per mil on average (Javoy and Pineau, 1991; Marty and Humbert, 1997). The similarity of the $\delta^{15}N$ distribution for MORB and diamond data as well as comparable C/N ratios of MORB and diamonds strongly suggest that both sets of mantle-derived materials have sampled a common mantle nitrogen component. In contrast, $\delta^{15}N$ values of mantle-derived magmatic rocks associated with continental or oceanic plumes as attested by their rare gas signature are positive within the range from 0 ‰ to +6 ‰ (Dauphas and Marty, 1999; Marty and Dauphas, 2003). The $\delta^{15}N$ values of plume-derived samples are comparable to those of oceanic nitrates, modern sediments, and high grade metamorphic minerals from paleo-subduction zones and, together with trace element concentrations, radiogenic isotopic compositions, and stable isotopic ratios in plume-related lavas, are best explained by addition of sediments or altered oceanic crust to the source of plumes. The origin of this light N signature in the MORB and diamond mantle could represent a surface N component that was recycled long ago since (i) nitrogen metabolized during the anoxic Archean and later on incorporated in the crust and sediments might have been light (Beaumont and Robert, 1999; Pinti et al., 2001), and (ii), there is petrologic evidence that nitrogen is indeed *pro parte* recycled into the mantle (Andersen et al., 1995). Comparable N/K ratios between the surface (sediments + crust) and the mantle constitute a strong argument for a recycled origin of nitrogen in the mantle (Marty and Dauphas, 2003).

The large-scale N isotope heterogeneity of the mantle may results from secular variation of the nitrogen isotope composition of recycled sediments, which is governed by specific metabolic paths having changed with the advent of oxygenated ocean. If this is the case, the contrast between mantle reservoirs reflects a profound change in the mantle convection regime through time. In the Archean, recycled material was stored in a mantle domain sampled by diamonds and by mid-ocean ridges. Starting from the Proterozoic, slabs reached deep, volatile-rich regions of the mantle which are now sampled by mantle plumes.

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Fluvial Fluxes to the Sea: What do Global Estimates tell us and how do they confuse us?

Milliman, J

Geochemists have used river sediment loads (both solid and dissolved) to estimate terrestrial erosion rates as well as the relative importance of various degradation processes. A thorough compilation and interpretation of existing data indicate that rivers presently discharge 35 x 10^3 km^3 of water annually, and 18 x 10^6 t of sediment and 3.9 x 10^6 t of dissolved solids. South Asia, particularly those regions draining young, wet mountains, account for most of the sediment input to the global ocean.

However, hidden within these numbers are many problems, as a brief listing can indicate:

- Human impact - nearly all rivers are impacted by man, Asian rivers, in particular, carrying much higher loads than before agriculture was organized. At the same time, dam construction has drastically reduced the sediment loads of many rivers. The problems are not restricted to sediment loads either: mining and industrial activities have elevated dissolved loads in many European rivers as much as an order of magnitude over natural levels.

- Short and inadequate data bases - despite having made the best estimates possible with the available data, we are unfortunately all to aware of the lack of long-term data bases, which would more accurately take into account climate shifts.
- Wrong assumptions - even if the numbers were perfect, we would have a problem in terms of relating these numbers to actual processes at the river's source. Much of the sediment eroded in the high mountains is stored along the way to the river mouth, and much of it is exchanged with older sediment, some of which may have been chemically or mechanically altered.

Understanding these problems, of course, helps us temper our estimates and sweeping conclusions regarding fluvial processes and fluxes. But the buyer must be aware of a potentially flawed product.

Two-Stage Melting of a Plum-Pudding Mantle: A Possible Explanation for why there is high He/Ne and He/Ar in MORB and low He/Ne and He/Ar in OIB

Morgan, W J; Phipps Morgan, J

Recent compilations of the ratios of rare gas abundances in ocean island basalts (OIB) and mid-ocean basalts (MORB) show complementary ratios of helium relative to the heavier noble gases (in both radiogenic and non-radiogenic isotopes). OIB has lower ratios of He/Ne, He/Ar, He/Kr, and He/Xe whereas MORB has a relative surplus of helium. This evidence conflicts with mantle evolution models that invoke isolated, distinct, long-lived reservoirs as the sources of OIB and MORB. For example, ^{4}He and ^{21}Ne are both produced by the decay of uranium and thorium (the ^{4}He is directly produced by the decay; the occasional alpha particle reaction $^{18}O(\alpha,n)^{21}Ne$ produces ^{21}Ne). In mantle silicates, the production ratio of $^{4}He/^{21}Ne$ is constant (~ $2x10^{7}$:1), yet the $^{4}He/^{21}Ne$ ratio is higher than this in MORB and lower than this in OIB. This evidence is consistent with our previously proposed two-stage melting hypothesis in which the MORB source are the leftovers of OIB/EMORB-melt extraction from typical plum-pudding mantle that upwells in mantle plumes (these ‘leftovers’ are the asthenosphere that later melts at mid-ocean ridges to form MORB). We think the most likely mechanism to preferentially retain helium in residues to OIB melt-extraction is its higher diffusivity. Helium diffuses orders of magnitude faster than the heavier noble gases. Thus during mantle stirring and plume ascent helium (both ^{3}He and ^{4}He) partially diffuses from the ‘lumps’ of primordial or highly enriched material (high in U and Th among other LIL’s) into the more refractory material surrounding these lumps but the heavier noble gases do not. When the easier-to-melt lumps melt to make OIB, their gases have a deficiency of He. At the more extensive melting at mid-ocean ridges, some of the refractory material (into which He but not the heavier gases of the lumps had diffused) melts, giving an excess of He in MORB.

The Ancient Oxygen Isotopic Composition of Seawater Recorded in Ophiolites

Muehlenbachs, K; Banerjee, N R; Furnes, H

The oxygen isotope history of seawater remains controversial despite decades of study. Unlike isotopic data from fossils and chemical sediments, the isotopic compositions of ophiolites indicate ancient oceans had an oxygen isotopic composition indistinguishable from today's. It is now well documented that ancient seafloor rocks (ophiolites) provide a faithful record of seawater-rock exchange that can serve as proxies for the $\delta^{18}O$ of seawater. This is due to the fact that alteration of the seafloor by seawater imparts a very characteristic oxygen isotope fingerprint. This fingerprint results from two competing processes, which control the oxygen isotope composition of seawater through seawater-rock reactions. The first is low-temperature weathering processes within the pillow basalt section, which lead to enrichment in ^{18}O of the volcanic sequence. This process is proportional to the amount of high-^{18}O, low-temperature minerals such as smectite and other phyllosilicates that form due to hydration of the basaltic crust. In contrast, high-temperature circulation of hydrothermal fluids within the sheeted dykes and gabbros lead to depletion in ^{18}O of these lower crustal units. Similarly, the magnitude of this exchange is relative to the modal proportion of low-^{18}O, high-temperature secondary minerals, such as chlorite and epidote. These trends are the consequence of the high water to rock ratio of seafloor alteration and the temperature dependence of the ^{18}O partitioning between minerals and water. Stratigraphic superposition of enriched $\delta^{18}O$ pillows above depleted $\delta^{18}O$ dykes and gabbros is unique to hydrothermally altered oceanic crust. This geochemical trend is easily recognized in well-preserved ophiolites and has been described from numerous locations. Furthermore ancient, dismembered, and highly metamorphosed ophiolite segments as well as eclogite nodules from kimberlites still commonly retain their original seawater imprint because subsequent metamorphism was relatively closed to isotopic exchange with external fluids. Inspection of published oxygen isotope data for modern seafloor and ophiolite samples reveals no secular trend in $\delta^{18}O$, indicating that the $\delta^{18}O$ of seawater has not changed throughout geological time. Since the $\delta^{18}O$ of seawater itself is fixed by seawater-rock exchange, the consistency of the $\delta^{18}O$ of seawater implies that the overall processes governing seawater-rock interaction, such as the style and scale of this exchange, has not changed over time.

Ophiolites are particularly useful since they record the time-integrated effects of hydrothermal alteration, including possible overprinting of high-temperature exchange as the crust moves off axis. However, most studies of ophiolites do not seem to support the hypothesis that oxygen isotope depletions due to high-temperature hydrothermal exchange are later overprinted by low-temperature seawater circulation in an off-axis environment. We attribute this to off-axis localization of deep seawater circulation in zones of high permeability, such as faults and fissures, resulting in relatively small and spatially restricted isotopic shifts, relative to deep, pervasive on-axis processes. This localization is in part due to sealing of the crust within a relatively short period of time after eruption due to precipitation of secondary minerals.

