… the **Geochemical Earth Reference Model** initiative is a grass-roots effort to establish consensus within the geosciences community on a chemical characterization of the Earth, its major reservoirs, and the fluxes between them …

# GERM at the AGU Fall Meeting 1999

## Program

**for**

**Wednesday, 15 December 1999**
**Thursday, 16 December 1999**

# Table of Contents

# Overview for Special Sessions

## ❖ GERM I: Oceans, Sediments, Arc Systems and Modeling

**V31E : Wednesday Morning 8:30 in MC 103**

## ❖ The Solid Earth's Chemistry: Global Inventories and Fluxes

**U32B : Wednesday Afternoon 13:30 in MC 131**

## ❖ GERM II: The Mantle

**V41E : Thursday Morning 8:30 in MC 103**

## ❖ GERM III: Data Bases, Modeling, Mantle MORB & OIB

**V42D : Thursday Afternoon 13:30 in MC 131**

## ❖ GERM IV: Posters

**V42A : Thursday Afternoon 13:30 in MC Hall D**

## GERM Information

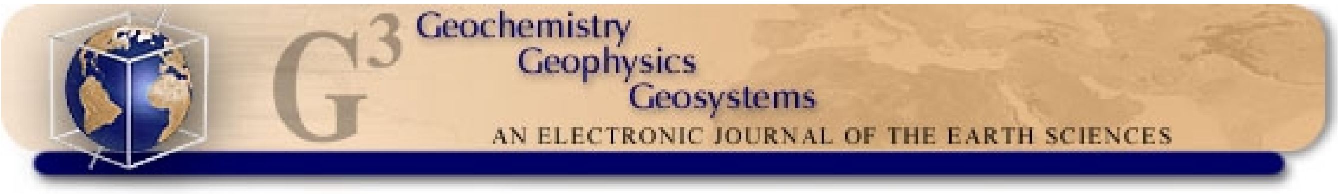
### *Free* GERM/G$^3$ *Beer at the VGP reception*
**Tuesday, December 14, MC-133, 6:15 pm**

### *GERM Information Meeting*
**Thursday, December 16, MC-103, 11:30 am**
Website Development, Funding for GERM, Geochemistry Data Bases, Publication of GERM contributions, Plans towards GERM 2001. Everybody is invited.

### *Please Note!*
**Germ 2001 Workshop, La Jolla, March 6-10, 2001**

## Call for Papers

The editors of Geochemistry, Geophysics and Geosystems solicit papers from the GERM sessions at the Fall 1999 AGU Meeting for the first **theme** volume of **G$^3$**.



**Guest Editors:** H. Staudigel, F. Albarede, L. Derry, and E. Hauri.

## Acknowledgements

GERM is an initiative that owes its existence to the contribution of an increasing number of individuals who donate their time and enthusiasm to this cause. Without this contribution GERM could not exist. GERM has received funding from the National Science Foundation, The Scripps Institution of Oceanography and the Quest for Truth Foundation. This document has been compiled from the AGU 1999 Fall Meeting program (EOS Transactions, AGU Volume 80, 1999), and we acknowledge the support of the AGU, and the program chairs Robert Duce, Toby Newell, and, in particular, Mary Reid, who helped put the program together. This document was produced by Patty Keizer from the **PACER** Center of the Scripps Institution of Oceanography at the UCSD.

# Daily Program

## ❖ GERM I: Oceans, Sediments, Arc Systems and Modeling

**Wednesday Morning 8:30 in MC 103**

| Time | Session | Title |
|---|---|---|
| 835 | V31E-01 | Atmospheric Transfer of Boron from Oceans to Continents: Boron Isotopic Composition of Rainwater |
| | | **E F Rose**, J Carignan, M Chaussidon |
| 850 | V31E-02 | Thermal Evidence of Water Exchange by Tidal Pumping in a Coastal Aquifer |
| | INVITED | **W S Moore** |
| 905 | V31E-03 | The PGE-Budget and Re-Os Isotope Systematics of the Eroding Continental Crust |
| | INVITED | **B Peucker-Ehrenbrink**, B Jahn |
| 920 | V31E-04 | Sources and Sinks of Osmium and Organic Carbon in the Gulf of Papua, New Guinea |
| | | **C E Martin**, B Peucker-Ehrenbrink, G Ravizza, G J Brunskill |
| 935 | V31E-05 | Unsupported 187Os in Cyprus Ochres: Evidence of Ephemeral Re Enrichment of Basal Sediments of the Oceanic Crust |
| | | **G Ravizza**, J S Blusztajn, H M Prichard |
| 950 | V31E-06 | Germanium - Silicon Fractionation During Silicate Weathering: Results from Field and Laboratory Studies |
| | | **A C Kurtz**, L A Derry, O A Chadwick |
| 1025 | V31E-07 | Hydrogen Isotope Profiles in Deep Sea Pore Fluids, and Speculations on the Global Hydrogen Cycle |
| | INVITED | **D P Schrag**, J L Alexander |
| 1040 | V31E-08 | Dispersed Volcanic Ash in Marine Sediments |
| | INVITED | **R W Murray**, S Carey, H Sigurdsson, J Peters, T Plank, Leg 185 Shipboard Party |
| 1055 | V31E-09 | Response of Near-Surface Earth Systems to a Superplume/Supercontinent Event at 1.9 Ga |
| | INVITED | **K C Condie**, D J Des Marais, D H Abbott |
| 1110 | V31E-10 | Birth, Death, and Resurrection: The Life Cycle of Supra-Subduction Zone Ophiolites |
| | | **J W Shervais** |
| 1125 | V31E-11 | Using Arc Geochemical Data to Evaluate Mass Fuxes and the Production of Continental Crust at Subduction Zones |
| | INVITED | **J Davidson** |
| 1140 | V31E-12 | A Next-Generation Model for Computing the Geochemical Evolution of Magma Undergoing Concurrent Recharge, Wallrock Partial Melt Assimilation, and Fractional Crystallization With Self-Consistent Energy Conservation (EC-RAFC) |
| | | **F J Spera**, W A Bohrson |

## The Solid Earth's Chemistry: Global Inventories and Fluxes

**Wednesday Afternoon 13:30 in MC 131**

| Time | Session | Title |
|---|---|---|
| 1330 | U32B-01 | The Composition of the Earth's Core |
| | INVITED | **B J Wood** |
| 1355 | U32B-02 | Dynamics of a hot abyssal layer in the mantle |
| | INVITED | **L H Kellogg**, D L Hunt, B H Hager, S Zhong |
| 1420 | U32B-03 | Osmium Isotopes and Mantle Dynamics |
| | INVITED | **E Hauri** |
| 1440 | U32B-04 | Helium flow in the mantle and mantle degassing |
| | | **M Ozima**, G Igarashi |
| 1455 | U32B-05 | Terrestrial Inventories of Light Rare-Gases and Heat Production |
| | INVITED | **F Albarede**, R D van der Hilst |
| 1535 | U32B-06 | Constraints on the mean composition and mantle source of MORB |
| | INVITED | **C H Langmuir**, Y Su, K E Donnelly, S L Goldstein |
| 1600 | U32B-07 | Crustal Fluxes to the Deep Mantle: Processing of Sediment Through the Subduction Factory |
| | INVITED | **T Plank**, M C Johnson |
| 1625 | U32B-08 | Composition of the Continental Crust and Implications for Global Geochemistry |
| | INVITED | **R L Rudnick** |
| 1650 | U32B-09 | Petrological and Geochemical Constraints on the State of the Archean Mantle |
| | INVITED | **N T Arndt** |

## GERM II: The Mantle

**Thursday Morning 8:30 in MC 103**

| Time | Session | Title |
|---|---|---|
| 830 | V41E-01 | Convection and the Formation of the Principal Reservoirs of the Earth's Silicate Mantle |
| | | **U Walzer**, R Hendel |
| 845 | V41E-02 | Mixing of Chemical Heterogeneities in the Earth's Mantle: A Study Incorporating Plate Dynamics |
| | | **J Schmalzl**, M Rehkämper, U Hansen |
| 900 | V41E-03 | Preservation of Local Source Heterogeneities Trough Convection and Remelting |
| | | **A V Sobolev**, A W Hofmann, I K Nikogosian, M Chaussidon, N Shimizu |
| 915 | V41E-04 | The Thermodynamics of Pressure-Release Melting a Plum-Pudding Mantle |
| | INVITED | **J Phipps Morgan** |
| 930 | V41E-05 | Pb Isotopic Evolution of the Earth |
| | | **W M White**, D Paul |
| 945 | V41E-06 | Thorium-Uranium-Lead Systematics, Heat Flow and the Second Lead Paradox |
| | | D Paul, **D L Turcotte**, W M White |

| | | |
|---|---|---|
| 1020 | V41E-07<br>INVITED | Trace chalcophile element geochemistry of the Earth<br>**A N Halliday**, W Yi, J C Alt, D Lee, D A Teagle, C H Langmuir, M O Garcia, M Rehkämper |
| 1035 | V41E-08<br>INVITED | The Geochemical Earth Reference Model: Composition and Evolution of the Depleted Mantle<br>**S B Jacobsen** |
| 1050 | V41E-09<br>INVITED | Hf-Nd Isotopic Behavior in the Silicate Earth<br>P J Patchett, **J D Vervoort** |
| 1105 | V41E-10 | Hotspots Sources and Fluxes: Insights from Fluid Mechanics Experiments<br>**A B Davaille** |

## GERM III: Data Bases, Modeling, Mantle MORB & OIB

**Thursday Afternoon 13:30 in MC 131**

| Time | Session | Title |
|---|---|---|
| 1330 | V42D-01 | Trace element compositions of ocean ridge basalts: evidence from a global compilation<br>**Y Su**, C H Langmuir, K E Donnelly, J Foriel, K Lehnert |
| 1345 | V42D-02 | The Gabbro-Harzburgite Connection in OIB Sources<br>**A W Hofmann** |
| 1400 | V42D-03 | Does the "Gabbroic" Component in Hawaiian Lavas Come From Oceanic Lower Crust?<br>**J E Snow**, K P Jochum, J Hoefs |
| 1415 | V42D-04 | Lead Isotope Anatomy of the Hawaiian Plume<br>**W Abouchami**, A W Hofmann, S J Galer |
| 1430 | V42D-05 | Geochemical Tracing of Flow Between Pacific and Atlantic Upper Mantle Reservoirs<br>**J A Pearce**, P T Leat, P F Barker, I L Millar |
| 1445 | V42D-06 | The RIDGE Petrological Database on the World Wide Web<br>**K A Lehnert**, Y Su, C H Langmuir |
| 1500 | V42D-07 | GEOROC, the MPI Geochemical Rock Database: A New Tool for Geochemists<br>**B Sarbas**, K P Jochum, U Nohl, A W Hofmann |

## GERM IV: Posters

**Thursday Afternoon 13:30 in MC Hall D**

| Time | Session | Title |
|---|---|---|
| 1330 | V42A-01 | The Ronov Database on Volumes and Masses of Sedimentary Rocks<br>**S Floegel**, W W Hay, A A Migdisov, A N Balukhovsky |
| 1330 | V42A-02 | Oxygen-Isotope Fractionation Between Al-Hydroxides and Water: Decade-long Synthesis Experiments at < 60 °C<br>**F Vitali**, F J Longstaffe, M I Bird, W Caldwell |
| 1330 | V42A-03 | Are Seafloor Hydrothermal Vent Fields Significant Geochemical Earth Reservoirs?<br>**T E McCandless**, J Ruiz, R D Mathur |
| 1330 | V42A-04 | Metalliferous Sediments at Ocean Ridges and the Distribution of High-Temperature Hydrothermal Vents<br>**E Gier**, C Langmuir |

| | | |
|---|---|---|
| 1330 | V42A-05 | Energy and Chemical Balances for Modern and Ancient Seafloor Hydrothermal Systems: Insights Into Their Rates of Formation and Implications for Magmatic Budgets<br>J R Cann, **S E Humphris** |
| 1330 | V42A-06 | Discovery of Hydrothermal Vent Sites in Bransfield Strait, Antarctica<br>**G P Klinkhammer**, C S Chin, R A Keller, A Daehlmann, H Sahling, G Sarthou, S Petersen, F Smith, C Wilson |
| 1330 | V42A-07 | The Evolution of Palagonite and its Effect on Element Budgets of Alteration Processes<br>**N A Stroncik-Treue**, H U Schmincke |
| 1330 | V42A-08 | Possible Mechanisms for Palagonitization of Basaltic Tephra: Evidence From the Keanakako'i Ash Member, Kilauea Volcano<br>**P Schiffman**, R J Southard, D A Swanson |
| 1330 | V42A-09 | U-Th-Ra Chronology of the TAG Hydrothermal Mound<br>M Bickle, **R Hughes**, C You |
| 1330 | V42A-10 | Chemical Structure of the Upper Mantle: Major Elements<br>**A Jambon** |
| 1330 | V42A-11 | Studying the Input to the West Pacific Subduction Factory: ODP-Leg 185<br>**J Ludden**, T Plank, C Escutia, Leg 185 Scientific Party |
| 1330 | V42A-12 | Osmium Isotopes in Vanuatu Arc-Lavas<br>**I J Parkinson**, C J Hawkesworth, D W Peate, S M Eggins |
| 1330 | V42A-13 | Os isotopic and thermobarometric evidence for recent delamination of subcontinental lithospheric mantle beneath the Sierra Nevada, California<br>**C Lee**, Q Yin, R L Rudnick, J T Chesley, S B Jacobsen |
| 1330 | V42A-14 | Ca-Eskola pyroxene in deeply subducted crustal rocks: Evidence from the Kokchetav massif, Kazakhstan<br>**I Katayama**, C D Parkinson, K Okamoto, Y Nakajima, S Maruyama |
| 1330 | V42A-15 | Composition and Stratification of the Slave Cratonic Upper Mantle<br>**M G Kopylova**, J K Russell |
| 1330 | V42A-16 | TnT2000: a Toolbox for Modeling the Geochemical Evolution of the Earth<br>**A Koppers**, J Phipps Morgan, H Staudigel |
| 1330 | V42A-17 | New Insight Into the Geochemical Consequences of Assimilation-Fractional Crystallization: Energy Constrained Assimilation-Fractional Crystallization (ECAFC)<br>**W A Bohrson**, F J Spera |
| 1330 | V42A-18 | Volcanic Glasses From Sea-floor Spreading Centers and Other Deep Sea Tectonic Settings: Major and Minor Element Compositons in the Smithsonian WWW Data set<br>**W G Melson**, T J O'Hearn, P Kimberly |
| 1330 | V42A-19 | GEOROC, the MPI Geochemical Rock Database: Introduction of the Web Interface<br>**U Nohl**, B Sarbas |
| 1330 | V42A-20 | Benford's Law: Surprising Distribution of Digits in Geochemical Data<br>**K P Jochum**, B Sarbas, A W Hofmann |
| 1330 | V42A-21 | Nitrogen Isotopes in the Mantle, Primordial or Fractionated?<br>**N Dauphas**, B Marty |
| 1330 | V42A-22 | $^{13}$C Depletion of Peridotitic Diamonds<br>**P Deines** |

# Abstracts

***listing in alphabetical order***

V42D-04; EOS 80(46):1,183

## Lead Isotope Anatomy of the Hawaiian Plume

**Abouchami, W; Hofmann, A W; Galer, S J**
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We report high precision Pb isotopic data $2\sigma_{ext} \leq 100$ ppm obtained with a triple spike (TS) on ~110 samples from six Hawaiian volcanoes. The samples come from Lanai, Mauna Loa, and Loihi volcanoes, which belong to the Loa trend, and from Kilauea, Mauna Kea and Kohala from the Kea trend. These isotopically distinct trends have been modeled as mixtures of two or three components (Chen and Frey, 1983; West et al., 1987; Eiler et al., 1998). Lead isotopes have the potential of yielding the maximum amount of information on the age and origin of source components present in the Hawaiian plume. Binary mixtures should form straight linear arrays in Pb isotope space, and deviations from straight lines require the existence of at least one additional component. In Pb isotope space, samples from individual volcanoes define tight, linear Pb isotopic arrays with distinct slopes. In $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ space, such arrays can be interpreted as either isochrons or mixing lines. If interpreted as isochrons, the $^{207}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ slopes of Loihi, Mauna Kea and Kohala correspond to ages of ~2 Ga, while the Kilauea slope indicates a younger age of 1.1 Ga. Exceptions are Lanai samples, which show a nearly horizontal line with $^{207}Pb/^{204}Pb$ ratios clustered around 15.44, and Mauna Loa data which display some scatter. A test of the isochron interpretation can be made using $^{208}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ systematics. Calculated $\kappa$ (= $^{232}Th/^{238}U$) values from the $^{208}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ slopes are inconsistent with those inferred from Th and U concentrations measured in the lavas themselves, suggesting that the $^{207}Pb/^{204}Pb$-$^{206}Pb/^{204}Pb$ slopes have no age significance. If, on the other hand, the Pb isotopic arrays are interpreted as binary mixing lines, then the observed Pb isotope systematics require far more than three components in the Hawaiian plume source. However, in each volcano, it seems that only two of these components are tapped --- a high $^{206}Pb/^{204}Pb$ and a low $^{206}Pb/^{204}Pb$ component --- resulting in a well-defined binary mixing line. Comparison of the Hawaiian Pb isotopic data with those of East Pacific Rise MORB glasses obtained using the TS technique (Galer et al., this volume) shows that there is no contribution of EPR-type oceanic lithosphere to shield building Hawaiian lavas. The existence of distinct linear arrays in Pb isotope space for individual volcanoes dictates the presence of several isotopically distinct mantle components within the Hawaiian plume. We conclude that the Hawaiian plume is a heterogeneous assemblage of residual mantle and recycled crustal components. Lastly, the concentrically-zoned plume model (Hauri et al., 1996; Lassiter et al., 1996) needs to be re-evaluated in the light of these new Pb isotopic data, which reveal that the isotopic anatomy of the Hawaiian plume is very complex in detail.