Here we review previously published analyses and present new data from the 1.95 billion-year-old Jormua ophiolite (Finland) and 160 million-year-old Mirdita ophiolite (Albania) that confirm seawater $\delta^{18}O$ has been buffered near $0 \pm 2‰$ since the early Proterozoic. Both of these ophiolites record enrichment of their extrusive volcanic sequences (pillow lavas) and concomitant depletions within the sheeted dykes and gabbros as observed in modern oceanic crust (Table 1). Calculated $\delta^{18}O$ compositions of the fluids in equilibrium with quartz and epidote mineral separates from highly altered samples of the

Mirdita ophiolite suggest an evolved seawater source. The fact that these ophiolites of widely varying ages preserve relatively similar oxygen isotopic profiles further supports the argument that ophiolites preserve their original seafloor oxygen isotopic alteration signatures.

	Mirdita Ophiolite (160 Ma)				Jormua Ophiolite (1.95 Ga)			
	Min.	Max.	Ave.	n	Min.	Max.	Ave.	n
Volcanics	6.5	12.4	8.7	29	4.0	8.5	7.2	30
Dykes	4.1	7.1	5.6	8	1.4	4.7	3.1	9
Gabbros	4.5	7.5	5.3	6	4.3	4.7	4.5	3

Table 1. Oxygen stable isotope analyses from the Mirdita and Jormua ophiolites.

The Continental Lithospheric Mantle

Pearson, D G

The continental lithospheric mantle (CLM) is an ancient low-volume Earth reservoir, currently estimated to comprise approximately 2.5% of the total mantle volume [1]. Despite its low volume, a combination of the distinctive bulk composition and antiquity has lead to models where the addition of this reservoir back into the convecting mantle is invoked to be the cause significant variations in the composition of magmas erupted in the oceans [2].

Our two main samples of CLM are massif peridotites and xenoliths. Massifs generally sample relatively shallow CLM, almost exclusively of post -Archean age. Xenoliths provide a larger range of depth sampling but the imprint of host-magma interaction needs to be removed before data can be interpreted. In general, CLM age correlates with the age of the overlying crust, i.e., Archean CLM underlies cratons, post-Archean CLM underlies non-cratonic areas [3]. In detail, the picture can be more complex.

A clear secular evolution of CLM bulk compositions is evident from xenolith studies. Younger CLM contains progressively more Fe-rich olivine such that Mg-number of olivine correlates positively with increasing age. Al and Ca contents show a negative correlation with melting age although this situation is complicated by the recent addition of diopside and garnet, plus orthopyroxene. The difference in bulk composition between Archean and fertile mantle gives the cratonic CLM a density difference of –2.4 %, imparting considerable buoyancy. The very high bulk Mg-number of cratonic peridotites can be interpreted in terms of an origin involving higher pressure (7-8 GPa) melt extraction. In contrast, the high Cr/Al of these rocks compared to non-cratonic peridotites could be interpreted in terms of shallow melting and subduction. These end-member models need to be resolved.

Much of the problem in understanding basic aspects of the genesis of many xenolith suites results from that fact that they have undergone considerable post-melt extraction modification of their mineralogy and bulk compositions. These changes affect the density of the CLM and its isotopic evolution. It is likely that significant garnet in cratonic garnet harzburgites exsolved from a higher pressure aluminous orthopyroxene precursor. New finds at the re-worked Bultfontein dumps show incontrovertible evidence for this. A remaining question is how much of this, and other orthopyroxene was introduced post-melting. The presence of large exsolved orthopyroxenes in normal granular harzburgites together with orthopyroxene banding found in some Kaapvaal peridotites suggests a melt-rock reaction, as advocated by Keleman et al. [4].

In addition to orthopyroxene, it seems likely that almost all diopside and significant amounts of extra garnet grew in cratonic peridotite xenoliths due to introduction of melts, probably associated with the host kimberlitic/alkalic magmatism [5,6]. Diopside and garnet in most lherzolites are not in major or trace element equilibrium and cannot be used on isochron plots with any confidence. The introduction of diopside during melt interaction is also likely in many non-cratonic, spinel-facies peridotites. These effects result in the present-day average isotopic composition of the CLM being close to Bulk Earth and not "enriched" as assumed in many petrogenetic models. Where CLM can be identified that has experienced less melt interaction, isotopic signatures can be "enriched" or "depleted" and the concentration of incompatible elements is very low (<< fertile mantle).

The CLM cannot be uniquely defined in terms of Nd, Sr or Pb isotopes. However, Os isotopes and emerging Hf isotope data show that the CLM is highly distinctive, with unradiogenic Os isotope compositions and radiogenic Hf compared to Nd isotopic compositions. This results in lithospheric peridotite compositions that are considerably above the mantle Nd- Hf array.

Elemental data for metasomatic rocks (MARID, PKP, glimmerites) show that they are enriched in HFSE and hence, on their own, are an unlikely source for the low Ti-Nb melts that erupt through continents. Olivine-poor, pyroxene-rich assemblages (eclogites, pyroxenites and variants) have greater enrichment in incompatible elements and immense isotopic variation. γOs values range to over 5000. Calculated bulk εHf values are commonly above +50, with rare garnet-rich assemblages having initial εHf up to + 25000 [7]. Similar, but less extreme isotopic variation is observed in pyroxenites from massif peridotites. Most samples scatter well off the mantle Nd-Hf isotope correlation line. Participation of such material during magma formation will obviously impart dramatic isotopic changes in the resulting melts and may well explain some of the Hf isotopic variability observed in MORB. Most estimates of the volume of olivine-poor lithologies in the CLM, based on both xenolith and massif studies, are in the region of 1 to 3 %. These volumes are insufficient to account for the "significant" volumes of refractory, HFSE-rich material suggested to complete the Bulk Earth mass balance [8]. However, isotopic and elemental studies of such CLM lithologies give an indication of their potential effects in convecting mantle magma source regions.

Although much can be said about the age and processes that generate and affect CLM through the study of mantle xenoliths, there is increasing evidence that post-melting melt infiltration and reaction has severely affected the mineralogy, elemental and isotopic composition of peridotites. Hence, the xenolith sample is a biased view. This makes the identification of representative lithospheric compositions speculative. Current average estimates almost certainly over-estimate the fertility and general level of incompatible element abundances of bulk CLM. Deeper, basal CLM is more fertile but approaches Bulk Earth in isotopic composition. These observations suggest that isotopically "enriched" CLM is a rarity and is usually very depleted in incompatible elements relative to fertile mantle. From these constraints it is far from obvious that recycled/delaminated CLM has a role to play in explaining the incompatible element and Sr-Nd-Hf isotopic composition of OIB.

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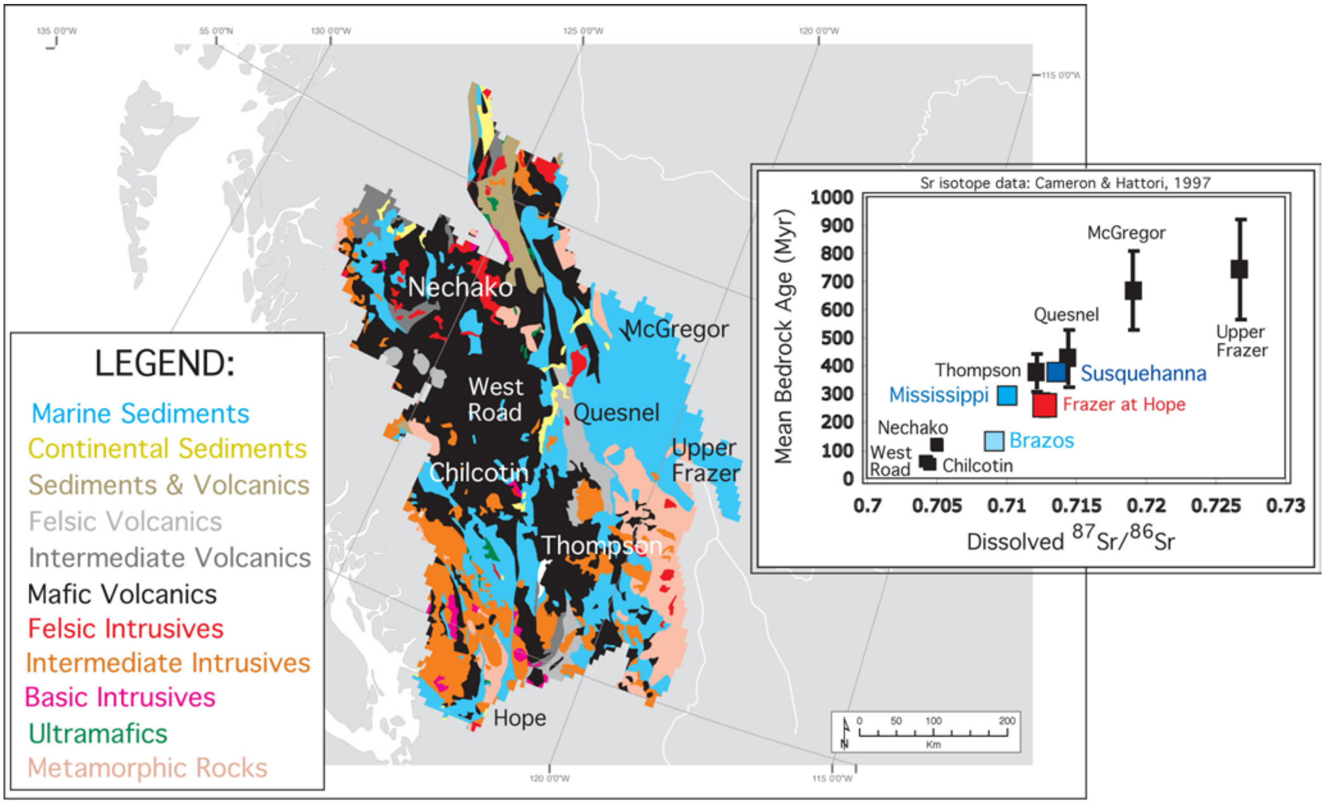
A New Initiative Investigating Links Between River Basin BedrockGeology and River Chemistry

Peucker-Ehrenbrink, B; Miller, M W

Interaction of rainwater with bedrock exerts a strong influence on the chemical and isotopic composition of river water. It should thus be possible to deduce important chemical and isotopic characteristics of river water from maps of bedrock geology. Unfortunately, detailed quantitative estimates of the Earth's surface geology are lacking. While some attempts have been made to quantify the lithologic composition of bedrock in individual river basins using coarse scale geologic maps and broad lithologic classifications (e.g., Reeder et al., 1972; Amiotte-Suchet et al., 2003), the geologic age distribution of bedrock in river basins has not been investigated. We have therefore initiated a project aimed at quantifying the lithologic composition and age structure of bedrock in river basins worldwide. For this project we use modern geographic information systems, digital geologic maps and a compilation of geochemical data to quantitatively investigate links between geology and river chemistry.

To date we have completed analysis of three digital data sets: 1) the geologic map of the conterminous United States of America (King and Beikman, 1974; 1:2,500,000; spatial resolution ~600 km^2 per polygon), made available in digital format by the USGS, 2) the geologic map of Alaska (Beikman, 1982; 1:2,5000,000; ~370 km^2 per polygon), also available in digital form through the USGS, and 3) the geologic map of Canada that is based on a revised and updated version of the geologic map by Douglas (1969; 1:5,000,000; ~780 km^2 per polygon), made available in digital format by the Geologic Survey of Canada (Wheeler et al., 1997). These data (Peucker-Ehrenbrink and Miller, 2002, 2003) have been used in conjunction with digital polygons of river drainage basins (Revenga et al., 1998) to compute the lithologic composition and geologic age structure of major river basins in North America. The lithologic compositions of 14 large (>40,000 km^2) river basins range from igneous rock-dominated (Frazer, Columbia), to sedimentary rock-dominated (Brazos, Susquehanna, Mississippi), to basins with an equal proportions of igneous, metamorphic and sedimentary bedrock (Thelon). A further subdivision of sedimentary rocks into marine and continental sedimentary rocks reveals that continental sediments account for no more than 25% of sedimentary rocks in these large river basins (e.g., Nelson, Colorado, Mississippi). A further subdivision of igneous rocks into intrusive and volcanic rocks reveals the entire range of igneous composition, from basins dominated by intrusive rocks (Hudson, Mackenzie, Nelson) to those dominated by volcanic rocks (Susquehanna, Colorado, Frazer, Columbia). Ultramafic bedrock covers significant areas in only a few basins (Susquehanna, Sacramento, Alabama and Tombigbee). Average bedrock ages range from ~130 Myr (Brazos) to ~2400 Myr (Thelon). We are currently analyzing the age distribution of major lithologic units in each river basin. An assessment of the spatial resolution of the digital data indicates that the resolution is adequate for investigating river basins larger than about 10,000 km^2 (i.e., ~20 polygons per basin).

For some river basins detailed hydrochemical data are available for the main stem and major tributaries (e.g., Frazer, Mississippi). For instance, detailed analysis of the Frazer River basin (British Columbia, Canada) and its tributaries yields a surprisingly linear correlation between mean bedrock age and the dissolved ^{87}Sr/^{86}Sr as well as the particulate ^{143}Nd/^{144}Nd (isotope data from Cameron and Hattori, 1997). Some other major river basins in North America, such as the Mississippi, the Susquehanna and the Brazos, plot on the same correlation (see Figure). Others, however, particularly those sourced in Precambrian terrains (e.g., Thelon, Nelson), deviated from the correlation defined by rivers draining predominantly Phanerozoic terrains (not shown). This indicates that parameterizations of riverine radiogenic isotope systematics need to take into account the susceptibility of bedrock (minerals) to weathering, the initial isotope composition and parent/daughter ratios of relevant bedrock (minerals).



Data Sources: Frazer Basin Polygon: World Resources Institute, 1998; Frazer Basin Geology: Geologic Survey of Canada, 1997; USGS, 1974.

Figure 1. Frazer river basin with major tributaries.

Depending on the availability of additional digital geologic maps we will expand the study to other continents, such as East and Southeast Asia (1:2,000,000; CCOP and Geologic Survey of Japan, 1997). Combining digital information on bedrock geology with digital maps of precipitation or runoff (e.g., Fekete et al., 2000) may allow us to use runoff-weighted bedrock area rather than simple area-lithology relationships. Depending on the availability of suitable digital data sets, other factors such as soil thickness, topography, land use (e.g., Revenga et al., 1998), and temperature can be added to the investigation at a later stage. Extending this analysis to pre-Quaternary periods is beyond the current focus of the project. However, we feel such a historic perspective is needed to fully utilize reconstructions of ocean paleochemistry (e.g., the marine Os-, Hf-, Nd-, and Sr -isotope records) in models of global biogeochemical cycles (e.g., Bluth and Kump, 1991).

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Modeling the Deep Earth’s Water Cycle

Phipps Morgan, J; Rüpke, L; Connolly, J

The water content of Earth’s oceans and mantle primarily reflects two processes; outgassing of mantle water during plume and ridge melting, and recycling of surface water after the incomplete dehydration of subducting slabs. Here we use the local thermochemical models we have developed for subduction zones (e.g. Rüpke et al., Geology, 2002) to parameterize potential water transport through the subduction barrier as a function of a plate’s speed and age when in enters the trench. If we assume that the paleo-Earth had similar numbers of plates moving at greater speeds (i.e. assume that for some reason it is difficult to initiate trenches so that the Earth has always had a parsimonious distribution of them), then the analysis in Phipps Morgan (Chem. Geol., 1998) can be extended to model the water content of the ocean and mantle through time. We find that prior to ~2 Ga, the majority of recycled water resided in incompletely dehydrated recycled crust, while during the most recent 2 Ga recycled slab serpentine has increasingly become the primary water-recycling lithology. We also find that if water melts as a fairly incompatible element, then for the scenarios considered here roughly ~80% of Earth’s post-moon-forming-impact water will be found in the present-day hydrosphere — almost independent of whether the initial post-impact oceans started with all or none of Earth’s remaining water. Finally, all models are in a present-day state of rehydrating the mantle, i.e. at present the mantle is receiving more water from subducting slabs than it is giving back in plume and mid-ocean ridge volcanism. This provides a possible explanation for the apparent sealevel drop of ~600m in the past 0.6Ga (Hallam, 1993).

Constraints on the Composition of the Subducting Slab at the Mariana Arc and the Evolution of Th/U Ratios in the Mantle

Porter, K; White, W M

Accurate modeling of the processes that shape the Earth's interior has been impeded by an incomplete picture of the nature and composition of crust-mantle fluxes at subduction zones. Although estimated compositions of subducting sediment (e.g. Plank and Langmuir, 1998) and altered oceanic crust (e.g. Staudigel et al, 1995) are available, it has been difficult to constrain the relative proportions of these components in the subducting slab. The composition of the "residual" slab – the fraction of subducted material that is incorporated into the convecting mantle – is also poorly defined. Here, we present new constraints on the nature of the subducting and residual slab based on trace element ratios and isotopic constraints.