[ back to program schedule ]

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U32B-05; INVITED; EOS 80(46):32

## Terrestrial Inventories of Light Rare-Gases and Heat Production

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Rare-gas isotopes and heat production inventories had a particularly strong impact on mantle convection models as they suggest, in particular, that (1) higher $^{3}He/^{4}He$ ratios in hot-spot basalts indicate a mantle source more primitive and undegassed than for MORB (2) a substantial fraction of the heat- producing elements is hidden in the deep mantle mantle and (3) nearly 50 % of the terrestrial radiogenic $^{40}Ar$ appears to be hidden in the lower mantle. Seismic tomography reveals, however, the penetration of subducting slabs into the deep mantle, while Os, O, Pb, and Hf isotopic evidence indicates that the source of hot-spot basalts contains the igneous and sedimentary components of ancient recycled oceanic crust. The apparent decoupling of refractory lithophile isotopes, rare gas isotope geochemistry, and heat constraints calls for the reassessment of some basic assumptions of mantle geochemistry, and, most notably, raises the following questions: (1) Is He incompatible enough upon melting that high $^{3}He/^{4}He$ ratios in basalts unambiguously signal a primordial mantle source? (2) Can a layer at the base of the mantle, such as the boundary layer described by Kellogg et al. (1999), be both rich enough in U, Th, and K to satisfy the Urey ratio constraint and yet acts as a source of He with high 3/4 ratios and unradiogenic Ar? (3) Are the elemental abundances of ordinary chondrites relevant to the discussion of terrestrial rare gases, heat-producing elements and heat inventories? (4) Did continuous geochemical fractionation at subduction zones and gravitational segregation of minerals from the plates (steady-state) since the Earth's accretion wipe off the geochemical distributions inherited from the early planetary differentiation (transient)? The brutal shift of the convection paradigm of the early 90's will not produce a unified theory of mantle dynamics until seismology, geochemistry, and mineral physics produce the critical observations required to answer these questions.

[ back to program schedule ]

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U32B-09; INVITED; EOS 80(46):33

## Petrological and Geochemical Constraints on the State of the Archean Mantle

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Archean basalts provide little direct information on conditions in the Archean mantle. There are no well-documented Archean MORB or OIB and we lack information on Archean equivalents of modern mantle reservoirs. Most Archean basalts formed in oceanic plateaus and have monotonous, evolved major-element compositions that are controlled by low-P fractionation and yield no information on temperatures in their mantle source. However their trace-element characteristics - relatively high Ni and low heavy REE - indicate that the parental magmas formed through high-degree melting at large depths which suggests that average source temperatures were high. More useful results come from komatiites. The liquidus temperatures of these near-anhydrous ultramagnesian liquids are so high that the primary magmas must have formed in deep-seated mantle plumes. Although they show little secular variation in MgO contents, the oldest 3.5 Ga komatiites generally have low Al/Ti and depleted HREE whereas the youngest 88 Ma komatiites have high Al/Ti and flat to enriched HREE. This variation reflects a decreasing role of residual garnet during melting, due to decreasing depth of melting, which indicates that source temperatures progressively declined. The Fe contents of Archean komatiites and picrites seem higher than in modern counterparts (Francis, 1999, EPSL 167: 197-213) due perhaps to secular change in source composition. A possible explanation is that unusually hot early Archean plumes contained a high proportion of Fe- and garnet-rich recycled oceanic crust. Age data for continental rocks show an unusual episodic, peak-and-trough spectra for the period 2.7 Ga to 1.8 Ga. Stein and Hofmann (1994, Nature 372: 63-68) argued that these peaks represent periods of accelerated crustal growth, each triggered by enhanced plume activity. If so, the implication is that the late Archean and early Proterozoic mantle operated in a plume-dominated mode quite different from during earlier and later periods.

[ back to program schedule ]

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V42A-09; EOS 80(46):1,175

## U-Th-Ra Chronology of the TAG Hydrothermal Mound

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Hydrothermal circulation of sea water at mid-ocean ridges results in the formation of black smoker fluid vents and associated large massive sulphide deposits. Ocean chemistry can be strongly affected by such fluid circulation, however, little is known about the structure of hydrothermal systems. Thermal budgets of hydrothermal systems require that venting is episodic and active no more than ~10% of the time. However, the frequency and duration of individual events is unresolved and the mechanism by which systems are reactivated unknown. The TAG hydrothermal mound, situated at 26°N on the Mid-Atlantic Ridge, is one of the largest and best studied of the known active hydrothermal mounds. The active structure is highly brecciated and shows distinct mineralogical zoning, dominated by pyrite-anhydrite-silica mixtures. We report new $^{234}$U-$^{230}$Th data analysed by TIMS, which, combined with published data, suggest the TAG hydrothermal mound may have been active recurrently on a 2000 year timescale for at least 40 ka. Some anhydrite samples have also yielded old ages which may contradict the traditional view that anhydrite will rapidly dissolve once high temperature fluid venting has ceased. However, $^{234}$U-$^{230}$Th ages may be compromised by the complex evolution of the mound. The significance of the U-Th ages is being tested by TIMS analyses of $^{226}$Ra in addition to analysis of $^{230}$Th, $^{234}$U and $^{238}$U. The Th-Ra system is sensitive to shorter timescales ( $\sim < 8$ ka) compared with the U-Th method ( $\sim < 400$ ka).

[ back to program schedule ]

V42A-17; EOS 80(46):1,176

## New Insight Into the Geochemical Consequences of Assimilation-Fractional Crystallization: Energy Constrained Assimilation-Fractional Crystallization (ECAFC)

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Geochemical data for igneous rocks provide definitive evidence for the occurrence of open-system processes in evolving magma bodies; among the most important of these is concurrent assimilation-fractional crystallization (AFC). Although numerous methods exist to quantify geochemical trends associated with AFC, most are of limited value since energy conservation is not incorporated self-consistently. Our energy-constrained model (ECAFC) relies on conservation of mass, species and energy to generate geochemical trends of a magma body undergoing AFC. Partial melting of wallrock, modeled as fractional melting, is also explicitly incorporated. Results of ECAFC simulations demonstrate that associated geochemical trends can differ greatly from those of classical AFC (defined as mass and species conservation models). (1) As magma initially cools, the mass of wallrock melt is potentially small/negligible if wallrock is at an initial T that is low compared to its solidus. Thus, although never recorded in classical AFC, the earliest stage of AFC is dominated geochemically by fractional crystallization. (2) For an element such as Sr, which might behave compatibly in magma but incompatibly in wallrock, fractional melting causes the first increments of wallrock melt to be very Sr-rich. Thus, for mantle-derived basalt undergoing assimilation of typical continental crust, when partial melting begins, both [Sr] and Sr isotopes *increase* despite Sr being compatible in magma. Eventually, Sr is depleted in wallrock residue, and magma [Sr] decreases. Because so little crustal Sr is being added, very little change in $^{87}$Sr/$^{86}$Sr occurs. A basalt-rhyodacite suite from near Long Valley, CA (Cousens 1996; Vogel et al. 1994), shows this complex pattern and is consistent with an ECAFC model where basaltic magma assimilates mafic-intermediate lower crust in which Sr behaves incompatibly. Significantly, no single classical AFC model can explain this trend. (3) For an element such as Nd, which may be incompatible in magma and wallrock, upon partial melting, [Nd] increases as $^{143}$Nd/$^{144}$Nd decreases, consistent with assimilation of continental crust. Eventually, [Nd] in wallrock residue is depleted and so little wallrock Nd is added to magma that [Nd] actually decreases due to a dilution effect. At this stage, magma characterized by the most crustal $^{143}$Nd/$^{144}$Nd does not have the most enriched [Nd]. A basalt-rhyolite suite from E. NV (Grunder 1992) may show this trend, which can not be modeled by classical AFC. (4) Classical AFC mass balance might suggest that relatively radiogenic Sr isotopes of some continental basalts can not be the product of AFC because addition of the large mass of crust required to generate the elevated $^{87}$Sr/$^{86}$Sr would yield magma that is no longer basaltic. However, for a basalt with 700 ppm Sr and $^{87}$Sr/$^{86}$Sr of 0.7035, assimilation of only 10 % (relative to mass of original magma) can yield contaminated magma with 950 ppm Sr and $^{87}$Sr/$^{86}$Sr of 0.7075; this mass, 3x smaller than that required by classical AFC, would have an inconsequential effect on the magma major element composition. In summary, distinctions in geochemical trends and mass balance for ECAFC vs. classical AFC suggest that new insight into AFC is critically dependent on consideration of energy conservation and wallrock partial melting. Our results indicate that a number of data sets merit reassessment with ECAFC to accurately document their petrological histories.

[ back to program schedule ]

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V42A-05; EOS 80(46):1,174

## Energy and Chemical Balances for Modern and Ancient Seafloor Hydrothermal Systems: Insights Into Their Rates of Formation and Implications for Magmatic Budgets

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We have examined energy and chemical budgets for a modern seafloor hydrothermal system and the ophiolite-hosted massive sulfide deposits of Cyprus to determine the requirements for the formation of large mineral deposits on the seafloor. The TAG active hydrothermal mound at 26°08"N on the slow-spreading Mid-Atlantic Ridge is among the largest 30% of massive sulfide deposits in Cyprus. The extensive investigations that have taken place at the TAG active hydrothermal mound have resulted in sufficient data to constrain the volume of rock that interacts with circulating fluids in the reaction zone, the growth rate of the deposit, and the size of the energy source necessary to build a large mineral deposit on the ocean floor. Our calculations show that mineral precipitation in seafloor hydrothermal

systems is extremely rapid, and can result in the formation of a 4 million tonnes deposit in ~ 600 years hundred years, assuming the energy fluxes measured at the currently active hydrothermal system. This would require a total of 2 x $10^{19}$ J of energy. If the mound formed through several episodes of activity as has been suggested by geochronological studies, then each episode must be on the order of tens, to perhaps a hundred, years. The metals in this seafloor deposit were derived from a reaction zone of ~ 0.4-0.7 $km^3$ in volume. The Skouriotissa massive sulfide deposit in the Troodos ophiolite in Cyprus contained 6 million tonnes of sulfide ore and, assuming that the proportions of metals that are transported into the water column rather than being precipitated in the deposit were similar to those at the TAG active mound, required alteration of 2 $km^3$ of rock, consistent with field evidence for the size of the associated reaction zone. Energy balances suggest that the steady state energy flux from solidifying and cooling newly intruded crust along the ridge axis is insufficient to provide the heat necessary to drive a 1000 MW hydrothermal system. Magma chambers of sufficient size to provide the energy from latent heat seem excluded by seismic results even at fast spreading ridges. Extraction of energy from a large pluton seems more possible, but the stratigraphic location of the reaction zones suggests that hydrothermal reaction during extensive downward cracking is unlikely. We propose that the short-lived episodes of activity of the hydrothermal system could be related to episodes of more rapid magma supply (1000 MW requires the supply of about 0.5 $m^3$ / s of magma) similar to that observed during eruptive periods of kilauea.

[ back to program schedule ]

V31E-09; INVITED; EOS 80(46):1,144

## Response of Near-Surface Earth Systems to a Superplume/Supercontinent Event at 1.9 Ga

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High production rates of juvenile continental crust at 1.9-1.7 Ga may reflect a combined mantle superplume and supercontinent event (SSE) at this time. Approximately coincident with this event are maxima in the abundance of black shales, BIF, sedimentary phosphates, and tidal flat carbonate crusts. In addition, at this time, high CIA values in shales record global warming, and a peak in the abundance of passive margin and intracratonic marine sediments reflects relatively high stands of sea level. Following SSE by 100-200 My is an increased abundance of eukaryotic microfossils and the first major massive sulfate evaporite deposits. Lithospheric deformation caused by mantle plumes may disrupt ocean currents, which, together with injection of large amounts of $CO_2$ and reduced species (e.g., $H_2$, sulfur, ferrous iron, etc.) into the atmosphere-ocean system from plume-related volcanism, could lead to more pervasive anoxia and an increase in bioproductivity, thus increasing rates of black shale deposition and enhancing global warming. Increases in seawater P, Fe, and $CO_2$ from plume-related hydrothermal vents and from enhanced erosion of a growing supercontinent could be responsible for peaks in phosphate, BIF, and tidal flat carbonate crust deposition during the SSE. High stands of sea level may be caused by the superplume effect (raising sea level) overwhelming the supercontinent effect (lowering sea level). No major carbon isotope anomaly is observed at 1.9-1.7 Ga, thus the ratio of burial rates of reduced and oxidized carbon remained relatively constant even as total rates increased. Waning of superplume activity by 1.7 Ga led to disappearance of widespread oceanic anoxia and to decreases in the input rates of $CO_2$, Fe and P into the oceans, resulting in declining rates of deposition of black shales, phosphates, and BIF. This waning also permitted seawater $O_2$ levels to increase, leading to sulfate evaporite deposition and perhaps also to the diversification of oxygen-requiring eukaryotes.