U-series disequilibria for the islands of the Mariana Arc suggest that U is partitioned from the mantle source and into Marianas magmas more efficiently than is Th (Elliott et al, 1997). This implies that the Th/U ratio of the Marianas magmas is lower than that of their source. Since non-arc magmas generally show the opposite trend (Th partitions into the melt more than U, requiring that the source have lower Th/U than the melt), it seems reasonable to assume this anomalous Th/U fractionation relates to slab-to-wedge transfer (.e.g, slab dehydration). This implies that the subducting slab has Th/U ratios greater than those of the island arc volcanics (IAV). These observations allow us to constrain the Th/U ratio of the subducting slab and, consequently, its implied composition.

Two samples, URA 5 and SAG 1 (Elliott et al, 1997), were chosen to represent the low- and medium-K lava series of the Marianas, respectively. A liquid line of descent for the crystallization of Mariana Arc magmas was calculated using the Java version of the MELTS program (http://penmelts.geology.washington.edu/index.html); the parental magma was assumed to have a composition equal to that of sample PS from the island of Pagan (Meijer, 1982). The trace element compositions of URA 5 and SAG 1 were corrected for fractionation using this liquid line of descent and partition coefficients from the GERM Partition Coefficient Database (http://earthref.org). Assuming a relative distribution of approximately 3:1 of medium- versus low-K rocks on the islands, an average Th/U ratio of 2.21 for the Marianas parental magmas was calculated.

An oceanic crustal thickness of 6 km was assumed; 475 m of sediment (Th/U = 4.52) was added to produce a total slab thickness of 6.475 km. The Th/U ratio of the bulk slab was calculated assuming varying ratios of NMORB (Th/U = 2.55) to altered crust (modeled as the "extrusive section" of Staudigel et al, 1995, with Th/U = 0.23). Slab compositions containing no more than 17% altered oceanic crust give feasible Th/U ratios. Figure 1 shows the range of possible slab compositions together with estimated "residual" slab compositions, which were calculated using

$$C^i_{res} = \frac{C^i_{init}F^i_{init} - C^i_{IAV}F^i_{IAV}}{F^i_{res}} \quad [1]$$

where $\boldsymbol{C_{ij}}$ denotes the concentration of element ***i*** in reservoir ***j*** and $\boldsymbol{F_{ij}}$ denotes the mass flux of element ***i*** to reservoir ***j***.

Using Th/U ratios to constrain the proportions of NMORB and altered crust in the subducting slab allows us to produce estimates of subduction fluxes of other elements. Figure 2 shows a trace element diagram for the various reservoirs under consideration. Slab concentrations are calculated as described above, assuming 7% sediment, 17% altered crust, and 76% NMORB. The IAV are modeled as being produced by a mixture between the mantle wedge (NMORB source composition) and a slab-derived component. The composition of the slab-derived component (SC) was calculated for each element using

$$C_{sc}^{i} = \frac{f^{i}C_{IAV}^{i} - C_{MORB}^{i}}{f^{i}} \quad [2]$$

where ***f*** f_i is a normalization factor calculated by dividing the concentration of Nb in MORB by that in the IAV. The residual slab compositions were calculated using equation 1 above.

Except for the large ion lithophile elements (LILE), Th, U, and Pb, the slab loses very little of its trace element inventory to the IAV. This result is consistent with previous studies of IAV (e.g. Hawkesworth et al, 1993), which implicate aqueous fluids in the transport of these elements from the slab to the IAV source. The results of this study certainly support the theory that aqueous fluids play an important role in the transport of elements between the slab and the source of IAV, since the LILE, Th, U, and Pb are all mobile in such fluids.

Collerson and Kamber (1999) argue that recycling of altered oceanic crust into the convecting mantle might produce the present-day observed low Th/U ratios in the mantle. The results of this study, however, do not support this theory. Although the inclusion of altered crust does lower the Th/U of the subducting slab, preferential extraction of U from the slab at the subduction zone results in an overall increase in residual slab Th/U. Since it is the residual slab material that is ultimately incorporated into the convecting mantle, these results suggest that the recycling of altered crust cannot produce the observed low Th/U ratios in MORB (figure 1), at least at the Mariana arc. The results of this study are more consistent with those of Paul et al (2002), who argue that the low mantle Th/U ratios are a result of magmatic fractionation during crustal differentiation.

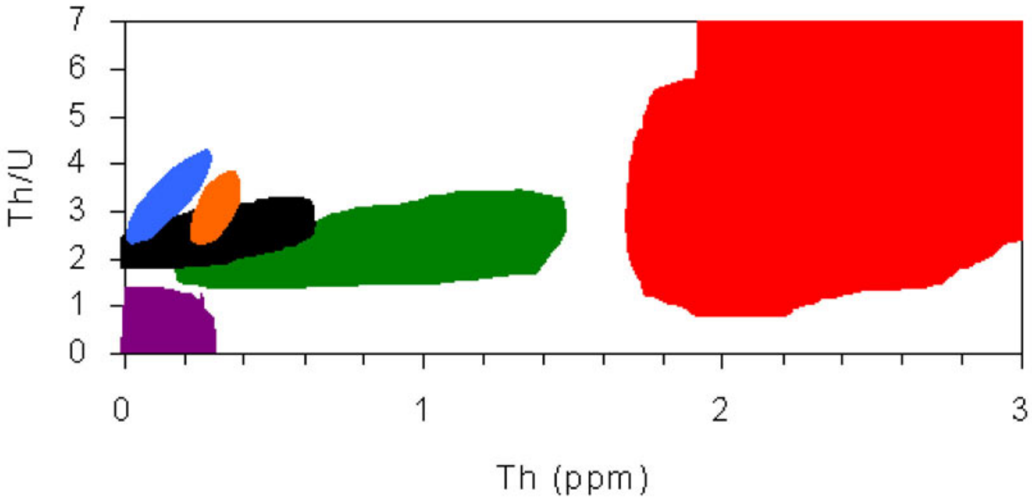

Figure 1. Variations in Th/U ratio and possible slab compositions. Red area is approximate distribution of sediment compositions; green denotes Mariana Island volcanics; black indicates NMORB; purple indicates altered crust; brown indicates range of initial slab compositions; blue indicates range of residual slab compositions.

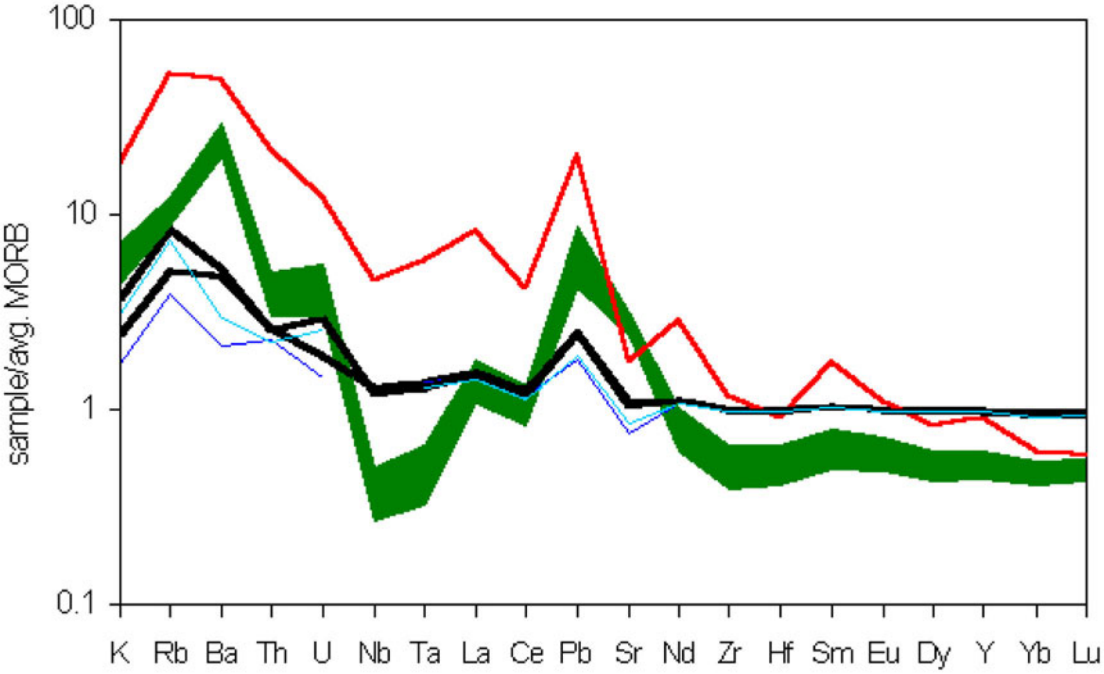

Figure 2. Trace element diagram for reservoirs under consideration. Green shaded region indicates approximate range of Mariana IAV compositions; red line indicates sediment composition; heavy black lines outline range of possible slab compositions; light- and dark blue lines outline range of residual slab compositions. Greater proportions of altered crust in the slab lead to higher concentrations of LILE in the subducting and residual slab material; very little change is seen otherwise.

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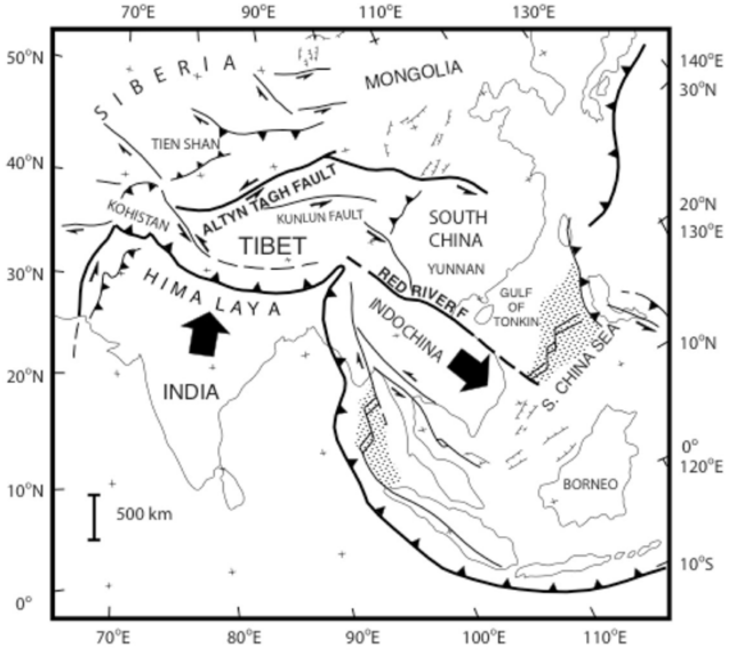
The Role of Strike-Slip Faulting during the Indo-Asian Collision: the Red River Shear Zone and the Altyn Tagh Fault

Ryerson, F J; Harrison, T M; Tapponnier, P; Leloup, P H; Meriaux, A-S; Finkel, R C; Van der Woerd, J

The Tibetan Plateau is surrounded by large strike-slip faults, such as the Altyn Tagh Fault (ATF) and the Red River Fault (RRSZ), whose role in accommodating Indo-Asian convergence, both today and throughout the history of the collision, is hotly debated. At one extreme, strike-slip faults are viewed as a by-product of distributed deformation in the lower crust and mantle. At the other, they are interpreted as localized lithospheric shear-zones, equivalent to intra-continental plate boundaries. These alternatives imply broadly different mechanical properties for the continental lithosphere. The resolution of this issue requires quantitative information, not only on the deep structure, but also on the slip-rates of these faults. Low slip-rates (mm/yr) have been taken to suggest distributed deformation, while higher rates (cm/yr) support localized deformation.



The Red River Shear Zone (RRSZ) extends from eastern Tibet to the South China Sea and comprises four elongated massifs. It plays a central role in the hypothesis that strike-slip extrusion of Indo-China accommodated a significant portion of Indo-Asian convergence immediately following onset of collision. In situ Th-Pb ion microprobe dating of monazite inclusions within garnets grown during high-temperature deformation allows direct assessment of the timing of amphibolite grade metamorphism and synchronous left-lateral shearing. Results from northern segments of the RRSZ in Yunnan, China indicate that garnet growth occurred between 34-21 Ma, and document late Oligocene metamorphism and left-lateral shearing in these high-grade metamorphic rocks. ^{40}Ar/^{39}Ar analysis of K-feldspars from ten transects perpendicular to the NW-SE strike of the Ailao Shan, the longest massif in the chain, yield a pattern of ages consistent with diachronous initiation of transtensional faulting along the RRSZ. The normal component of this faulting occurs along the eastern boundary of the shear zone, the locus of the active Range Front fault. Numerical modeling of isotopically-derived cooling histories yields a dip-slip rate of ~6 mm/yr. A 400-km long segment of the Ailao Shan reveals a pattern of ages that increase smoothly from 17 Ma in the northwest Ailao Shan to 25 Ma in Vietnam. This relationship indicates that the onset of extension was diachronous, beginning in the southeast and propagating northwest at a rate of ~4.5 cm/yr. This rate and the spatial and temporal variability of extension are consistent with predictions, based on Oligocene-Early Miocene magnetic anomalies from the South China Sea, that the RRSZ experienced strike-slip rates of ~4 cm/a and that its present position does not represent a small circle about the Indochina/South China poles of rotation. As a consequence, a strike-perpendicular component of compression would have existed in the northern portion of the belt, and an increasing component of strike-perpendicular extension to the southeast across the Ailao Shan.

The northern edge of the Tibetan Plateau is defined by the active, sinistral Altyn Tagh Fault. Estimates of the slip-rate on the Altyn Tagh Fault vary from 2 mm/yr to 40 mm/yr. "Morphochronological" rate measurements in which the ages of tectonically offset landscape features such as moraines, alluvial fan, and fluvial terrace risers are constrained by ^{10}Be and ^{26}Al cosmic-ray exposure dating, support the higher estimate. The rate is fastest near Tura, on the central segment of the fault (85-89ºE). Here, offsets of fluvial terrace risers and abandoned channels (~420 m) and glacial features (~3.5 km) are constrained by both radiocarbon and cosmogenic dating and yield a slip rate of ~30 mm/yr. This long-term rate indicates that, at this longitude, the Altyn Tagh fault on the north edge of Tibet absorbs as much of India's convergence relative to Siberia as the Himalayan Main Frontal Thrust does on the southern edge of the plateau.

Millennial slip-rate measurements over a length of ~1000 km on the ATF display a systematic eastward decrease in the slip-rate, from 30 mm/yr near Tura to 4 mm/yr at Shibao Cheng (96ºE) west of the junction with the Qilian Shan Front (Meyer et al., 1996). At a more detailed level, the ATF slip rate decrease suggests a stepwise decrease at the junctions between the ATF and branching, sub-perpendicular, active thrusts south of the fault, indicative of the transfer of lateral slip to vertical uplift and thickening. Hence, the growth of young fold and thrust mountain belts on the northeastern edge of the plateau appear to be a direct consequence of the eastward propagation and the sinistral motion of the ATF. This behavior is in contrast to that on the Kunlun Fault where the rate over a similar length of the fault appears to have remained constant over the last 45 Ka (Van der Woerd et al, 2000), and suggests that the Kunlun Fault is no longer propagating eastward.

Motion of RRSZ and the ATF can be associated with rifting and mountain building, respectively. The relative ages of these features indicates the strike-slip faulting has propagated northwards over the course of the collision, and the strike slip motion and crustal thickening have been and continue to be contemporaneous processes. The high slip rates are consistent with localized deformation of the continental lithosphere, in agreement with recent seismic data, supporting the hypothesis that these are lithospheric faults. As such, deformation within the continental lithosphere resembles that of the oceanic lithosphere in which deformation is localized along the boundaries of largely undeformed blocks.

The Composition of the Depleted Mantle

Salters, V J M; Stracke, A

We present an estimate for the composition of the depleted mantle (DM), the source for midocean ridge basalts. Several avenues are used to derive the estimated composition of DM. Since trace element ratios can be better determined than absolute concentrations, absolute concentrations are only estimated for a few elements and the majority of the trace element concentrations are based on trace element ratios. The most reliable estimates of trace element ratios are estimates of parent-daughter ratios which are based on the isotopic composition of mid-ocean ridge basalts.