[ back to program schedule ]

V42A-21; EOS 80(46):1,177

## Nitrogen Isotopes in the Mantle, Primordial or Fractionated?

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The upper-mantle is depleted in $^{15}N$ relative to air by *ca*. -5 ‰, which has long been ascribed to a primordial heterogeneity of the Earth. To further investigate this hypothesis, we have analysed N and Ar isotopes in plume-derived samples. Gases trapped in fluid inclusions and

vesicles were extracted by on-line crushing, were purified in an ultra-low blank line developed at the CRPG (Nancy), and were subsequently analysed with a static-vacuum mass-spectrometer. These analyses allow first to propose a not-model-dependent estimate of the N content of the mantle derived from K-Ar-N systematics (1.0 ± 0.4 ppm). The important findings of this study are that the deep mantle (sampled by plumes) is enriched in $^{15}N$ relative to air by *ca.* +3 ‰, and that the $N_2/^{36}Ar$ ratio differs by one order of magnitude between the deep mantle and the shallow mantle. The N isotopic heterogeneity of the Earth is hardly primordial in origin, and may rather result from one of these processes. (i) Recycling of surface-derived N in the mantle throughout the Earth's history. Dissimilatory nitrate reduction leads to an enrichment in $^{15}N$ of the residual $NO_3^-$, which is the main N bearing nutrient, so that the present-day sedimentary organic matter is enriched in $^{15}N$ relative to air. Such isotopic fractionation can readily account for the N isotopic composition of the deep mantle. During Archean times, when the atmosphere was more reducing than today, $NO_3^-$ was not readily available, and sediments were presumably depleted in $^{15}N$ relative to air, which could account for the N isotope signature of the shallow mantle. (ii) Metal-silicate isotope fractionation of N at the time of core formation. The solubility of N in iron-nickel alloys follows Sieverts' law ($N_2$ gas ↔ 2N dissolved), which is theoretically associated with a fractionation of N isotopes. Each of these interpretations has important geological implications on either the recycling efficiency through time or the mechanism of core formation.

[ back to program schedule ]

V41E-10; EOS 80(46):1,173

## Hotspots Sources and Fluxes: Insights from Fluid Mechanics Experiments

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Laboratory experiments have been performed to study thermal convection in a fluid stratified in density and viscosity. The presence of chemical heterogeneities helps to focuss heat and stabilize the convective features. Thus, strong stratification produces narrow and cylindrical hot thermochemical plumes. They are generated in the thermal boundary layer above the interface between the two reservoirs, and they entrain by viscous coupling thin schlieren of the lower denser layer. I suggest that such plumes could be responsible for hotspots on Earth. Scaling laws for the entrainement rate and the characteristics of the plumes have been derived and checked upon the experimental data. They show that a mantle plume would entrain chemically dense material at a rate between 0.1 and 15% of its total volume flux. The time required to homogenize a given stratification can also be estimated: it would take between 0.3 Ga (for a thin CMBL) and 4.0 Ga (for strong stratification at mid-mantle depth) to erase the heterogeneities. These times are lower bounds because the experiments do not include the effect of continuous reinjection of heterogeneous material into the mantle by subduction. Long-lived geochemical reservoirs are therefore to be expected in a chemically heterogeneous convecting mantle.

[ back to program schedule ]

V31E-11; INVITED; EOS 80(46):1,144

## Using Arc Geochemical Data to Evaluate Mass Fuxes and the Production of Continental Crust at Subduction Zones

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One of the most vital roles of geochemical data from arc magmatic rocks is in constraining the mass fluxes between slab, wedge and crust at convergent margins. Much effort has recently been devoted to quantifying the contributions of sediment and fluid from the slab. These estimates must be tempered by some uncertainty in the composition of the mantle wedge to which the slab component is added, although a depleted MORB source appears to be the most appropriate choice in most instances. A more serious note of caution should be raised in using volcanic rocks from arcs to evaluate source processes, since most have been strongly affected by the filtering effects of the crust through which they pass. The influence of open system differentiation, while widely recognized, may not be easy to account for. Detailed studies of individual volcanoes invariably highlight the role of open system processing of magmas - recharge and contamination - during over the lifetimes of the edifice. Isotopic disequilibrium among magmatic phases in many arc rocks provide further confirmation of open system processing. Core-to-rim $^{87}Sr/^{86}Sr$ profiles of plagioclase phenocrysts combined with well-defined textural features such as irregular dissolution surfaces, indicate that magma compositions changed during phenocryst growth. Added to this complexity is the realization, now experimentally confirmed, that crustal melting during contamination may produce melt(s) that is not in isotopic equilibrium with the bulk rock protolith. Conceding that differentiation is an important process that modifies or in some cases primarily defines the geochemical characteristics of erupted magmas, we must attempt to track the history of magmas traversing the crust. In this regard a simple picture of one-stage magma chamber storage is typically rejected in favor of multi-level storage and differentiation, more likely achieved in sub-volcanic dike-sill complexes. Subduction zone magmatism currently represents the main long-term flux of material from the mantle, and it

has therefore commonly been asserted that the continental crust has been generated primarily at arcs. This assertion is not consistent with the composition of primary arc magmas produced below the Moho, which are demonstrably dominantly basaltic. Recycling of ultramafic cumulate complements to intermediate composition differentiates is an essential additional process if continental crust is to be generated at subduction zones. Even this, however, is incapable of producing the isotope and trace element characteristics of average crust, which require open system processing. Thus the processes of crust-magma interaction that we observe today may represent a fundamental mechanism in the maturation of continental crust subsequent to distillation from the mantle.

[ back to program schedule ]

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V42A-22; EOS 80(46):1,177

# $^{13}$C Depletion of Peridotitic Diamonds

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Silicate inclusions in diamonds either belong to a peridotitic (P-Type),an eclogitic (E-Type) or transitional, websteritic, (W-Type) paragenesis. 162 P-type diamonds from the Venetia kimberlite, South Africa, whose mineral inclusion chemistry had been measured (Viljoen et al. 1998) were analyzed for their carbon isotopic composition. The large number of samples available permitted, for the first time, a more detailed analysis of the relationships between P-Type inclusion chemistry and the carbon isotopic composition of the diamond host. The carbon isotopic composition ranges from $\delta^{13}C = -2.5$ to -18 ‰ vs. PDB. The $^{13}$C sampling frequency distribution is multi modal. Examination of the inclusion chemistry (chromite, olivine, garnet) as a function of the carbon isotope composition mode to which the host belongs, as well as multi variate regression analyses, revealed no correlation between inclusion chemistry and $^{13}$C content. The inclusion compositions in diamonds of low $^{13}$C content are not distinctive. For a given carbon isotopic composition the combination of Ni/Fe and Mg/(Mg+Fe) of olivine inclusions varies systematically along fractionation trends. The composition of the olivine inclusions and the $^{13}$C content of their hosts can be interpreted as reflecting similar petrogenetic processes occurring in several mantle environments differing, on average, in their carbon isotopic composition. The iron/magnesium distribution between coexisting garnets and olivines permits an estimate of their pressure/temperature equilibration conditions. Diamonds, whose inclusions were equilibrated at lower temperatures and pressures tend to have, on average, lower $^{13}$C contents. The compositions of coexisting olivines and chromites suggest oxygen fugacities between 2.9 and 5.8 log units below the quartz-fayalite-magnetite buffer at 50 kbar and temperatures between 1280 and 1490 °C. Inclusions from diamonds of lower $^{13}$C content do not indicate systematically lower $fO_2$ conditions. The evaluated $fO_2/T$ conditions suggest minimal (0.0 to -0.5 ‰) isotope fractionation between a C-H-O vapor phase (methane, water, hydrogen) and diamond. The large $^{13}$C depletion of some Venetia P-Type diamonds appears to be unrelated to the composition of their inclusions, igneous fractionation trends, oxygen fugacity, and vapor isotope fractionation processes. This conclusion is consistent with evidence deduced from more limited data sets from other kimberlites. Viljoen K.S., Phillips, D., Harris J.W. and Robinson D.N. (1998) Mineral inclusions in diamonds from the Venetia kimberlites, Northern Province, South Africa Seventh International Kimberlite Conference, Cape Town 1988, Extended Abstracts 943-945.

[ back to program schedule ]

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V42A-01; EOS 80(46):1,173

# The Ronov Database on Volumes and Masses of Sedimentary Rocks

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Alexander Borisovitch Ronov, Viktor Efimovitch Khain, and their co-workers at the Vernadsky Institute of Geochemistry in Moscow compiled data on the distribution of sedimentary and volcanic rocks over a period of 50 years. The data were originally gathered for each geologic period of the Phanerozoic except the Quaternary, and for each continent except Antarctica. Each continent was divided into three tectonic environments - platform, geosyncline, and orogenic regions, and most of the Periods were divided into Subperiods. These initial compilations were published during the 1960's and 70's. A major global summary was published in 1980. It was translated and published as a reprint by the American Geological Institute and has been the data source for many global studies of the evolution of sedimentary rocks. Data on the continental margins and ocean floor were added to the global inventory in the 1980's. The data were revised and updated in a publication in 1993. The Phanerozoic stratigraphic units are more refined Subperiods/Epochs (31) of the Periods (11). Three Precambrian units, Vendian and Late and Middle/Early Riphean have been added to the compilation. The tectonic classification is in terms of platforms, geosynclines, and orogenic belts for the continental blocks for the entire Phanerozoic. The data are presented in terms of twelve sediment types and six kinds of volcanic rock. Seven new tectonic regions, shelf and slope for the platforms, geosynclines, and orogenic regions, and

ocean floor were added for Subperiods/Epochs from the Late Jurassic through Pliocene. A total of 26 categories of sediment and sedimentary rock are given for the Late Jurassic through Pliocene. The 1993 data are available as a GERM data set. The original data were collected at a subcontinental scale but have never been published. They are currently being prepared for inclusion in the GERM database. A compilation of Pleistocene sediment volumes and is also underway.

[ back to program schedule ]

V42A-04; EOS 80(46):1,174

## Metalliferous Sediments at Ocean Ridges and the Distribution of High-Temperature Hydrothermal Vents

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Determining the distribution of hydrothermal activity is important in understanding the chemical and thermal fluxes through the mid-ocean ridge system. Water column studies have been used to constrain the distribution and global systematics of high temperature vents along portions of the ridge system, but inevitably these data reflect a very short and recent time increment. Plumes formed at vents carry Fe and Mn-rich particles away from their sources. The particles settle and create Fe and Mn-rich sediment. These sediments reflect the time-integrated plumes and a much greater time interval. Sediment and plume studies are a valuable comparison. A correlation exists between plume incidence and spreading rate (Baker et al 1995), and a qualitative correlation exists between spreading rate and (Fe+Mn)/Al. The latter relationship is influenced by variable detrital sources and deposition rates in different regions, which leads to complex relationships between sediment composition and spreading rate. Along short intervals of individual ridges, however, a more detailed comparison can be made because the detrital background varies far less. Estimates of vent frequency from water column studies along the Mid-Atlantic Ridge (MAR) range from one vent per 25-30 km (36- 38˚N) to one vent per 360 km (27-- 30˚N), depending on the region studied. Sediments along the MAR from 36- 38˚N have high (Fe+Mn)/Al (up to five) and high plume-derived trace elements and reflect the presence of multiple high temperature hydrothermal sources. In contrast, sediments to the north (38-- 40.5˚N) and south (33- 35.6˚N) have low (Fe+Mn)/Al (about one). Hydrothermal activity is likely very limited in these regions as there is no apparent signature in the sediment. Along the MAR, water column and sediment studies are consistent, suggesting a concentration of vents within a small latitude window for a substantial period of time. For the East Pacific Rise (EPR) from 5- 35˚S, superfast spreading rates and high vent density combined with low detrital input result in a huge hydrothermal influence on the sediment composition. Surface sediments collected along or very close to the axial summit show extremely high (Fe+Mn)/Al (up to 230). Along strike, the sediment compositions vary consistently with water column studies. The highest (Fe+Mn)/Al occurs near 17˚S coinciding with a magmatic maximum and the highest vent frequency. The data thus far show a remarkable coherence between inferences from plume incidence and sediment composition, despite the different time scales that are sampled.

[ back to program schedule ]

V41E-07; INVITED; EOS 80(46):1,172

## Trace chalcophile element geochemistry of the Earth

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The concentrations of S, Cu, Cd, In, Sn, Te and the platinum group elements (PGEs) in submarine basaltic glasses, altered ocean floor basalts and subaerial OIB are now providing a clearer picture of the dominant processes that control the inventories of the trace chalcophile elements in the earth. Tellurium, like S, can be lost by low pressure degassing processes and most subaerial OIB data do not reflect

magmatic compositions. Cadmium shows signs of minor depletion in subaerial volcanic rocks, whereas In and Sn are less problematic. Sulfide fractionation renders Cu, Te and the PGEs compatible during fractional crystallization. Their behavior during partial melting is likely to be strongly influenced by whether or not residual sulfide was present. Sulfur, Te and PGEs are higher in Hawaiian magmas than in MORB. These data cannot be explained by a flux from the outer core to the mantle. However, assimilation of cumulate sulfide appears to be an important process that has a major effect on the Cu, S and Te (and presumably PGE) budgets of Loihi magmas. Cadmium, Sn and In behave as moderately incompatible elements in all environments. Cadmium and, to a lesser extent In concentrations are uniform in all basaltic glasses. Cadmium concentrations are similar for Pacific (131 ± 25), Atlantic (110 ± 14) and Indian (115 ± 21) MORB, Loihi OIB (136 ± 18) and Mariana arc and back arc (108 ± 9 ppb) (all ± 1 $\sigma$ ppb). Therefore, the mantle is very homogeneous in Cd concentration. In contrast, the hydrothermally altered upper 2 km of the ocean floor, as sampled from DSDP holes 504B and 896A, is extremely variable in Cd (14 to 326 ppb) and Cd/In ratio (0.6 to 5), despite constant In concentrations like those of pristine MORB. If OIB sources such as those supplying Loihi are the products of recycling altered oceanic crust these gross heterogeneities must become extremely well mixed by mantle convection. The calculated budgets for volatile chalcophile elements in the primitive mantle give cause for concern about the degree to which we understand the state of material that accreted to form the earth. Indium, Pb, Hg, Cd, Tl, Bi and C have similar half-mass condensation temperatures (~500K). However, the calculated primitive mantle inventories of all of these siderophile and chalcophile elements vary through two orders of magnitude from In, which appears to be even less depleted than predicted from the supposed lithophile element volatile depletion trend, to C, which appears to be highly siderophile. The budgets of the highly siderophile volatile elements Te, S, Se and C are as expected from the late accretion of a veneer that was not as depleted in these volatile elements as the average composition of the earth. The moon, despite strong depletion in certain volatile chalcophile elements like Cd and In, does not appear to be so depleted in Te. A possible explanation for this is that the earth continued to fractionate chalcophile and siderophile elements like Te into core-forming liquids for a significant period after the giant impact generally considered responsible for the formation of the moon.