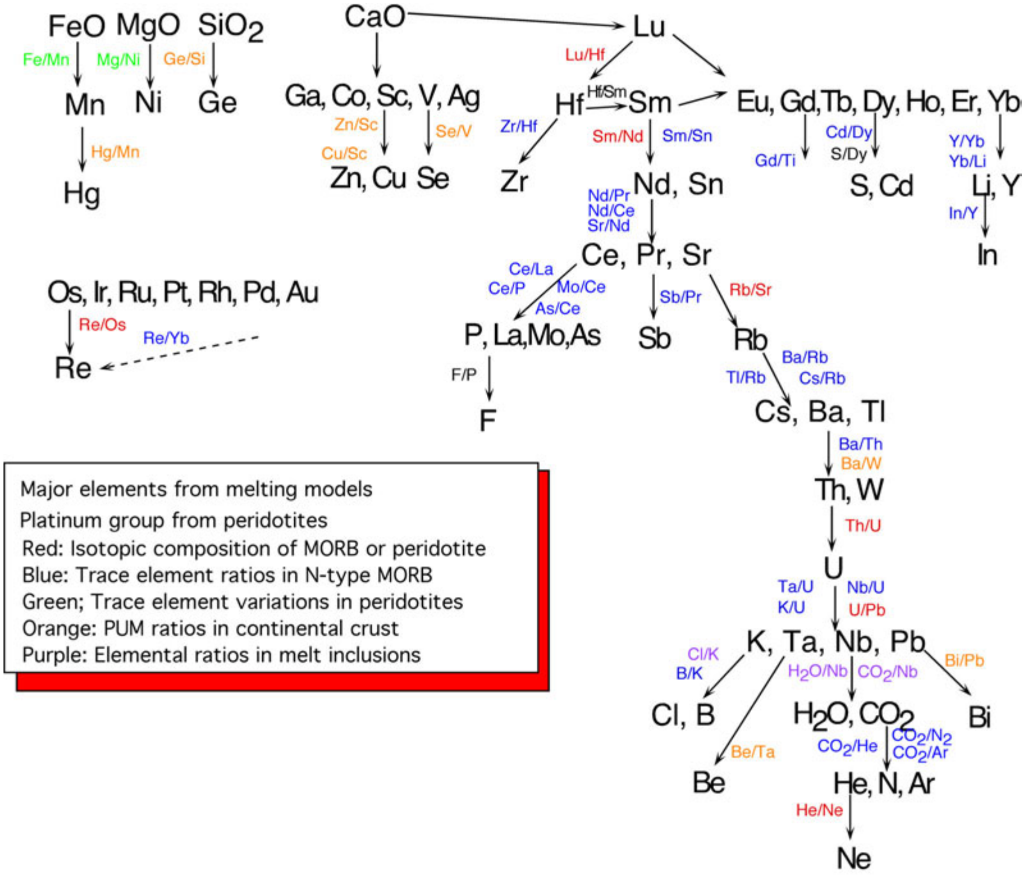


Figure 1. Genealogy of the elements in the depleted mantle. Charts showing the dependencies of the concentrations on the trace element ratios.

Fig.1 shows how the estimates of the elements are derived and dependent on each other. These estimates form the “backbone of our trace element estimates. A second way of estimating trace element ratios is through the average composition of primitive normal-type mid ocean ridge basalts. Figure 2 shows the location of the samples use for the average composition. We have used the following criteria for basalts to be included in the average: basalts - are classified as fresh rock or glass; are retrieved from depths in excess of 2000m; have MgO>8.0 wt%; have $(La/Sm)_N<1$. In addition, samples were filtered for REE pattern as at least six REE needed to be determined; non-smooth REE patterns were excluded. The major element composition is obtained by subtraction of a low degree melt from a bulk silicate Earth composition. A fourth group of estimates, which includes some of the transition elements and the PGE is derived from the elemental and isotopic composition of peridotites. A last group of trace element ratios is derived from continental crust. Continental crust is thought to be complementary to the depleted mantle and ratios that are chondritic in the continental crust are expected to also be chondritic in the depleted mantle.

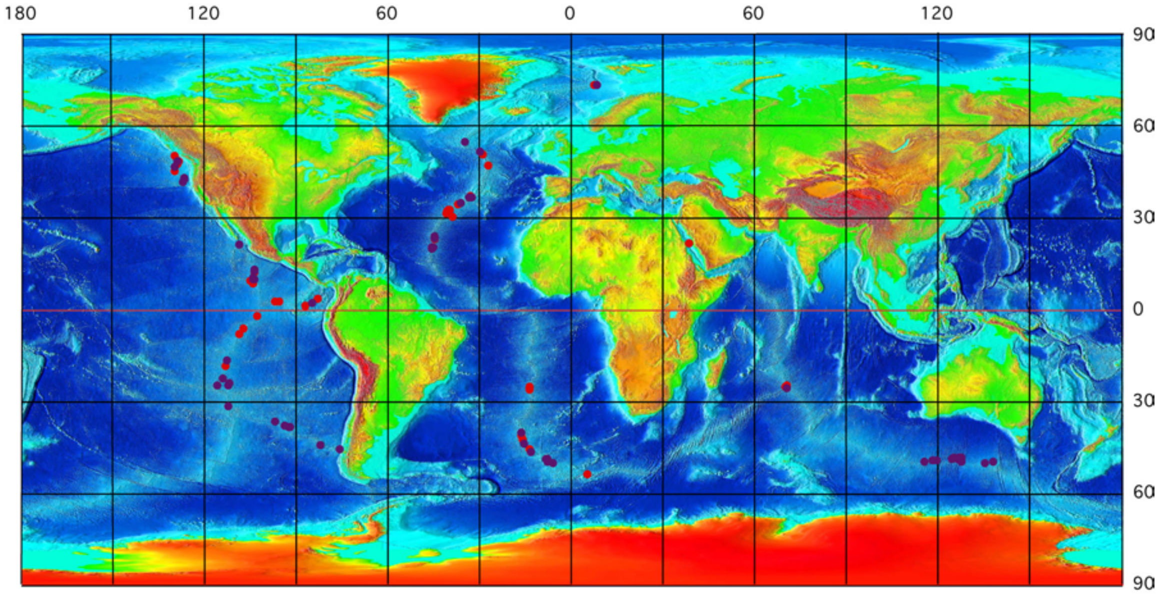


Figure 2. Sample locations of N-type MORB used to make an average composition. Purple circles are glass data, red circles are whole rock.

We have varied the average depletion age of the mantle and the isotopic composition of the depleted mantle to bring La/Nb and Ce/Pb within the range observed in primitive mid-ocean ridge basalts. Only a narrow range of ages, 2.0-2.4Ga, yields appropriate trace element ratios. In addition only a limited range of isotopic compositions yield appropriate trace element ratios and the isotopic composition is at the depleted end of mid-ocean ridge basalts.

Why we should worry about the Bio in Geochemistry

Schlesinger, W H

The chemical arena at the surface of the Earth has determined the milieu for life for the past 3.5 billion years or so, and, in turn, biology has had a major impact on its characteristics. Many paleoecologists speculate how the first oxygen-producing photoautotrophs must have changed the chemical environment of the anoxic Precambrian seas. The introduction of oxygen may have been the first time that the action of a few species made life miserable for most of the other inhabitants on the planet. Now, at least since the Industrial Revolution, we find ourselves in another era in which a single species, in this case Homo sapiens, is casting an enormous pall on the Earth's chemical composition.

Studies of the planet's biogeochemistry should compare the circulation of chemical elements on a hypothetical lifeless Earth, to an Earth with its full complement of biota short of humans, and to the modern Earth, on which humans control the flux of most of the "light" elements of the periodic table. For example, in the carbon cycle, the flux of CO_2 between the atmosphere and the Earth's crust is measured in 0.1 x 10^{15} gC/yr. The flux between the atmosphere and the biosphere is ~2000 times larger—200 x 10^{15} gC/yr. The human perturbation from fossil fuel combustion and deforestation results in a net flux of about 7 x 10^{15} gC/yr to the atmosphere. On the one hand, this flux would seem to be a small perturbation of the natural biogeochemical cycle of carbon--< 5% of the biospheric flux. On the other hand, this flux has resulted in a 30% increase in the concentration of atmospheric CO_2 since the beginning of the Industrial Revolution, with concentrations now increasing about 0.5%/yr and global, political attention focused on the potential for climatic warming.

For various elements of biogeochemical interest (C, N, S, P, B) and water, I will compare the surface geochemical flux on a hypothetical abiotic Earth with today's functional characteristics, to the flux to and from the biosphere on the Preindustrial Earth, and to today's human perturbation of the biospheric flux.

GERM and EarthRef.org

Staudigel, H; Koppers, A A P; Helly, J

The Geochemcial Earth Reference Model (GERM) initiative is a grass roots initiative that uses the vision of a reference model to provide an intellectual and Information Technology (IT) infrastructure to geochemistry. The GERM initiative emphasizes the marriage of scientific context with the development of an IT or "Cyber" infrastructure in geochemistry: A functional infrastructure can only grow out of an interdisciplinary and scientific Earth science vision in geochemistry. GERM workshops offer interdisciplinary keynotes that link geophysical, geochemical and geobiological sciences. Such linkages are essential in the design of geochemical databases, in terms of their metadata needs and semantic linkages. Much attention has been paid to these issues in setting up the GERM website and the EarthRef.org infrastructure, in addition to making available digital legacy data sets.

The GERM website and its host EarthRef.org are based on relational (Oracle) database hosted and supported by the San Diego Supercomputing Center (SDSC). SDSC serves http://earthref.org/ as an intellectual, server hardware and software support. More recently, MagIC (the Magnetics Information Consortium) has been established within EarthRef.org, serving as a nucleus for development of metadata in paleomagnetism and for the establishment of some specific paleomagnetic databases.

GERM and EarthRef.org have supported and/or developed several important initiatives in geochemistry and Earth Sciences:

1. Beginning with its 1998 meeting six GERM Steering Committee members developed G-cubed.org — a new electronic journal in Earth sciences. G-cubed is designed as a traditional, high quality journal that has many special features that serve important needs and eliminate problems perceived in scientific publishing. Special features include publication types that allow for the publication of data or technical advances, low cost, rapid publication, publication of electronic products (such as websites, animations, etc.) and a copyright policy that offers maximum access to published materials. With respect to the GERM reference model materials, relevant G-cubed papers are freely available when accessed from the EarthRef.org website.

2. GERM has been active in the development of metadata concepts and formats for geochemistry and Earth sciences in general. This work has resulted in a series of publications or manuscripts that are available for discussion at this workshop and through EarthRef.org at http://earthref.org/metadata/GERM/. Main points of these concepts include a logical structure (for Earth scientists) and a modular nature of the metadata that provides access to these data from

a range of search types, such as by location, rock type, tectonic setting or relevance to a particular expert level (K-12, college, research). Metadata also include more standard concepts like analytical procedures and archiving-related metadata.

3. GERM and EarthRef.org have established relational databases that archive every type of contributed and legacy data. Legacy data are archived including images of the relevant aspects of the original papers, as well as the data themselves in Microsoft Excel and ASCII text formats. This archival setup has been chosen to allow for easy upload and download of all materials that support scholarly publications.

4. EarthRef.org has developed a series of other databases and web computational tools. For example, EarthRef.org hosts the Seamount Catalog (SC) that archives geographic and morphological information on seamounts in a relational database and file archive. For each seamount in this catalog four base maps (i.e. multibeam, altimetry, merged multibeam and altimetry and residual maps) are available for downloading in the PS, AI, PDF and JPEG formats. These base maps display the sample locations of dredges, boxcores, ODP and DSDP sites, etc. and they are automatically re-generated from the database, in case new multibeam data and/or sample locations become available for the seamount. Related data files on the seamounts (i.e. other than the base maps) are directly linked in from the EarthRef Digital Archive (ERDA) to which scientists can upload their own contributions for the seamounts, and link them in with a publication.

5. Ongoing efforts include the development of concepts to archive legacy geochemical data, the beginning of a MagIC website that offers support for metadata development and the establishment of an IT infrastructure for paleo/rock magnetism. In a similar fashion, we are also establishing an important node for Radiometric Ages (RAD) that will be linked to the CHRONOS initiative and GERM will be directly involved in the setup of a chemical stratigraphy node for the same CHRONOS initiative.

EarthRef.org has benefited greatly from linkages with AGU's newest electronic journal G-cubed. G-cubed copyright allows specifically the use and the posting (free linkage) of GERM related articles, and data from articles submitted to any AGU journals may be deposited at EarthRef.org with a direct link to a URL in ERDA.

The Lu-Hf and Sm-Nd Isotopic Composition of Chondrites: Implications for Determining the Hf-Nd Isotopic Composition of Bulk Silicate Earth

Vervoort, J; Söderlund, U; Patchett, P J

The Sm-Nd and Lu-Hf isotope systems have been useful tools in trying to understand the differentiation and evolution of the silicate Earth. One important aspect of coupling these two isotopic systems in crust-mantle studies is due to the lithophile, refractory nature of parent and daughter elements in both systems. Because these elements were not subject to volatile loss during planetary formation or sequestration to the core during core formation, the bulk silicate Earth (BSE) composition should provide an important initial point upon which all subsequent processes can be based. For example, the Hf-Nd isotopic compositions of a wide variety of crust and mantle derived materials are, with few exceptions, extremely well correlated in both crust and mantle samples. Regression lines drawn through these data, however, are offset from the current Hf-Nd CHUR values by about 3 ε_{Hf} units. This is true whether the data are considered collectively, or as separate reservoirs (e.g., crust vs. mantle), or whether present-day or initial values for the terrestrial samples are used (Vervoort et al., 1999). This statistically valid mismatch has potentially profound implications for the Earth and has been used to argue for the existence of a missing reservoir, perhaps hidden in the lower mantle, in order to balance the terrestrial Hf-Nd array with BSE (Blichert-Toft and Albarède, 1997). Implicit in the "hidden reservoir" theory is the assumption that we know the chondritic Hf-Nd values for the Earth precisely and unambiguously. In this presentation, we contend that this is not the case and that there is considerable uncertainty in the current Lu-Hf isotopic parameters.

In order to address this issue we have determined Lu-Hf and Sm-Nd isotopic compositions of 6 carbonaceous (Allende, Kainsaz, Karoonda, Mighei, Murchison, and Murray) and 13 ordinary (Allegan, Ankober, Avanhandava, Bjurböle, Bruderheim, Forest City, Girgenti, Holbrook, Homestead, Indarch, Ochansk, Pultusk, and Richardton) chondrites. Our approach has been to dissolve the samples in high-pressure dissolution vessels, spike the samples with mixed Lu-Hf and Sm-Nd tracers and determine both Lu-Hf and Sm-Nd isotopic compositions on the same solutions.

The Sm-Nd isotopic compositions of all chondrites we have analyzed have a narrow range of isotopic compositions that fall along a 4.55 Ga reference isochron and are centered on the values currently in use (^{143}Nd/^{144}Nd = 0.512638, ^{147}Sm/^{144}Nd = 0.1966 with fractionation correction based on ^{143}Nd/^{144}Nd = 0.7219; Jacobsen and Wasserburg, 1980; 1984). Excluding Bjurböle (low ^{143}Nd/^{144}Nd and ^{147}Sm/^{144}Nd) all other chondrites vary in ^{143}Nd/^{144}Nd from 0.512602 to 0.512678 with an average of 0.512639. This is a total present-day variation of less than 1.5 ε_{Nd} units and a total variation in ^{147}Sm/^{144}Nd of 2.5%. These results verify the current Sm-Nd values for CHUR and, due to the limited variation in the data, also indicate that the Sm-Nd isotopic reference is rather insensitive to how the CHUR values were determined.

The situation for the Lu-Hf isotopic system is different. The chondrites span a very large range in ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf and fall along an isochron (using a decay constant of 1.865 x 10-11; Scherer et al., 2002; Söderlund et al., 2003) with an intercept of ~0.2798 and a slope of 0.0884. All chondrites form a continuous trend with ^{176}Hf/^{177}Hf from 0.282678 to 0.282949 and ^{176}Lu/^{177}Hf from 0.03014 to 0.03539. This represents a total range of ~18 ε_{Hf} units and a variation in Lu/Hf of ~17%. Essentially, our results are the same as those of Bizzarro et al. (2003), except that their data extend to even lower Lu/Hf for chondrites than do ours. There also appears to be a systematic difference between carbonaceous and ordinary chondrites. The carbonaceous chondrites have ^{176}Hf/^{177}Hf and ^{176}Lu/^{177}Hf values that average 0.282849 and 0.03422, respectively, compared with 0.282678 and 0.03216 for ordinary chondrites. This is a difference between the two chondrite groups of more than 6 ε_{Hf} units and 6.4% in Lu/Hf ratios.

These results have profound implications for the determination of the Hf-Nd isotopic composition of bulk silicate Earth. The Sm-Nd values of BSE can be interpreted in a straightforward way from the chondritic data due to their restricted present-day range and the overlap of carbonaceous and ordinary compositions. The situation with the Lu-Hf system, however, is more complex. Because of the spread in the Lu-Hf isotopic composition of chondrites and the systematic differences between ordinary and carbonaceous chondrites, the Lu-Hf isotopic composition of BSE cannot be determined unambiguously. For example, if we take the average of all our chondrite data to determine BSE, we arrive at a value close to the current Lu-Hf values for CHUR (^{176}Hf/^{177}Hf = 0.282772, ^{176}Lu/^{177}Hf = 0.0332; Blichert-Toft and Albarède, 1997). If, on the other hand, we take Lu-Hf values for BSE more consistent with carbonaceous chondrites, this present-day value would lie ~2.7 ε_{Hf} units above the current value. This adjustment to the CHUR value would place it near the center of the terrestrial array and thereby obviate any need for a missing reservoir in the Earth to balance the array with BSE. The selection of a BSE value from the chondrite data cannot be made a priori based on just the Hf-Nd data themselves, but must consider the broader question of what type or types of chondrites, if any, the Earth is made of.