[ back to program schedule ]

U32B-03; INVITED; EOS 80(46):31

# Osmium Isotopes and Mantle Dynamics

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Decompression melting is the most fundamental mantle process on Earth, and the isotopic variations of osmium (Os) provide a critical record of mantle melting to a degree unmatched by any other single isotope system. This advantage is due to two fundamental properties of the osmium isotopic system, namely (1) Os is a compatible element in mantle peridotite, and is thus a highly conservative tracer of basic mantle processes (melting, mixing), and (2) the parent elements rhenium ($^{187}$Re- > $^{187}$Os) and, to a lesser degree, platinum ($^{190}$Pt- > $^{186}$Os) are incompatible elements during magma formation. Re and Pt are not highly incompatible, but instead have a degree of magma compatibility similar to major elements such as Ca, Al, and Fe. These properties result in very large and perfectly complimentary differences in the Re/Os and Pt/Os ratios in mantle melts (high) and their residues (low). These differences are directly correlated with major element differentiation during melting, and are further magnified over time by variations in the ratios $^{187}$Os/$^{188}$Os and $^{186}$Os/$^{188}$Os. Because of the very high Re/Os ratio of all mantle melts, any terrestrial reservoir which can be classified as "crust" will rapidly evolve to very high $^{187}$Os/$^{188}$Os, making Os isotopes a uniquely sensitive tracer of crustal recycling into the mantle. Because Re is only mildly partitioned into melts, an increase in the mantle Re/Os ratio of any mantle reservoir requires a substantial addition of crustal material ( > 10%, Hauri & Hart, 1993). A Re-Os mass balance of the primitive upper mantle (PUM), depleted mantle (DMM) and continental crust (CC) demonstrates that the Re-depletion of the upper mantle is ten times larger than the Re-enrichment of the continents, requiring an additional reservoir of Re (Hauri & Hart, 1997). The ubiquitous elevation of $^{187}$Os/$^{188}$Os in mantle plumes, coupled with other geochemical tracers, strongly suggests that this additional reservoir is represented by crustal material stored in the deep mantle. Similar arguments can be made for the Pt-Os system, but the magnitude of the isotopic signal is muted by the very slow decay and low abundance of $^{190}$Pt. The correlated increases in $^{187}$Os and $^{186}$Os in some Hawaiian picrites (Brandon et al., 1999) suggest the presence of a Hawaiian reservoir with Pt/Re elevated by 50-100% over chondritic, a signature which is not easily attained in modern MORB. However, melting in the presence of garnet, coupled with oxidative Re loss in subduction zones, can create all the observed Hawaiian Os isotope variations by recycling of oceanic crust. This likelihood complicates interpretation of Os isotopes in terms of core-mantle exchange. In summary, Os isotopes should be widely recognized as sensitive tracers of the existence of terrestrial reservoirs with elevated crust/mantle ratios. Such reservoirs should be intrinsically more dense than the surrounding mantle, and gravitate toward the core-mantle boundary where they can be regionally aggregated by the large-scale convective flow. These reservoirs, which probably give rise to high-$^{187}$Os hotspot magmas, may satisfy the recent paradoxes implied by the terrestrial heat budget (Kellogg et al., 1999) and by the seismic properties of the lower mantle and D" (Albarede & Van der Hilst, 1999).

[ back to program schedule ]

V42D-02; EOS 80(46):1,182

## The Gabbro-Harzburgite Connection in OIB Sources

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Source compositions of mantle plume basalts are commonly ascribed to recycled oceanic crust (Hofmann and White, 1982), and specific recycled rock types, such as basaltic crust, pelagic sediments and terrigenous sediments, have been invoked to explain the isotopic "species" of Zindler and Hart (1986), HIMU, EM-1 and EM-2 (e.g. Chauvel et al., 1992). Another voluminous rock association subject to subduction is the gabbro-harzburgite assemblage that forms the lower part of the oceanic crust in contact with uppermost mantle, and such assemblages should also be recycled. What are the Sr-Nd-Pb isotopic characteristics of such a source? Feldspar-rich ophiolite gabbros from Oman have low (Th,U)/Pb, Rb/Sr and Nd/Sm ratios (Kelemen, 1998; Godard, 1998, both personal communication), and therefore recycled gabbros (with or without the associated harzburgite) might be isotopically rather similar to the DMM (depleted MORB mantle) of Zindler and Hart, and they might therefore be difficult to distinguish from present-day MORB. However, hydrothermal circulation may affect some of the relevant parent-daughter ratios, for example by removing lead or adding rubidium. DMM-like isotope characteristics are indeed found in basalts from Hawaii, Iceland and Galapagos Islands, but there is no consensus whether these "depleted" components are part of plume or whether they are derived from entrained or assimilated present-day upper mantle. Hofmann and Jochum (1996) and Sobolev et al. (1999) argued that Hawaiian basalts contain recycled gabbroic source components because of anomalously low (Th,U)/(La,Ba) and high Sr/Nd ratios, both common characteristics of ophiolitic gabbros. Further examination of published basalt data from Iceland and the Galapagos islands and new data from Iceland (Chauvel et al. 1999) shows that many of these basalts also have anomalously high Sr/Nd ratios. On both Iceland and Galapagos, Sr/Nd correlates positively with Mg-numbers and negatively with absolute REE concentrations. Conventional petrological interpretation would suggest that primary high Sr/Nd and Mg-numbers are both reduced during fractional crystallization processes. However, on Iceland (and on some of the Galapagos Islands (e.g. Santa Cruz), the Mg-number also correlates strongly with $^{143}Nd/^{144}Nd$. This suggests that Mg-rich basalts and picrites are derived from Mg-rich sources such as harzburgite. Overall, these relationships suggest that the sources of many basalts and picrites from Iceland and Galapagos are dominated by a recycled gabbro-harzburgite mixture which has been converted by recycling to an eclogite-harzburgite assemblage. Overall, this source type is more refractory than, for example, recycled basalt-peridotite associations. This is presumably the reason why melts produced from eclogite-harzburgite are common only in plumes where the degree of melting is relatively high, either because of high plume flux (Hawaii) or because the plume ascends to relatively shallow levels during melting (Galapagos and Iceland). Chauvel, C. et al., Earth Planet. Sci. Lett. 110, 99-119 (1992). Chauvel, C. et al. Geochem., Geophys., Geosystems, submitted 1999. Hofmann, A. W. & White, W. M. Earth Planet. Sci. Lett. 57, 421-436 (1982).. Hofmann, A. W. & Jochum, K. P. J. Geophys. Res. 101, 11,831-811,839 (1996). Sobolev, A.V. et al. Submitted to Nature, Aug. (1999). White, W.M. et al. (1993) J. Geophys. Res. 98, 19,533-19,563 (1993). Zindler, A. Hart S.R. Ann. Rev. Earth Planet. Sci. 14, 493-571 (1986).

[ back to program schedule ]

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V41E-08; INVITED; EOS 80(46):1,173

## The Geochemical Earth Reference Model: Composition and Evolution of the Depleted Mantle

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The mantle source of mid-ocean ridge basalts (MORB) is usually referred to as the "Depleted Mantle" (DM), since it is depleted in many important incompatible trace elements. In contrast, moderately incompatible and compatible element abundances in this reservoir are similar to estimates for "primitive mantle" or bulk silicate Earth. Both the chemical fractionation patterns as well as the isotopic compositions of DM are consistent with an origin by repeated melting of an initially primitive mantle to produce the continental crust and at least certain components of the atmosphere and oceans. The available constraints for the composition and volume of the DM, as well as its isotopic and chemical evolution through Earth history will be reviewed. The fluxes into and out of the DM are obtained by modeling its interaction with other reservoirs through time. This includes chemical and isotopic modeling of mantle-crust evolution based in particular on certain incompatible trace elements (Nd, Sr, Hf, and Pb), as well as degassing models based on noble gases (He, Ne, Ar and Xe). The result is a relatively simple Geochemical Earth Reference Model.

[ back to program schedule ]

V42A-10; EOS 80(46):1,175

# Chemical Structure of the Upper Mantle: Major Elements

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A data base containing 1109 chemical analyses of mantle samples was constructed. The analyses were divided according to their geological nature (xenoliths or specimens from massifs), origin (oceanic or continental), and petrological facies (spinel or garnet). These distinctions led to five sets: continental and oceanic xenoliths, continental or oceanic massifs samples (all four spinel facies) and garnet-bearing specimens. Only major components were considered: $SiO_2$, MgO, $Al_2O_3$, CaO, FeO, $Na_2O$, $TiO_2$, MnO, Ni and Cr. An excellent correlation is observed between the two ratios $MgO/Al_2O_3$ *vs* $SiO_2/Al_2O_3$. In the case of continental massifs the correlation can be described by the equation:\centerline{$MgO/Al_2O_3 = 1.089 (SiO_2/Al_2O_3)-3.170$} with a squared correlation coefficient $R^2 = 0.999$. For the four other sets previously defined the values of $R^2$ are: 0.995 (continental xenoliths), 0.990 (oceanic massifs), 0.991 (oceanic xenoliths); 0.990 (garnet-bearing xenoliths ). Seven additional correlations can be derived with values of $R^2$ ranging from 0.998 to 0.65. For any set of two component ratios the relationship obtained is identical from one set to the other. This relationship implies that all analyses belong to one single population, the upper mantle. The nine sets of correlations relating the ten independent variables point to a binary mixture of a mafic end member (mostly olivine) and a basaltic component: any known mantle sample is a specific mixture of these two end-members. Oceanic crust differentiation and lithospheric recycling are certainly the processes that control the chemistry of mantle samples. Extraction of the continental crust (or its recycling) cannot explain the chemical variation demonstrated by samples from the mantle.

[ back to program schedule ]

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V42A-20; EOS 80(46):1,174

# Benford’s Law: Surprising Distribution of Digits in Geochemical Data

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Benford (1938) was the first to popularize that the frequencies of digits in the first, second, third, ... place of many large sets of multi-digit numbers do not follow a uniform distribution as suggested by intuition. For example, the distribution of first digits of numbers generated by no known systematic process follows the logarithmic relation: Probability (1st digit = a) = log(1 + 1/a). This function leads to a monotonical decline from 30.1% for the 1's down to 4.6% for the 9's. The second-place and the higher-place digits where the zero has to be taken into account are much more uniform (e.g., frequencies for digits in the second position vary from 12% for the 0's to 8.5% for the 9's). Benford's law is a consequence of lognormal distributions of numbers. Benford ' s law has been used as an aid in analytical procedures in many fields, for example for detection of fraud or irregularities in tax returns and accounting systems, but not in geochemical research. As shown by Ahrens (1954), concentrations of trace elements in rocks are lognormally distributed. Lognormal distributions are generated by fractionation-dominated processes (Allègre & Lewin, 1995). Trace element data of rocks are therefore suitable to test Benford's law in geochemistry. For this purpose, we used data from some JGR publications on the results of the Hawaii Scientific Drilling Project (HSDP), analyses of MORB and OIB of the Max-Planck-Institut (MPI) SSMS laboratory, and more than 75000 trace element data from our MPI Geochemical Rock Database (GEOROC, Sarbas et al., 1999) containing OIB trace element data from about 300 publications. Our results show that the observed frequencies of the HSDP data fit the computed distribution law very well. For example, the evaluation of 2730 and 606 concentration data of Albarède (1996) and Hofmann & Jochum (1996), respectively, shows that the mean differences between observed and theoretical frequencies of the 1st digit are about 1.4, of the 2nd digit about 0.6, and of the 3rd digit about 0.4 percentage points. The difference is even lower (1.2 percent for the 1st digit) for the large data set (75000 values) of the GEOROC Database. We used Benford ' s law to verify the incompatibility sequence of trace elements. Very incompatible elements (e.g., Cs, Ba, U) span concentration ranges of several orders of magnitude in MORB and OIB samples and therefore fit the distribution law much more closely than compatible elements (e.g., Sc) whose element abundances in oceanic basalts are much more uniform. Other geochemical applications of Benford ' s law may be the detection of anomalies and spurious values possibly caused by sample contamination, analytical difficulties or unknown geological processes. L H Ahrens (1954), Geochim. Cosmochim. Acta 5, 49-73; F Albarède (1996), J. Geophys. Res. 101, 11841-11853; C J Allègre & E Lewin (1995), Earth Planet. Sci. Lett. 132, 1-13; F Benford (1938), Proc. Amer. Phil. Soc. 78, 551-572; A W Hofmann & K P Jochum (1996), J. Geophys. Res. 101, 11831-11839; B Sarbas et al. (1999), EOS, this volume.

[ back to program schedule ]

V42A-14; EOS 80(46):1,176

## Ca-Eskola pyroxene in deeply subducted crustal rocks: Evidence from the Kokchetav massif, Kazakhstan

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The discovery of metamorphic diamonds in the Kokchetav massif has greatly increased estimates of the maximum pressures attained by crustal metamorphic rocks. These rocks provide an unparalleled opportunity for understanding the mantle dynamics attending subduction of continental lithosphere. One of the unique textures in ultrahigh-pressure (UHP) minerals is quartz rods in clinopyroxene. This texture has been observed in eclogite not only from the Kokchetav massif, but also from the other UHP terranes. Smith (1984) interpreted the quartz rods to be exsolution products from a pre-existing supersilicic clinopyroxene which contained excess silica at peak metamorphic conditions. Zircon is an excellent container, which effectively sequesters of peak UHP metamorphic phases from retrogression. Therefore, in order to ascertain the pre-exsolution composition of the clinopyroxene, we analyzed clinopyroxene inclusions in zircon of the eclogite and a diamond-bearing biotite gneiss from the Kokchetav massif. Clinopyroxene inclusion in zircon has an excess of $Fe^{3+}$ + $Al^{VI}$ over $Al^{IV}$ + Na + K, and calculated cation totals significantly less than 4.0 per 6 oxygens. The stoichiometry of these pyroxenes can be reconciled if the end-member Ca-Eskola; $Ca_{0.5}AlSi_2O_6$ is considered. This end-member contains vacancy on the M2 site, and was first hypothesized by Vogel (1966), based on the need to explain isochemical symplectic breakdown of omphacites to diopside plus feldspar. The zircon-hosted clinopyroxene contains up to 9.6 mol% of the Ca-Eskola component for the eclogite, and 18.2 mol% for the biotite gneiss, whereas the matrix clinopyroxene contains much less (1.3 mol%, on average). Recalculation of the composition of the matrix clinopyroxene prior to exsolution of quartz rods yields 6.8 mol% Ca-Eskola component, which is consistent with the composition of the clinopyroxene inclusions in zircon. We conclude that the Ca-Eskola component in the peak metamorphic clinopyroxenes broke down by the retrograde reaction: 2 $Ca_{0.5}AlSi_2O_6$ = $CaAl_2$ $lSi_2O_6$ + 3 $SiO_2$ resulting in exsolution of the quartz rods in the matrix clinopyroxene. Significant quantities of the Ca-Eskola clinopyroxene in subducted crustal rocks may have an important bearing on physico-chemical properties of the slab at great depth.

[ back to program schedule ]

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U32B-02; INVITED; EOS 80(46):31

## Dynamics of a hot abyssal layer in the mantle

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There is evidence of compositional heterogeneity in the deep mantle, based on the geochemical signatures, heat flow and seismic imaging of the lower mantle. Dynamical modeling suggests that this heterogeneity likely takes the form of a hot abyssal layer of variable thickness, starting at a depth of about 1500 km. Such a layer should be enriched in heat producing elements (compared to the MORB source) to provide sufficient heat flow from the mantle to satisfy the observed global heat flux. For a hot absyssal layer to remain stable, it must be instrinscally dense enough to avoid entrainment and mixing into the overlying layer. We test the conditions for stability of a hot, abyssal layer using numerical models of two-component convection. We use two methods to model the dense layer: a double diffusive method, in which the intrinsically dense material is modeled with a "dye" that is governed by an advection-diffusion equation, and a "marker-chain" method which tracks a sharp interface between two different components. The latter has advantages over the double diffusive method which overestimates the amount of mixing between the two components. The models are heated internally and from the core-mantle boundary, with a higher rate of internal heating in the lower layer. Our models indicate that an intrinsic density contrast of ~ 4% or more yields a stable layer in these models. The layer is thicker under hot rising plumes and may provide a stable "anchor" which will control the heat and mass flux in plumes. Introducing a temperature- and depth-dependent viscosity (similar to the presumed rheology of the mantle) into the model decreases the intrinsic density contrast required to maintain the stable layer. We observe thermal coupling; that is, upwellings in the lower layer are correlated with plumes in the upper layer. We will address several factors affecting the evolution, structure and persistence of a dense layer at the base of the mantle, and examine the resulting fluxes of heat and mass.

[ back to program schedule ]

V42A-06; EOS 80(46):1,174

## Discovery of Hydrothermal Vent Sites in Bransfield Strait, Antarctica

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Bransfield Strait is a marginal basin between the South Shetland Islands and the Antarctic Peninsula. In April-May of this year we carried out a search for vents on board the RVIB NB Palmer. We used the ZAPS instrument sled (OSU), OFOS camera sled, and TV-grab (GEOMAR) to explore the water column and underlying sea floor. We also undertook a series of dredges to sample rocks. Previous investigations had found hydrothermal plumes at several locations in Central Basin. The plumes typically consist of particles, dissolved Mn maxima, varying amounts of $^3$He and $CH_4$, and sometimes temperature anomalies. The plumes are associated with volcanic ridges that characterize the central rift zone of this back-arc basin. This study focused on two such areas: Hook Ridge and Three Sisters. The turbidity plumes at Hook Ridge detected with the ZAPS package were larger and more complex than previously documented. In fact the largest were as large as any found on the MAR. Interestingly the dissolved Mn anomaly, as measured with the ZAPS chemical sensor and on-board techniques, was modest (less than 5 nM). Plumes only occurred in a small area (1x1km) on the southern flank of the E-W ridge segment. The plumes were complex and sometimes contained two maxima, one at 1100-1200m and a much smaller and more localized maximum at 700-800m. We traced the shallower maximum to a sunken crater near the ridge crest. Two TV-grabs from this feature recovered hot, soupy sediment (42-49°C) underlain by a thick layer of volcanic ash. Hard, siliceous crusts partially cover sediments in the crater. We also recovered pieces of massive sulfide resembling chimney fragments. Their mineralogy and texture indicate venting temperatures of in excess of 250°C during formation. Native sulfur and Fe-sulfides occur in fractures and porous layers. The source of the large deeper plume remains a mystery. We can not rule out the occurrence of dense brine formation higher up on the ridge. More likely there is a very large and very robust site yet undiscovered. We spent much less time at Three Sisters. Nevertheless we detected water column anomalies and recovered hydrothermal barites and sulfides from this area. In many ways the Bransfield sites remain enigmatic examples of backarc vents in a polar region.

[ back to program schedule ]

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V42A-16; EOS 80(46):1,176

## TnT2000: a Toolbox for Modeling the Geochemical Evolution of the Earth

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The geochemical evolution of the Earth is determined by the depletion of the mantle due to partial melting at hotspots, mid-oceanic ridges and island arcs, the formation of continental crust and the recycling of oceanic and continental lithosphere at subduction zones. Geochemical modeling approaches for these processes tend to focus on a relatively small number of processes, and they tend to be restrictive in modeling boundary conditions and the number and types of geochemical parameters considered. The fragmentation and incomplete geochemical modeling has limited our understanding of the Earth as a dynamic, geochemical system. These limitations led to development of the Terra Nova Toolbox (TnT2000) hoping to provide a flexible modeling environment that ultimately will allow us to explore both simple and sophisticated geochemical scenarios for a variety of chemical and physical processes that shape the Earth. TnT2000 uses a box model approach, expanded from the two stage melting model of Phipps-Morgan and Morgan (1999, EPSL 170:215-239), and includes all chemical elements ($n$=92) and natural isotopes for these elements ($n$=287). TnT2000 includes different models of partial melting and recycling, as well as variable assumptions about global reservoir geometry (whole mantle *vs*. layered mantle) and fluxes between them. Chemical fractionation by batch, fractional or dynamic partial melting, metasomatism and water-rock exchange are described with the help of empirical or experimental partition coefficients. The rate of chemical fractionation within the Earth can be

adjusted back through Earth history, whereby the current version uses a square-root heat loss model based on a 9.5 Gyr mantle overturn rate (P-M&M, 1999). The parent-daughter isotopes are constantly corrected for radioactive decay. TnT2000 provides a simple graphical user interface for the MatLab 5.2 environment and through graphical tools the fractionation patterns for different reservoirs can be monitored. Its modular nature allows for the future addition of other geochemical and geophysical processes. We will present the first version of TnT2000 that includes a basic set of tools and the geochemical parameters, to show a comparison of the two-stage melting model (P-M&M, 1999) with a conventional two-layered mantle model. These results and the interactive toolbox itself will be available at http://www-pacer.ucsd.edu/tnt.htm.

[ back to program schedule ]

V42A-15; EOS 80(46):1,176

## Composition and Stratification of the Slave Cratonic Upper Mantle

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We describe the mineralogical and chemical composition of the Slave mantle as deduced from xenoliths of peridotite within the Jericho kimberlite, Northwest Territories. Our data set includes major, trace and rare earth element compositions of bulk samples of spinel peridotite, low-T and high-T garnet peridotite and minor pyroxenite. Mineral modes for individual samples are estimated by computer-aided image analysis of conventional thin sections and by recalculation of bulk chemistry into a mineral basis equivalent to the constituent phases. Compared to primitive upper mantle, Slave peridotite shows depletion in the major elements and enrichment in incompatible elements (except for HREE). The Slave mantle is also uniquely stratified. Older, depleted spinel peridotite extends to a depth of 80-100 km and is underlain by garnet peridotite which shows a gradual decrease in Mg# with depth to 200 km. The youngest layer of fertile garnet peridotite, enriched in clinopyroxene and garnet, is underlain by a pyroxenite-rich horizon at the base of the petrological lithosphere. The Slave is further distinquished from the Kaapvaal and Siberian upper mantle by a marked vertical stratification in Mg#, lower abundances of orthopyroxene and higher abundances of clinopyroxene. In addition, a deeper layer of garnet peridotite below Slave shows less depletion than low-T peridotite from other cratons. The Slave peridotite results from a series of chemical events that includes a craton-scale process causing major element depletion. The low-T garnet peridotite is explained by 20-40% partial melting of pyrolite at P > 3 Gpa; the high-T peridotite requires lower pressure melting of the same pyrolite source. Another recognizable event in the formation of low-T Slave peridotite is enrichment in orthopyroxene by metamorphic or magmatic process. Samples of peridotite and pyroxenite have also been metasomatically enriched by K, Na, LREE-rich kimberlite-related fluids. Cratons can be classified into two varieties based on the presence (Type 1; Tanzania, Slave) or absence (Type 2; Kaapvaal, Siberia) of chemical and age stratification. Our analysis suggests that the Slave craton is Type 1 characterized by a gradual increase in fertility with depth and evidence for incremental downward growth of the continental mantle with time.

[ back to program schedule ]

V31E-06; EOS 80(46):1,143

## Germanium - Silicon Fractionation During Silicate Weathering: Results from Field and Laboratory Studies

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We present the first detailed study of germanium behavior in the soil environment as an important step toward making the Ge/Si system a useful tracer of weathering processes in both modern and ancient environments. Intensely weathered soils developed on Hawaiian basalts have bulk soil Ge/Si ratios a factor of 4 or more higher than basalt (e.g. 10-20 mol /mol *vs*. 2.5 mol/mol). Bulk soil Ge concentrations increase with Si, not with Fe, implying that the primary mechanism for Ge sequestration is related to secondary soil silicates, rather than soil Fe-sesquioxides. Soil organic matter is not a significant reservoir of Ge. Sequential extraction experiments on these soils indicate that Ge is preferentially incorporated relative to Si during the initial precipitation of secondary soil aluminosilicates (principally allophane). Further Si loss as these soils age, and related changes in mineralogy, involves little additional Ge/Si fractionation. A complementary study of granitic weathering from Luquillo, Puerto Rico shows that differences in Ge/Si and weathering rates in granitic minerals are an important control on Ge/Si in granitic saprolites. Retention of primary quartz prevents these soils from developing very high Ge/Si ratios. The most important weathering reaction in these saprolites is the weathering of plagioclase (and hornblende) and precipitation of secondary

kaolinite. Neoformed kaolinite has a Ge/Si ratio (5.7) higher than the actively weathering minerals (3.9). A geochemical mass balance requires that the solution released from this reaction carries a low, highly fractionated Ge/Si ratio (0.15 mol /mol). Initial results from laboratory synthesis of allophane confirms that secondary aluminosilicates fractionate Ge/Si during their precipitation. Allophane precipitated from a solution with an initial Ge/Si ratio of 0.9 æmol/mol had a Ge/Si ratio of 1.2 mol /mol. The final solution Ge/Si ratio was 0.5 mol /mol. Ge/Si fractionation during precipitation of secondary aluminosilicates is consistent with a thermodynamic model of Ge/Si solid solutions.

[ back to program schedule ]

U32B-06; INVITED; EOS 80(46):32

## Constraints on the mean composition and mantle source of MORB

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The chemical composition of MORB provides one of the best constraints on the composition of the upper mantle. In general, major element characteristics are remarkably coherent: the mantle source is fertile in major elements and moderately depleted in highly incompatible elements; there are mantle temperature variations of some 200 degrees beneath ridges. In addition, there are long wave-length gradients in mantle composition associated with hot spots, and there is small scale heterogeneity that appears to be ubiquitous (but not uniform in amount). The RIDGE database now provides the opportunity to generate far more meaningful estimates of the mean composition of the ocean crust for both major and trace elements for the different ocean basins. Detailed comparison of this composition with continental crust and bulk earth provides constraints on the size of both MORB and OIB reservoirs. There are several first order constraints for mantle models. First, the major element fertility of the MORB source and the modest incompatible element depletion mean that the source has only lost the equivalent of a very small degree melt to other reservoirs. This requires that over time most of the ocean crust has been effectively recycled into the upper mantle. Second, apparent ages for isotope systems suggest that heterogeneities along ocean ridges have ages of less than a few hundred million years. These two lines of evidence suggest a major role for efficient stirring in the upper mantle of recycled plates. The origin of the local heterogeneity of MORB and its implications for the upper mantle is currently under debate. The most popular model is the "veined mantle" from Hanson (J. Geol. Soc. London 1977). Current versions of this model make these veins pyroxenite or eclogite from recycled ocean crust that can be independently sampled by the melting process. Aspects of this latter model pose difficulties: most recycled crust should be depleted gabbro with highly distinctive trace element compositions, but evidence for such material is rarely found; how veins can melt and transport melt independently from the surrounding mantle matrix is unclear; enriched basalts at ridges are highly enriched in incompatible elements, and large extents of melting of recycled crust are unlikely to yield such trace element patterns; since the pyroxenite melts at lower tempertatures, ridges derived by lower extents of melting should show a greater vein component and hence evidence of a more fertile major element source, which is not apparent in the data. An alternative model takes into account the fact that low degree melts in equilibrium with garnet lherzolite are likely to be abundant in the upper mantle- in the "wings" of melting regimes, through upwelling off-axis, from interaction with off-axis hot spots. Such melts have many of the requisite chemical characteristics to create local small scale hetrogenities in the upper mantle, and would not lead to substantial major effects.

[ back to program schedule ]

V42A-13; EOS 80(46):1,175

## Os isotopic and thermobarometric evidence for recent delamination of subcontinental lithospheric mantle beneath the Sierra Nevada, California

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Delamination of the subcontinental lithospheric mantle has been predicted on the basis of various geodynamic models, but the supporting evidence has been circumstantial. Beneath the extinct Sierra Nevadan arc, California, high elevations, alkalic magmatism, and low sub-Moho seismic velocities suggest that the lower crust and lithospheric mantle have recently delaminated. Sm-Nd model ages of lower crustal (garnet clinopyroxenites) and upper mantle cumulate xenoliths (garnet websterites) indicate that this region was once underlain by Proterozoic juvenile crust and lithospheric mantle. The lower crustal and upper mantle cumulate xenoliths are present in late Miocene lava flows but absent in late Pliocene flows; this temporal change in xenolith demographics has been used to suggest that the lower crust and lithospheric mantle were delaminated during the Pliocene. However, peridotite xenoliths from both late Miocene and late Pliocene flows

have $^{187}$Os/$^{188}$Os in the range 0.1263-0.132, which is typical of the range of modern-day asthenospheric mantle. Because some of these peridotites are highly refractory (Fo up to 92.5), the radiogenic Os requires recent extraction from the convecting mantle, suggesting that most of the original Proterozoic lithospheric mantle was removed prior to the late Miocene, even though the lower crust had not yet delaminated. These peridotites show chemical and textural evidence for cooling: orthopyroxenes with high Ca and Al cores, exsolution of garnet from pyroxene, and garnet rimming spinel. Thermobarometry indicates that they originated at temperatures as high as 1400°C and subsequently cooled to or below temperatures of 800°C, coinciding with the equilibration temperatures of garnet clinopyroxenites and garnet websterites. The lengthscale of the diffusion profiles suggest that such disequilibria could not have persisted much longer than 150 Ma at 800°C. Thus, these peridotites are interpreted to represent "frozen" intrusions of hot, asthenospheric mantle that upwelled into the void created by delamination of older lithospheric mantle during Cretaceous or early Tertiary times.

[ back to program schedule ]

V42D-06; EOS 80(46):1,183

## The RIDGE Petrological Database on the World Wide Web

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Systematic compilations of data are essential both for the preservation and documentation of existing data, and as a useful tool for the scientific community to synthesize and build upon prior work. Publishing databases on the internet provides global and convenient access to data independent of computer platforms and location. Here we present a web interface applied to the RIDGE Petrological Database (URL: http://www.ldeo.columbia.edu/RidgePetDB ), a relational database for geochemical data on rocks from mid-ocean ridges, back-arc basins and seamounts. The structure of this database, originally designed at LDEO and modified in a joint effort with the Max-Planck-Institut for Chemistry (MPI) in Mainz1, permits far more general application to accommodate any type of chemical data for whole rocks, glasses, minerals and inclusions along with a wide variety of metadata including geographical location, sampling procedures, cruise, rock texture, modal composition, analytical method, precision, standard values etc.. The identical structure is used for GEOROC, the geochemical rock database of the MPI2,3. The web interface consists of a series of web pages that allow the user to fully explore the contents of the database. Query pages supply the user with tools such as dynamically created lists and menus to define criteria for queries. The user's input is incorporated into SQL queries that return data tables in HTML, text or Excel csv format. The web interface is designed to be flexible and efficient for the user: - The search queries are structured in a way that the user can define any combination of criteria such as lat/long, geographical names, rock types, tectonic setting, cruise, ship, sampling year, reference, person and compositional characteristics. - Interactive query results let the user browse through related information by point and click - The user can customize tables including metadata of his choice. - Precompiled data tables are available for faster access to data. - Tables from original papers can be retrieved as published. The utility of the full suite of queries is currently limited by incomplete metadata which is often missing from publications and difficult to obtain from individuals. Future publications need to have more rigorous guidelines regarding the inclusion of metadata if the growing amount of geochemical data is to be preserved and used for maximum benefit. In addition, unique sample identifiers, which are possible for submarine samples, need to be adopted for all publications and sample types to optimize data linkage and retrieval. 1. K Lehnert, C H Langmuir, W B Ryan, W Jin, Y Su, B Sarbas, U Nohl, K P Jochum, J Snow, S Galer, A W Hofmann EOS, Trans AGU 79 (45) Fall Meet. Suppl, 44 (1998) 2. B Sarbas, K P Jochum, U Nohl, A W Hofmann EOS, Trans AGU (this volume).