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Li Isotope Fractionation in Rivers Draining Silicate Lithologies

Vigier, N; Burton, K W; Reynolds, B; Gislason, S R; Rogers, N W; James, R H

Weathering of Ca-Mg silicates is considered as a significant sink of atmospheric CO_2, and the importance of basalt weathering, particularly on the seafloor and in volcanic islands, has been recently highlighted (Louvat and Allègre, 1998; Brady et Gislason, 1997). Nevertheless, because of the lack of convenient proxies, no consensus exists on the paleo-variations and controlling factors of large scale silicate weathering rates. It has recently been proposed that Li isotopic ratios measured in large rivers could mainly reflect the degree of silicate weathering, because of the high Li contents in silicate minerals and of the preferential uptake of ‘Li into secondary clays (Huh et al., 2001). Therefore, in parallel to studies concerning large river basins, it is important to quantify and understand the natural fractionations of lithium isotopes during silicate weathering, by studying small catchments of dominantly silicate lithologies.

For this purpose, about 30 rivers have been sampled in Iceland in 2001. Also, 15 Scottish rivers with little evidence for anthropogenic contamination and that mainly drain old silicate terrains (>500Ma) have been sampled twice, in May and October 2002. Despite low-levels of trace elements in the dissolved phases of these rivers (e.g. about half of the sampled rivers display Li contents of less than 200 ng.l^{-1}), recent developments with the Multicollector ICP-MS 'Nu-Instruments' allow σ^7Li to be measured with a 2σ uncertainty of about 0.3‰ and a reproducibility of about 0.5‰ for 10ng Li. Each sample has been filtered in order to analyze the dissolved phase and the corresponding suspended particles when possible. Bottom sands have also been collected and analyzed in order to better constrain the composition of the parent lithology for each watershed. Colloids from Scottish organic-rich rivers have also been separated using an ultra-filtering technique for isotope analyses.

The σ^7Li values for dissolved phases of Icelandic rivers display a large range (between 10‰ and 28‰) suggesting that ^{7}Li/^{6}Li ratios fractionate during weathering of the parent basalts (~4.5‰). Volcanically active areas, characterized by young basalts and intensive weathering display the lowest σ^7Li in contrast to rivers draining old basalts in areas characterized by significantly lower weathering rates (Gislason et al., 1996). Measurements of a melted superficial ice core located in Langjokull show that any atmospheric contribution is negligible for dissolved lithium. Rivers draining old silicate terrains in Northern Scotland show a more restricted range for σ^7Li (from 16‰ to 22‰). All rivers have low Ca/Na and Mg/Na ratios (average of 0.4 and 0.2 respectively) corresponding to the end-member previously defined for silicate rivers (Gaillardet et al., 1999), suggesting a negligible contribution from carbonate dissolution. Li contents measured in 0.2µm filtered waters are higher than for Icelandic rivers (0.2-1.2ppb), and are very similar in the ultra-filtered waters (<10kD). First results show little seasonal variation in σ^7Li. Ultra-filtered waters display identical or higher σ^7Li than 0.2µm filtered waters, suggesting possible isotopic exchange processes, and in particular the preferential adsorption or complexation of ^{6}Li by organic matter.

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REE Geochemistry of the Changjiang (Yangtze) and Huanghe (Yellow) River Sediments: Comparison and Constraints

Yang, S Y; Li, C X; Jung, H S

Rare earth element (REE) compositions of sediments of world major rivers were well documented to probe into the chemical evolutions of upper continental crust (UCC) and shale composites (NASC, PAAS) (Goldstein and Jacobsen, 1988; Sholkovitz, 1988, 1990). As the two largest rivers in China with the total drainage area of about one forth of China continent area (2.55×10^6 km^2), the Changjiang and Huanghe are both sourced from the Tibetan Plateau, but span quite different geologic, geographic and climate regimes. Bottom, bank and suspended sediments collected from the middle and lower parts of the Changjiang and Huanghe rivers were measured for REEs and other elements as well as mineral and grain size compositions.

The Changjiang and Huanghe sediments differ from other world river-borne sediments not only in average REE abundances but also in REE fractionation, although typical REE patterns of LREE (light REE) enrichment relative to NASC are observed in these rivers. The Amazon and Mississippi sediments exhibit stronger REE fractionations than Chinese river sediments (Fig. 1). While leached by 2 M HCl plus 0.5 M HNO_3, both the Changjiang and Huanghe sediments show relative enrichment of MREEs (middle REEs) in UCC-normalized patterns in the leachable fractions, and flat UCC patterns in the residual fractions (Fig. 2).

The source rock compositions in the drainage basins are the main factor controlling the REE compositions of both river sediments. The Huanghe sediments inherit the REE compositions from the loess deposit, whereas the Changjiang sediments bear similar REE compositions with those of source

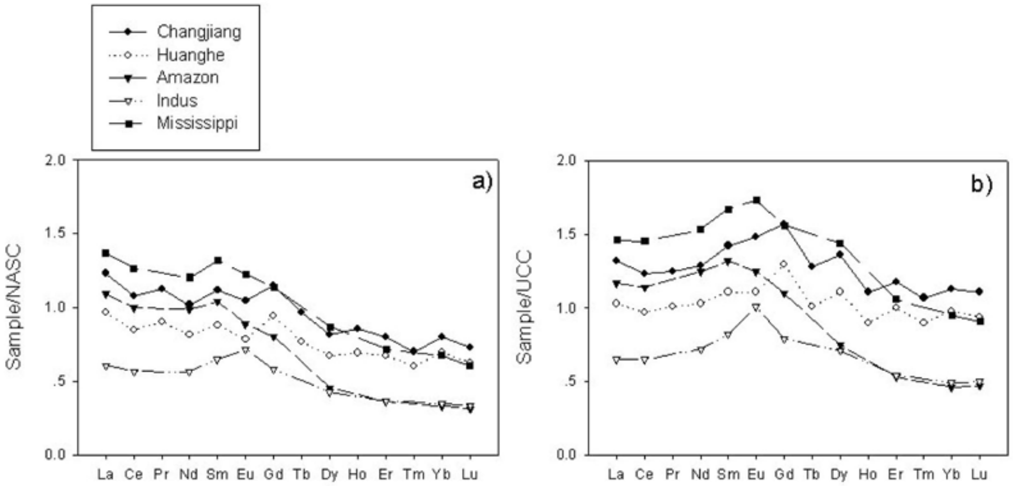

Figure 1. Comparisons of REE patterns between the Chinese and other world river sediments. World river date after Goldstein and Jacobsen (1988), Sholkovitz (1992) and Elderfield et al. (1990).

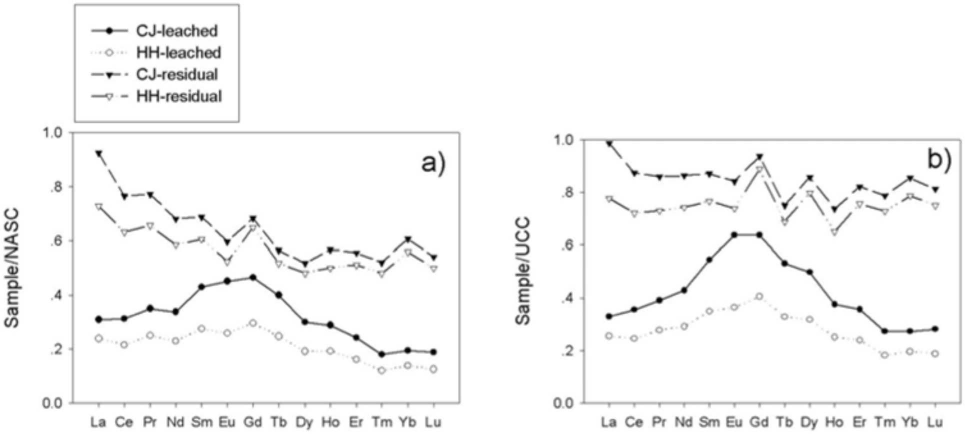

Figure 2. Distribution diagrams of REE patterns in the leachable and residual fractions after normalized with NASC (a) and UCC (b).

sediments in the upper basin. Overall, chemical weathering exerts a minor influence on REE compositions of both river sediments although stronger MREE fractionation in the Changjiang sediments is likely related to the stronger chemical weathering in the Changjiang basin. Mineral partitioning has a considerable control on REE compositions. Clay minerals are rich in REEs, especially in LREEs, whereas heavy minerals such as zircon, sphene, and allanite are important hosts of residual REEs. Fe-Mn oxide-bound phases account for a large proportion of acid-leachable REEs in the Changjiang and Huanghe sediments. The UCC patterns of the Huanghe sediments are more linear with weak fractionation than those of the Changjiang and other river sediments, which suggesting that the Huanghe sediments have very similar compositions of REEs with the upper continental crust. Therefore, the Huanghe sediment can be referred as the representative of the UCC and terrigenous material into the sea in order to study the REE compositions and fractionations of the sediments of other world major rivers.

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