[ back to program schedule ]

V42A-11; EOS 80(46):1,175

## Studying the Input to the West Pacific Subduction Factory: ODP-Leg 185

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Extensive studies in the Izu-Bonin and Mariana arc systems had already laid the foundation for much of the geochemical flux equation in the West Pacific, and the missing part of the flux equation was largely the input. The incoming sediment and basaltic sections approaching the Izu-Bonin Trench, were sampled for the first time on Leg 185 at Site 1149 (~ 400 m sediment and ~130 m of basement), and the

oceanic crust seaward of the Mariana Trench was sampled by deepening ODP Site 801 (the oldest oceanic crust ever drilled) to almost 500 m into Layer 2A. Both of these sites are located along the same flow line in Mesozoic Pacific oceanic crust, from about 170 to 130 Ma, and provide an unparalleled opportunity to study the geochemical and physical nature of old Pacific crust and sediments. The West Pacific subduction factory is particularly "efficient" in that most of the sediment is subducted, and may control differences in outputs of the arcs. The sedimentary section at the Izu-Bonin trench lacks the mid-Cretaceous volcaniclastic section, and contains more siliceous and carbonate-rich biogenic material than the Marianas section. Notably, almost 60% of the Izu section consists of chert and porcellanite-rich lithologies. Samples and detailed logging data now available for both sites will be combined with seismic profiles and used to calculate the flux of key elements carried in the sedimentary column into the Subduction Factory. In addition to part of the C and S fluxes, Pb-isotopes, Ba, U, Th and REE budgets in arcs are probably controlled by the sediment input to the system. Sites 801C and 1149 provide the first significant sections drilled into Mesozoic fast spreading crust. Contrary to simple downhole decreases in the extent of alteration observed at other sites, alteration of the volcanic section at 801C is related to several discrete zones associated with ocherous Si- Fe-hydrothermal deposits and thick massive flows, within zones of remarkably unaltered basalt which contains fresh glass. Shipboard measurements for $K_2O$ and estimates of the vol% alteration (1.7% halos, 1.5% breccia and hyaloclastite, 0.05% celadonite veins) indicate a 17% increase in $K_2O$ and Rb contents in the total volcanic section at Site 801C as the result of patent alteration. Adding interpillow sediment to this estimate increases the bulk $K_2O$ content of the Leg 185 section to 60% greater than in fresh basalt alone. A second estimate of the $K_2O$ budget was made by calibrating the natural gamma ray measurements made on whole-round cores (MST-NGR) with shipboard AA data on discrete samples. The bulk $K_2O$ calculated from the MST-NGR data for the entire tholeiitic section is 0.31 wt%, similar to the average obtained from the logging data (0.36 wt%). These estimate are lower than those for DSDP 417 in old Atlantic crust (0.56 wt%), the only other site where alteration budgets have been attempted. These preliminary estimates are only the first of an extensive geochemical program to be integrated with geophysical logs and aimed at the reconstructing of the fluxes for most of the elements of interest for subduction recycling studies.

[ back to program schedule ]

V31E-04; EOS 80(46):1,143

# Sources and Sinks of Osmium and Organic Carbon in the Gulf of Papua, New Guinea

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Much of the Os in marine sediments is associated with organic carbon, leading to the proposition that the Os isotopic composition of seawater over time is strongly affected by the weathering of ancient organic matter. The Os isotopic composition of surficial sediments from the Gulf of Papua, located in the wet tropics, demonstrate that both seawater and terrestrial Os are sequestered in the estuarine environment in conjunction with organic carbon burial. There is a negative correlation between the Os isotopic composition of the bulk sediment and the fraction of organic matter of terrestrial origin. The Os/Corg of the Gulf of Papua surface sediments is intermediate between that of other modern and ancient sediments. Approximately $10^{11}$mol/yr of Corg and 20-57 mol/yr of Os are buried in the inner shelf ( < 50m depth) of the Gulf of Papua, in an area of only 21,000 $km^2$. Where marginal marine sediments such as these undergo rapid uplift and weathering, as in convergent margins, they can contribute substantially to the Os isotope budget of the oceans. The Fly and Sepik Rivers are two of the largest rivers draining the island of New Guinea and among the world's top rivers in terms of discharge and sediment yield. The sediment supplied by these rivers as well as the most terrestrial of the Gulf of Papua sediments are remarkably unradiogenic ($^{187}Os/^{188}Os < 0.40$) compared to the very high values usually contributed to the oceans by continental crust ($^{187}Os/^{188}Os > 1.2$). Osmium isotopic budgets for the oceans have previously considered the balance between a low concentration radiogenic upper continental crustal source supplied by rivers and a higher concentration unradiogenic source dominated by hydrothermal and meteoritic influxes. These results indicate that New Guinea and presumably much of the landmass of the Oceania region of the SW Pacific is in fact a significant source of nonradiogenic Os to the oceans.

[ back to program schedule ]

V42A-03; EOS 80(46):1,174

## Are Seafloor Hydrothermal Vent Fields Significant Geochemical Earth Reservoirs?

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Seafloor hydrothermal vent fields (SHVF) are one of the most significant earth science discoveries of the century. They have been studied for nearly two decades, but their potential contribution to the chemical dynamics of the earth has been largely overlooked. At active spreading ridges, the prolific chemosynthetic biota constitute large reservoirs of $^{13}$C-depleted carbon mainly as bacteria. Sulfides that precipitate from the venting hydrothermal fluids are similar to or enriched in Re and Os (up to 4 ppb Re; 4 ppb Os), relative to MORB (up to 1 ppb Re; 7 ppb Os), with radiogenic $^{187}$Os/$^{188}$Os ratios indicating a seawater contribution. Ancient analogues of the SHVF (from 0.8-2.1 Ga), have sulfides with Re and Os concentrations up to 90 ppb and 3 ppb respectively, with initial $^{187}$Os/$^{188}$Os ratios as high as 0.5. The subduction of ancient $^{13}$C-depleted SHVF with altered MORB can account for the apparent major element versus carbon isotopic contradictions in diamond eclogite genesis, and provides a model to explain the poor Re-Os age systematics reported for many mantle eclogites. SHVF are abundant on ocean ridges, and must have existed in abundance since at least the mid-Proterozoic, when increased ocean depth pushed hot seawater to its critical P and T, maximizing rock fracture and hydrothermal circulation. SHVF are significant geological features and their subduction is inevitable. Whether they are important contributors to the chemical dynamics of the earth depends on more than their total volume or mass alone. Rhenium, osmium, and carbon are present in non-silicate phases that are not taken into account in equilibrium models based largely on silicate phases. The contribution of the SHVF reservoir to the overall Re-Os and carbon isotopic budget of the crust-mantle system thus requires a re-thinking of previous equilibrium mixing models based largely on igneous reasoning.

[ back to program schedule ]

V42A-18; EOS 80(46):1,177

## Volcanic Glasses From Sea-floor Spreading Centers and Other Deep Sea Tectonic Settings: Major and Minor Element Compositons in the Smithsonian WWW Data set

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The Smithsonian MORB glass data for major and minor element analyses are now available on the web http://www.nmnh.si.edu/minsci/research/glass/. This is a larger version of one of the most widely cited data sets and sample collections used to understand magmatic and tectonic processes beneath the mid-ocean ridges on a global scale. One of these papers are listed on the website. The analyses were done in the Department of Mineral Sciences on samples contributed by numerous marine geologists and geophysicists over the past 27 years and includes samples from 2085 localities: 664 from the Atlantic, 28 from the Caribbean, 89 from the Indian, and 1304 from the Pacific. There are two data sets: a Magma Batch File (MBF) and an Individual Analysis File (IAF). Our approach to acquiring and analyzing the glasses was formulated to cover the world sea-floor spreading centers and to identify and report the composition of homogenous magma batches, an approach typically used in studies of subareal eruptive rocks. Thus analyses with compositions within analytical precision and from a continuous sequence in a deep-sea core, or a single dredge, or a single unit identified by observers in a submersible, were averaged: such data make up the MBF (2703 analyses). The IAF on which the groups are based are in a separate file (9035 analyses). The analyses are by the electron microprobe, using the same standards and same normalization procedures, and most by the same analyst (Tim O'Hearn). The major elements have been normalized to VG-2, a widely used Smithsonian MORB glass standard analyzed by classical wet methods by E. Jaresowich. We have found consistent but small analytical differences with other labs working on MORB glasses. Our data are a highly coherent set intended to give the precision required to identify the often subtle but important differences among spreading center eruptive rocks as clues to their tectonic and petrogenetic significance.

[ back to program schedule ]

V31E-08; INVITED; EOS 80(46): 1,144

## Dispersed Volcanic Ash in Marine Sediments

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Drawing on sedimentary sequences recovered during ODP Leg 165 (Caribbean Sea) and Leg 185 (Izu-Bonin Arc), we will discuss chemical and statistical techniques used to recognize and quantify dispersed volcanic ash in marine sediments. Dispersed ash consists of formerly discrete layers that have been bioturbated or otherwise physically mixed into the bulk sediment as well as ash that has been deposited directly to the seafloor as part of the pelagic rain. Such chemical quantification is important because petrographic studies are often limited to qualitative assessments ("abundant", "present", "rare"). Determining the abundance of both discrete and dispersed ash in marine sediments is vital to global chemical budgets of volcanic ash production, the consumption of dissolved species such as Mg from porewaters during ash alteration, and for temporally determining episodes of Earth history that experienced elevated volcanic outputs. We will show, based on normative calculations and multielement statistical treatments, that our approach yields precise, geologically reasonable, and consistent results for quantification of dispersed ash. In the Caribbean, dispersed ash commonly accounts for 15-20 wt% of the bulk sediment, and in some cases up to 45 wt%. The accumulation of dispersed ash typically leads the accumulation of discrete layers by 2-10 m.y. These changes could signify distance from the volcanic source, periods of small volume volcanic activity preceding the large eruptions, or the transportation to the deep sea of terrestrially deposited ash preceding the larger eruptions. In the Izu-Bonin system, our results indicate the presence of 35-50 wt% dispersed ash of probable mixed composition. Both the Caribbean and Izu-Bonin results agree with qualitative petrographic estimates, but tend to be slightly higher (by 5-10 wt%). This suggests that the visual smear-slide estimates are not recognizing an altered ash component. Our preliminary results suggest that the chemical and statistical approach is worth pursuing. Systematically sampling the downwind regions of the major arc systems of the world will greatly improve our understanding of temporal and spatial patterns of volcanism, the global composition of marine sediment, and the extent to which arc material is subducted and cannibalized at convergent margins.

[ back to program schedule ]

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V31E-02; INVITED; EOS 80(46): 1,143

## Thermal Evidence of Water Exchange by Tidal Pumping in a Coastal Aquifer

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Mixing of meteoric and sea water produces brackish to saline water in coastal aquifers. In this mixing zone, chemical reactions of the salty water with aquifer solids modify the composition of the water. In some cases these reactions enrich the fluid in nutrients, metals and radioactive tracers. By quantifying the tracer signal in the coastal ocean, the quantity of fluid exchanging may be inferred. Based on the tracer signals, I have concluded that large volumes of water exchange between the coastal ocean and underlying aquifers. Little is known regarding the mechanism of the exchange process. During vibra coring operations off the southeast US coast, we found several sites within the upper 5 meters of the seabed where a layer of salty water lay between an overlying clay layer and the limestone basement. At these sites the core penetrated sand, shells, and dense clay, then dropped a meter or more before hitting limestone. There was no core recovery between the clay and limestone. In May 1999 we dove on one of these sites about 20 km SE of Little River Inlet (NC/SC border) and drove a PVC pipe through the sand and clay into the water layer. Using a hand pump we pumped water from this layer at 5 L/min. The water near the limestone was enriched in sulfide, radium, ammonia, and phosphate. Water 1 m above the limestone was low to zero in sulfide but enriched in radium. With the top of the well sealed, we recorded the temperature in the well in July 1999. The anoxic water at the bottom yielded a constant temperature of 19.5°C for 2 days. A recorder placed 1 m above the anoxic water measured a semidiurnal cycle of 1°C for 96 hours. Low temperature (20.5°C) occurred within 1 hour of low tide, and higher temperature (21.1-21.5°C) occurred at high tide. Bottom ocean water during this period was 25-26°C with no cycle. These data can only be explained by tidal pumping. During low tide water emerges from the limestone and drives some of the overlying water into the coastal ocean through high permeability sediments. During high tide water is forced back into the limestone. The temperature data suggest a significant fraction of the water above the limestone must exchange each day. As the water exchanges it provides nutrients and radium to these coastal waters. Based on the number of vibra cores that recorded this sedimentary sequence, it is fairly common along the coast from North Carolina to Florida.

[ back to program schedule ]

V42A-19; EOS 80(46): 1,177

# GEOROC, the MPI Geochemical Rock Database: Introduction of the Web Interface

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Geochemists are faced with a rapidly growing volume of published analytical chemical data. Therefore, an easily accessible and reliable tool is needed for fast access and efficient selection and sorting of these data. These requirements initiated the Max-Planck-Institute for Chemistry (MPI) in Mainz to establish GEOROC (**GEO**chemistry of **R**ocks of the **O**ceans and **C**ontinents), a relational geochemical database that contains available published chemical analyses of whole rocks, glasses, minerals, and inclusions. In cooperation with the Lamont-Doherty Earth Observatory (Lehnert et al., 1998), we have developed a database structure that combines chemical analyses with additional information (metadata) that are necessary for proper interpretation. These metadata include geographical location, rock type, age, analytical method, precision and/or accuracy, and standard measurements. All data are linked to the primary reference source. Currently, the GEOROC database covers most of the ocean-island occurrences. It includes the analyses of about 12,000 whole rocks, 10,000 minerals, 1,000 volcanic glasses and 1,000 melt and mineral inclusions, published in more than 500 papers. In the future, data on other oceanic as well as continental rocks will be added. The identical structure is used for the RidgePetDB of Lamont, presented in this session (Lehnert et al., 1999). The GEOROC database is a MS Access database that will be accessible over the world wide web. The database runs on a Windows NT server. The web interface uses "Active Server Pages", an application environment that combines HTML and server-side Visual Basic scripts to create dynamic web pages. The server-side scripting has the advantage of compatibility with various types of browsers and client machines (MAC and PC). The GEOROC web interface offers the possibility to select data by bibliographical, geographical, petrographical, and chemical criteria. The resulting datasets can be downloaded as text or HTML file and can be saved by the client as Excel spreadsheets. K Lehnert et al. (1998), EOS, Trans AGU 79 (45) Fall Meet. Suppl.,44 K Lehnert et al. (1999), EOS, Trans AGU (this volume).

[ back to program schedule ]

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U32B-04; EOS 80(46): 32

# Helium flow in the mantle and mantle degassing

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We made extensive compilation of noble gas data obtained for mantle derived-materials such as MORB, OIB, OIB-xenolith and diamond. An examination of this data set reveals some interesting features of terrestrial noble gases, which have not hitherto been inferred from existing limited data bases. While concentrations of Ne (except for MORB), Ar, Kr, and Xe in mantle-derived materials are well correlated with each other, He concentration is totally uncorrelated with the concentration of other noble gases, confirming the previous suggestions by various authors that He in the mantle is essentially decoupled from the heavier noble gases. Moreover, a $^{4}$He - $^{40}$Ar plot shows clear distinction between MORB and OIB; while MORB is characterized by excess He relative to a closed system evolution value ($^{4}$He/$^{40}$Ar ~ 3), OIB is overwhelmingly deficient in $^{4}$He. This complementary characteristic in He abundance is also seen in a radiogenic $^{4}$He to $^{21}$Ne ratio; the ratio should show a constant production ratio in a closed system evolution. The nature of the excess (or deficient) He can be constrained from the consideration of their isotopic compositions. He in MORB and OIB are characterized by very narrowly-confined $^{3}$He/$^{4}$He isotopic ratios, about $10^{-5}$ for MORB and $(1 - 4)\times10^{-5}$ for OIB, and they are not much different from solar He ($1.5 \times 10^{-4}$). In contrast, a similar radiogenic isotopic ratio, $^{40}$Ar/$^{36}$Ar, in the mantle shows several orders of magnitude larger values than the primordial $^{40}$Ar/$^{36}$Ar ratio (~$10^{-4}$). The latter difference can be reasonably attributed to fractionation in K/$^{36}$Ar in the Earth from the solar composition and subsequent accumulation of radiogenic $^{40}$Ar. It is then difficult to attribute the observed modest difference between terrestrial He-isotopic ratio and that of solar He to the same fractionation event responsible to the Ar isotopic ratio, since at least a similar magnitude of fractionation in (U+Th)/$^{3}$He as in K/$^{36}$Ar, and hence a similar magnitude of difference in $^{3}$He/$^{4}$He isotopic ratio as in Ar would be expected. As a consistent explanation for the above observations, we propose that He is being continuously released from OIB source materials and migrating upward. The He-flow is quite independent of other noble gases which are essentially retained in mantle materials and would move "congruently" with mantle convection. Magma produced in MORB source mantle would entrain the migrating He to give rise to the excess He in MORB, while OIB source mantle is continuously deprived of He. In contrast to the $^{3}$He/$^{22}$Ne ratio which differs by more than

an order of magnitude between MORB and OIB, elemental ratios Ne/Ar, Kr/Ar, and Xe/Ar show little difference between MORB and OIB, and they are very close to the air ratios. The latter facts suggest that the mantle degassing was not due to commonly assumed equilibrium processes such as crystal/melt or melt/vapor noble gas partitions, but more likely to kinetic process.

[ back to program schedule ]

V42A-12; EOS 80(46): 1,175

## Osmium Isotopes in Vanuatu Arc-Lavas

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Os isotopic studies of arc lavas have the potential to resolve the amount and nature of recycled crustal material in subduction zones because of the large contrast between mantle and subducting plate $^{187}Os/^{188}Os$ ratios. The compatible nature of Os during partial melting and melt migration means that Os isotopic measurements can also discriminate whether arc melts migrate through the mantle wedge via percolation or channelled flow. In order to address these issues we analysed a suite of primitive arc lavas ( > 9% MgO) from the intraoceanic Vanuatu Island arc which unambiguously record information about mantle wedge processes. To determine the sub-arc mantle composition we analysed two mantle xenoliths from Merelava island and the local subducted sediment component was constrained by analyses of sediments from DSDP Hole 286. All the lavas have supra-chondritic $^{187}Os/^{188}Os$ ratios ranging from 0.1280-0.1391, Os concentrations of 35.8 to 710.4 ppt and Re concentrations of 141.0 to 508.7 ppt. The two mantle xenoliths have sub-chondritic $^{187}Os/^{188}Os$ ratios of 0.1241 and 0.1263. Sediments from Hole 286 have highly variable Os contents (4.5-345.5 ppt) and age corrected $^{187}Os/^{188}Os$ ratios of 0.2260-0.4818. These data constrain several key aspects of melt genesis in subduction zones. 1) Os contents correlate with Ni and MgO indicating that Os behaves as a compatible element, even during the relative oxidised conditions in the mantle wedge (FMQ+2). This is supported by the normal mantle Os contents of the xenoliths. 2) The least radiogenic $^{187}Os/^{188}Os$ (0.1280-0.1310) can be explained by recycling of a small amount of subducted sediment although from mass balance considerations the Os-rich upper section of the sediment would have to be subducted and recycled. 3) The lack of sub-chondritic Os isotope values in the lavas indicates that melt transport through the sub-arc lithosphere was by channelled flow. Although sediment recycling can explain some of the Vanuatu data the relatively unradiogenic nature of the subducted sediment beneath Vanuatu allows some assessment of the Os isotopic composition of Pacific and Indian MORB mantle which are both present in the mantle wedge.

[ back to program schedule ]

V41E-09; INVITED; EOS 80(46): 1,173

## Hf-Nd Isotopic Behavior in the Silicate Earth

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Most terrestrial samples that we have analyzed to date (juvenile, mantle-derived rocks, early Archean to present; sediments, Archean to recent from a range of depositional environments; crustally derived Precambrian granitoids; modern ocean island arcs; lower-crustal xenoliths) plot along a single Hf-Nd isotopic array. The coherence of the terrestrial array for the crust is the result of broadly similar time-integrated $f_{Lu/Hf}/f_{Sm/Nd}$ ratios (approximately 1.5) in most crustal samples. This dominant Lu/Hf - Sm/Nd fractionation is ultimately due to incompatible-element enrichment in magmas during melting processes and occurs regardless of whether the samples are mantle melts and are new to the crust, are melts of existing crust, or have had a long crustal history and are now part of the sedimentary record. The coherence of the mantle array is due in part to the complementary incompatible-element depletion in the mantle but perhaps more importantly, reflects the long-term effects of crustal recycling. Thus the overall crust-mantle coherency in the terrestrial Hf-Nd array reflects efficient mixing processes of a dynamic Earth: mantle convection, homogenization in the crust via sedimentary processes, and recycling of crustal materials back into the mantle. This strongly coupled Hf-Nd isotopic behavior in the silicate Earth contrasts dramatically with that of lunar samples which record highly divergent Lu-Hf and Sm-Nd fractionations following early lunar differentiation. Several important unresolved issues exist regarding terrestrial Hf-Nd isotopic systematics. Most obvious is the position of the terrestrial array relative to the Bulk Silicate Earth (BSE) reference. All arrays calculated for any subsets of our data consistently lie about 3 $\varepsilon_{Hf}$ units above BSE. This mismatch implies that either: (1) there is a hidden reservoir in the Earth, not analyzed to date, that balances the terrestrial Hf-Nd array; (2) the chondritic reference values for the Sm-Nd and Lu-Hf isotopic systems, either individually or

collectively, do not accurately represent a BSE composition; or (3) the silicate Earth is not chondritic with respect to Hf and Nd. To better constrain mixing trajectories between crust and mantle, we have re-estimated crustal Hf/Nd based on our Hf and Nd isotope dilution values for the > 300 crustal samples that comprise the terrestrial array. All sediments, excluding Fe-Mn crusts and associated red clays, yield a Hf/Nd value of 0.21. This value is identical to the average Hf/Nd value (0.21) for all crustal samples we have analyzed, including all juvenile rocks, sediments, granitoids, and lower crustal xenoliths, but excluding early Archean high-grade gneisses. Our collection of lower crustal samples also have an average Hf/Nd of 0.21, significantly higher than a previous estimate of 0.17 [Rudnick and Fountain, 1995, Rev. Geophys.]. The overall crustal Hf/Nd estimate of 0.21 is somewhat higher than previous estimates of 0.19 for the continental crust [e.g., Rudnick and Fountain, 1995, Rev. Geophys.], and lies closer to the BSE Hf/Nd of 0.23 and the estimate for the depleted mantle reservoir of 0.27 [Blichert-Toft and Albarede, 1997, EPSL]. These values will result in limited curvature in mixing trajectories between crust and mantle and are consistent with the empirical observation ot the isotopic record in which all terrestrial samples appear to lie along a single, linear array.

[ back to program schedule ]

V41E-06; EOS 80(46): 1,172

## Thorium-Uranium-Lead Systematics, Heat Flow and the Second Lead Paradox

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It is evident that the Earth's crust is an enriched chemical reservoir, enriched in incompatible elements. It is also evident that the mantle is the complementary depleted reservoir. But is the mantle a single homogeneous reservoir, a strongly heterogeneous reservoir, or is the mantle composed of two or more essentially isolated reservoirs, including a primordial or near primordial reservoir? The systematics of the radiogenic uranium-thorium-lead isotopic system provide essential constraints on and answers to these questions. The thorium-uranium ratio, $\kappa$, can be measured both directly and indirectly from lead $^{208}$Pb/$^{206}$Pb ratios. Bulk silicate earth values from studies of meteorites give values for $\kappa$ in the range $\kappa = 4.0 \pm 0.2$. However, it has now been established beyond question that the source region for MORB has $\kappa = 2.0$-2.5. Thus the upper mantle reservoir that is the source for MORB is highly depleted in thorium. This may be due to the deposition of continental derived uranium into the oceanic crust by hydrothermal circulations and its subsequent subduction and mixing into the MORB source reservoir. Two fundamental questions can be asked: (1) How large is the MORB source reservoir and (2) where is the complementary reservoir that is enriched in thorium (this is the second lead paradox)? Presumably, if the excess uranium in the MORB source reservoir has been extracted from the upper continental crust, then the upper continental crust should be the complementary enriched thorium reservoir. But there are strong limits on the amount of thorium enrichment that can be accommodated in the upper continental crust. We have solved a series of box models in order to study this problem. We have utilized heat flow constraints, considered various values of the Urey number, and considered whole mantle convection with various mass ratios. We conclude that the whole mantle cannot have the composition of the MORB source reservoir. Our results strongly favor a relatively small MORB source reservoir (about 25% of the mantle) that remains essentially isolated from the remainder of the mantle. The interchange between this reservoir and the rest of the mantle must be less than a few percent of the plate tectonic flux. This data requires (1) that the subducted oceanic crust must enter the upper mantle MORB source reservoir and (2) that this reservoir remains essentially isolated from the rest of the mantle. The maximum allowed size of the MORB source reservoir is close to the size of the upper mantle above the 660 km seismic discontinuity .

[ back to program schedule ]

V42D-05: EOS 80(46): 1,183

## Geochemical Tracing of Flow Between Pacific and Atlantic Upper Mantle Reservoirs

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The Earth's convecting upper mantle can be viewed to a first approximation as a system comprising three main (sub-oceanic) reservoirs: the Pacific, the Atlantic and the Indian. Because of the uneven global distribution of ridges and subduction zones, the surface area of the Pacific reservoir is contracting (at about 0.6 km$^2$/yr) while the surface areas of the other reservoirs are increasing. Garfunkel and others have argued that this causes net mantle flow from the Pacific to the Atlantic and Indian reservoirs to maintain mass balance. Alvarez has further argued that this flow should be restricted to those parts of the Pacific rim where there are no deep continental roots or subduction zones that would act as barriers to mantle flow, i.e. to the SE Indian Ocean, the Caribbean, and the Drake Passage. The Drake Passage and

Scotia Sea contain some $10^6$ $km^2$ of oceanic lithosphere created within the past 30 Ma, mainly by extension behind the rapidly retreating South Sandwich Trench. Here, we use isotope geochemistry of dredged MORB evaluate the nature and magnitude of Pacific-Atlantic mantle flux through this region. The existing global MORB isotope geochemistry database demonstrates that South Pacific mantle can be effectively discriminated from South Atlantic mantle on the basis of its high Nd and low Pb8/4 isotope ratios for a given Pb6/4 ratio. Our new data show that MORB from the Phoenix-Antarctic spreading centre and the Quest Fracture Zone within the Drake Passage have clear Pacific affinities. By contrast, samples from the westernmost South American-Antarctic Ridge and the East Scotia Sea have South Atlantic affinities. The results thus indicate that Pacific mantle did penetrate the South Atlantic, but that westward flow of Atlantic mantle away from the Bouvet plume and around the sinking slab may currently be more significant than eastward flow of Pacific mantle. Quantitatively, the mantle flux through the Drake Passage over the past 30 Ma can only account for some 5% of Atlantic expansion. Unless the Caribbean had a much greater flux, plume input from the lower mantle may provide a better explanation than Pacific-Atlantic flow for the expansion of the Atlantic upper mantle reservoir.

[ back to program schedule ]

V31E-03 INVITED; EOS 80(46): 1,143

## The PGE-Budget and Re-Os Isotope Systematics of the Eroding Continental Crust

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Loess has been used extensively as a proxy for the chemical composition of the upper continental crust (UCC), particularly for major elements and lithophile trace elements. In this study we test the applicability of this concept for the platinum group elements (PGE) and the Re-Os isotope systematics. Due to the siderophile and chalcophile nature of PGE and their affinity for trace mineral phases it is not (a priori) clear if sedimentary deposits such as loess are valid proxies for the PGE budget of the eroding UCC. Sixteen loess samples from China, Argentina, Central Europe and Spitzbergen, spanning a wide range in Sr-Nd isotope space, yield an average $^{187}Os/^{188}Os$ of $1.05\pm0.23$ (1 $\sigma$ ). This value is similar to present-day sea water (1.06) and slightly less radiogenic than previous estimates for the eroding upper continental crust (1.20-1.32, Esser and Turekian, 1993). Average $^{187}Re/^{188}Os$ of 45.4 and $^{190}Pt/^{188}Os$ of 0.0195 are lower than previous estimates as well. Calculated Re-depletion ages show significant scatter and are, on average, slightly older (2.2 Gyr) than Nd-model ages (1.6 Gyr), and significantly older than average Sr-model ages (0.78 Gyr). Rhenium depletion ages appear to be affected by in situ weathering, as Re-Os data for three paleosols from the Chinese loess plateau yield significantly younger model ages (0.55-1.9 Gyr) than intercalated loess deposits (2.09-2.84 Gyr). This model age discrepancy is caused by preferential mobility of Re relative to Os. Paleosols are characterized by significantly higher Re concentrations (181-617 pg/g) than loess (89-169 pg/g), probably caused by scavenging of Re onto organic matter during soil formation. Primitive mantle normalized PGE pattern show striking regional differences. For instance, a loess sample from Spitzbergen is characterized by Os/Ir of 4.5 and the highest $^{187}Re/^{188}Os$ (200) of all analyzed loess samples. This pattern is typical of organic-rich sediments and can be linked to extensive outcrops of organic-rich sediments in Spitzbergen. Chinese loess, isotopically similar to average loess, shows highly fractionated PGE pattern with Os (31 pg/g) and Ir (25 pg/g) concentrations typical of UCC (e.g., Schmitz et al., 1997). The slightly supra-chondritic Os/Ir of average loess most likely is characteristic of UCC in general, as radiogenic ingrowth of $^{187}Os$ as well as preferential mobility of Os relative to Ir in subduction zones will increase the Os/Ir in the continental crust with time. Average Ru (407 pg/g), Pt (390 pg/g), Pd (653 pg/g) and Re (237 pg/g) concentrations in Chinese loess, however, are lower than previous estimates of UCC (Schmitz et al., 1997) and reflect either preferential loss of these elements during weathering or overestimation of Ru-, Pt-, and Pd-concentrations in previous UCC estimates.

[ back to program schedule ]

V41E-04; INVITED; EOS 80(46): 1,172

## The Thermodynamics of Pressure-Release Melting a Plum-Pudding Mantle

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The idea that the mantle may consist of a periditite matrix with embedded pyroxenite `plum' phase assemblages is currently being reexamined to see whether this may be a key idea to explain various geochemical contrasts between mid-ocean ridge and ocean island basalts. The geochemical composition of pyroxenite and peridotite components has received most attention recently. However, how a plum-pudding mantle melts could play an equally large role in determining the composition of ocean island basalts. Here I reexamine the thermodynamics of this melting process, building on previous work by Sleep (JGR, 1984) and Hirschmann, Asimow, Stolper and coworkers (e.g. J. Pet., 1999). In these models peridotite and pyroxenite phases are assumed to be interlayered on a less-than-km scale so they melt in thermal equilibrium. Each phase assemblage is assumed to have a solid-solution (e.g. Forsterite-Fayalite-like) melting behavior. While in thermal contact, each phase assemblage is assumed to melt in chemical isolation from the other. The resulting thermodynamics is straightforward, yet yields some interesting results about the possible melting behaviour of a plum-pudding assemblage that may have important implications for the geochemical evolution of the mantle. As noted previously by Asimow et al. (Phil. Trans. Roy. Soc., 1998) in a different form, for pressure-release melting the solidus-depletion gradient (the increase in solidus temperature $\delta T^m$ with progressive melt-extraction-induced depletion $\delta f$) can play a significant role in reducing the melt productivity of a single ascending phase assemblage, contributing an effective thermal-entropy sink as much as a quarter to a half of the latent heat of melting. At a given pressure, the magnitude of the solidus-depletion gradient can be measured from a standard T vs. composition phase diagram as the product of the local slope of the solidus times the width of the phase loop. While having a noticable effect on the melting of a single solid-solution phase assemblage, the solidus-depletion gradient has an even more important effect on the melting of a small-volume, lower-solidus plum phase assemblage embedded within a more refractory (higher solidus temperature) matrix. Here heat-flow from the surrounding matrix will tend to enhance plum-melting, and the solidus-depletion gradient of the plum phase-assemblage becomes the key parameter controlling the pressure-release melting productivity of the plum phase-assemblage. Crude estimates suggest that the productivity of plum melting is likely to be roughly threefold that expected for the productivity of a single peridotite phase-assemblage. These effects are presented by discussing several idealized scenarios of plum-pudding melting during ascent beneath a ridge or hotspot. An interesting effect seen in some scenarios is that, if a plum phase-assemblage has a steeper solidus-pressure gradient than the peridotite matrix so that the plum begins to melt at a greater depth than the matrix, then once the peridotite matrix begins to melt there will be little or no melting of embedded refractory plums (because the periditite's P-T path lies below the solidus of the residual plum phase-assemblage). This effect may play an important role in the subsequent modification of a plum-pudding mantle by pressure-release partial melting.

[ back to program schedule ]

U32B-07; INVITED; EOS 80(46): 32

# Crustal Fluxes to the Deep Mantle: Processing of Sediment Through the Subduction Factory

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The trace element compositions of some ocean island basalts (OIBs), notably those from Pitcairn and Society islands, provide evidence for recycling of subducted sediment into the deep mantle. For example, while Ce/Pb ratios in most oceanic basalts are > 25, some Society basalts are as low as 15 (White and Duncan, 1996) and appear to be shifted in many compositional parameters toward continental crust. Sediments are clearly subducted > 100 km beneath volcanic arcs and may provide an efficient way to inject continental material with low Ce/Pb (ave. subducting sediment = 2.9) into the deeper mantle. Nonetheless, most models that create low Ce/Pb in this way do not take into account the fractionation that occurs as sediment is processed through the subduction factory. For example, if Pb is removed preferentially to Ce during sediment dehydration and/or melting in the subduction zone, then sediment residues may have high Ce/Pb compositions that fail to form an adequate mixing end-member for low Ce/Pb OIB. We evaluate subduction processing based on our recent experiments on trace element partitioning during sediment dehydration and melting at high pressure. These experiments involve diamond traps and ICP-MS analyses of trap fluid material and sediment residues for a red clay starting composition at temperatures crossing the solidus from 600-900˚C and 2.0 GPa and 13% $H_2O$. Bulk partition coefficients (D's) are calculated from measured residue and trap concentrations, corrected for diamond dilution by mass balance using over 30 elements. Although in some experiments, Pb dissolves in the gold capsule, others preserve approximate mass balance of Pb in the charge. DCe = 4.0 and DPb = 0.69 below the solidus ( 650˚C), while DCe = 3.0 and DPb =0.88 above the solidus ( 800˚C). Thus, Pb is more incompatible than Ce during both sediment dehydration and melting. However, because the D's are near 1 or greater, Ce/Pb in the residue is not increased significantly for reasonable amounts of fluid and melt loss: assuming 10% fluid loss followed by 20% melt loss, Ce/Pb increases from 5 to 7. Thus, it is likely that sediment fully processed through the subduction factory may still have considerable leverage in creating low Ce/Pb domains in the mantle.

[ back to program schedule ]

V31E-05; EOS 80(46): 1,143

## Unsupported 187Os in Cyprus Ochres: Evidence of Ephemeral Re Enrichment of Basal Sediments of the Oceanic Crust

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As part of our efforts to reconstruct the $^{187}$Os/$^{188}$Os record of ancient seawater we have been investigating the Re-Os systematics of metalliferous sediments associated with the Troodos ophiolite in Cyprus. During the course of this work we have documented unexpectedly high $^{187}$Os/$^{188}$Os ratios associated with oxidized hydrothermal sulfides from Skouriotissa. Measured $^{187}$Os/$^{188}$Os ratios in this material range from 3.60 to 13.2 (n=6). All of these ratios exceed estimates of average upper crustal $^{187}$Os/$^{188}$Os, with the most radiogenic values being 10X larger than typical upper crustal values. Os concentrations also exceed average crustal values, ranging from (0.27 - 1.1 ppb) Only about 10% of the $^{187}$Os in these samples can have been produced by in situ Re decay during the 90 m. y. history of these deposits, requiring a multi-stage history. Based on the very large Re/Os ratios of primary hydrothermal pyrite, (Brugmann et al. 1998 ODP Sci. Results 158 p91-100) we estimate that the measured $^{187}$Os/$^{188}$Os of the Skouriotissa oxidized sulfides could have been produced in as little 2 million years within an unaltered pyrite. Consequently we suggest that the unsupported Os was produced prior to sulfide oxidation on the seafloor and that significant Re loss occurred at the time of sulfide oxidation. With respect to the GERM effort these data have potentially important implications in that they provide evidence of ephemeral Re enrichment with the upper most oceanic crust and associated basal sediments. They also demonstrate the existence of reservoirs within the oceanic crustal section with $^{187}$Os/$^{188}$Os ratios far larger than would be predicted by any simple models based on oceanic crustal age. Moreover the Os concentrations of these samples are as much as 100 times larger than those commonly measured in MORBs, rendering this material a potentially important contaminant of mantle melts. Thus although our estimates of hydrothermal sulfide inventories within the oceanic crust indicate it is unlikely that deposits analogous to those studied here are abundant enough to modify the Re or Os budget of the oceanic crustal section as a whole, assimilation of analogous material may be locally important, particularly if the upper crust and basal sediments can melted or assimilated selectively.

[ back to program schedule ]

V31E-01; EOS 80(46): 1,142

## Atmospheric Transfer of Boron from Oceans to Continents: Boron Isotopic Composition of Rainwater

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The atmospheric geochemical cycle of B is still poorly constrained and the fractionation of B isotopes during seawater evaporation has never been documented, primarily because of difficulties in its measurements. Atmospheric B is mostly present as a gaseous phase (90%), the remaining 10% being associated to aerosol particles (Fogg and Duce, 1985). Although part of atmospheric boron originates from volcanic emissions and continental mineral dust, seawater is probably the main source of B. However, it was also suggested, based on experimental studies, that seawater may be a sink for atmospheric B (Nishimura et al., 1973). Because of the large difference in B isotopic composition between marine and continental environment (Schwarcz et al., 1969; Chaussidon and Albarede, 1992), the isotopic composition of rainwater may help to constrain processes which transfer B from oceans to continents. Rain and snow were sampled in different coastal and continent interior areas in Nepal, Bangladesh and Quebec and were analyzed for B concentrations and isotopic compositions. Isotopic analyses were performed on evaporated samples by ion microprobe. The average precision for each measurement is ±1.5 ‰. Measured concentrations (ICPMS) range from 0.01 to 4 micromol/l and $^{11}$B/$^{10}$B ratio (given in delta notation relative to NBS951) range from +3.8 to +9.1 ‰ for the rains and from +18.5 to +23.0 ‰ for the snows. Preliminary laboratory experiments consisting in a monitored evaporation of seawater show that the vapor produced by evaporation of seawater is enriched in $^{10}$B which is compatible with the results obtained on natural rainwater samples. The B isotopic composition and the distribution of B concentrations obtained for rainwater samples suggest that oceans are most likely a major supply of atmospheric B over the continents.

[ back to program schedule ]

U32B-08 INVITED; EOS 80(46): 32

## Composition of the Continental Crust and Implications for Global Geochemistry

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The composition of the continental crust has been derived from models of crustal growth (andesite model and bimodal Archean model of Taylor and McLennan), from studies of granulite terranes (Weaver and Tarney, Shaw) and, more recently, from interpretation of seismic velocity models of the deep crust in terms of the compositions of high-grade rock types (Christensen and Mooney, Wedepohl, Rudnick and Fountain, Gao et al.). Similarities between compositional models provide insight into how the crust formed and the major processes of Earth differentiation. These similarities include: an andesitic bulk composition, strong enrichment of incompatible trace elements compared to the bulk silicate Earth, a marked depletion of Nb relative to other incompatible trace elements and a low Nb/Ta ratio. The implications of these observations are: 1) The andesitic bulk crust composition requires recycling of mafic to ultramafic components from the crust to the mantle via delamination/foundering, subduction and/or chemical transport in altered oceanic crust. 2) The enrichment of incompatible elements in the continents is too large to reconcile with derivation of the crust from only the upper mantle, requiring contributions from mantle below the 660 km seismic discontinuity, and therefore convective communication between upper and lower mantle. 3) The Nb depletion of the continents indicates they formed in convergent margin settings; direct plume contributions are likely to be less than 20% by mass. 4) The depletion of Nb in both continental crust and depleted mantle and the low Nb/Ta of both requires that an additional reservoir exists in the silicate Earth that is enriched in Nb and Nb/Ta. This reservoir is likely to be refractory eclogite formed during crust formation in subduction zones and sequestered deep within the Earth.

[ back to program schedule ]

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V42D-07; EOS 80(46): 1,184

## GEOROC, the MPI Geochemical Rock Database: A New Tool for Geochemists

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The estimation of the chemical and isotopic inventories of the Earth's reservoirs and of the chemical fluxes between them is one of the aims of the GERM initiative. It requires the collection and evaluation of a large and rapidly growing volume of published analytical chemical data. The success of GERM thus depends on the availability of tools that provide these data in easily accessible form. Through a joint effort with the Lamont-Doherty Earth Observatory (Lehnert et al., 1998), the Max-Planck-Institute for Chemistry (MPI) in Mainz developed a relational geochemical database accessible over the world wide web that contains available chemical analyses of whole rocks, glasses, minerals, and inclusions as well as additional information (metadata) necessary for proper interpretation, including geographical, petrographical, and analytical details. Currently, the MPI database GEOROC (**GEO**chemistry of **R**ocks of the **O**ceans and **C**ontinents) covers ocean-island occurrences. In the future, data on other oceanic as well as continental rocks will be added. The identical database structure is used for the RidgePetDB of Lamont, presented in this session (Lehnert et al., 1999). Applications of the GEOROC database are, for example, the comparison of new measurements with literature data, the characterization of OIB sources, the establishment of distinctive trace element and isotopic signatures of the OIB end members, and the study of the geochemical distribution of the elements by statistical means. It also offers opportunities to evaluate and guide existing projects and to develop new research initiatives. Essential for a reasonable usage of the database are complete chemical analyses and an unequivocal correlation of chemical data and metadata. These metadata often provide crucially important criteria for extracting and limiting chemical data, in order to meet specific requirements of data quality and other parameters. Data collected thus far reveal a serious deficit in this respect. Therefore, we provide a set of Excel forms that include fields for all necessary data that should be used by future authors as guideline for publications. The GEOROC database will be presented and demonstrated, including an introduction of the (preliminary) web interface during a poster session of this meeting (Nohl & Sarbas, 1999). K Lehnert et al. (1998), EOS, Trans AGU 79 (45) Fall Meet. Suppl.,44 K Lehnert et al. (1999), EOS, Trans AGU (this volume).

[ back to program schedule ]

V42A-08; EOS 80(46): 1,175

## Possible Mechanisms for Palagonitization of Basaltic Tephra: Evidence From the Keanakako'i Ash Member, Kilauea Volcano

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In the region surrounding Kilauea Caldera, a wide range of weathering and/or alteration products, including palagonite, is developing within 200-500-year-old vitric tuffs of the Keanakako'i Ash Member. These deposits are unusually well suited for investigating the physical/chemical controls on palagonitization because they were distributed across a region with pronounced ranges in rainfall ( < 50 to > 300 cm/yr), soil pH (3.5 to 7.5), and hydrothermal input from steam vents. In the driest region sampled (50 cm/yr at Nanahu Arroyo, 11 km south of Kilauea Caldera), glassy pyroclasts are recrystallizing under slightly alkaline conditions (pH=7.8) into a complex pedogenic mineral assemblage of di- and tri-octahedral smectites, kaolins, and opal. However, under similar rainfall conditions, but extremely low soil pH (3.5) created by sulfuric acid aerosol fall-out immediately down-wind from Kilauea Caldera (at Sand Wash, 1 km southwest of the caldera), vitric pyroclasts are undergoing nearly congruent dissolution, with opaline crusts locally forming on the faces of tephra outcrops. On the windward side of Kilauea Caldera, where soil pH is uniformly close to neutral (7.1 to 7.5) and rainfall exceeds 200 cm/yr, tephra is altering into leached, aluminous pedogenic clays: halloysite or kaolinite at Volcano Village (2 km from the rim of the caldera; 250 cm/yr), and the short-range-order aluminosilicates allophane and imogolite, in outcrops along Wright Road (4 km from the caldera; 300 cm/yr). Tephra alteration products in these cases are consistent with intensities of pedogenic desilication predicted from the precipitation gradient and soil acidity. In the region just south of the caldera and west of Keanakako'i Crater, 10 m-thick deposits of the Keanakako'i Ash are exposed in scarps along circumferential faults bounding the caldera. In this locality, glassy ash fragments are ubiquitously coated with rinds of palagonitized glass, averaging 20 mm thick, and the tuffs are moderately consolidated. Bedding-parallel layers of authigenic calcite precipitated in pores between palagonitized grains have $\delta^{18}O$ values of between -14 and -13‰ (PDB). If the calcite exchanged with local meteoric water, isotopic equilibrium occurred at temperatures between 60 and 65°C. This would be consistent with a hydrothermal origin for the calcite (and palagonite), presumably related to steam discharge along fault scarps.

[ back to program schedule ]

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V41E-02; EOS 80(46): 1,171

## Mixing of Chemical Heterogeneities in the Earth's Mantle: A Study Incorporating Plate Dynamics

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An improved understanding of the destruction of chemical heterogeneities by mantle convection is required, to better link geochemical and geophysical models of the Earth's mantle. This is desireable, because seismic tomography and numeric modeling of convection provide important information about the present-day spatial structure of the mantle, whereas geochemical investigations mainly provide information on the temporal evolution of different mantle reservoirs. Numerical investigations in two dimensional (2D) geometry indicate that convective flow mixes efficiently on all length scales, and this suggests that the mantle should be well mixed within a relatively short time scale. Investigations of simples convective flows in a three dimensional (3D) geometry do not confirm the 2D results. In contrast, they indicate that mixing within a single convective cell is effective, whereas mixing across cell boundaries is poor. Potentially, this could explain the existence of different chemical reservoirs, without calling for vertical layering of the mantle. In a recent paper, Ferrachard and Ricard (1998) pointed out that simple 3D models do not account for a toroidal component in the velocity field, and such a component is introduced if the movement of lithospheric plates is considered. This indicates that plate-tectonics may enhance mixing and lead to faster convective homogenization of the mantle. Advances in numerical techniques and available computer resources have only very recently permitted the simulation of the generation and subduction of lithospheric plates in a self-consisting manner (Trompert and Hansen, 1998). We have used such a model to investigate the effect of lithospheric plates on the mixing properties of the mantle. Our results indicate that

geochemical heterogeneities can survive on length scales exceeding the size of a convective cell for several plate-subduction cycles. Small-scale mixing within one convective cell was observed to be efficient. Moreover, we find that the movement of the plates enhances mixing in the direction of plate motion, and this is leads to the formation of large-scale mantle anisotropies. References: Ferrachat, S. and Y. Ricard, Regular vs. chaotic mixing, Earth Planet. Sci. Lett., 155, 1998 Trompert, R. and U. Hansen, Mantle convection simulations with rheologies that generate plate-like behaviour, Nature, 395, 1998.

[ back to program schedule ]

V31E-07; INVITED; EOS 80(46): 1,144

## Hydrogen Isotope Profiles in Deep Sea Pore Fluids, and Speculations on the Global Hydrogen Cycle

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Hydrogen isotope ratios in deep sea pore fluids may be influenced by the composition of the overlying ocean, interactions within the sediments, and fluxes from the underlying oceanic crust. Ocean Drilling Program (ODP) sites from the North Atlantic gateways (Sites 981 and 984), the Bermuda Rise (Site 1063), the Benguela Current upwelling system (Sites 1081, 1083 and 1084) and the sub-Antarctic (Sites 1088, 1089, 1090 and 1093) all show a common pattern with delta-D values decreasing with depth. A finite difference model was developed to help determine the relative importance different processes and interpret the deuterium profiles. A series of generic simulations demonstrate the influence of porosity and sedimentation rates on the diffusion of paleo-seawater, and the effects on the profile of fluxes of water depleted in deuterium. The model is then adapted to simulate each of the ODP sites analyzed, so that the measured profiles may be explained. The profiles are best explained by a flux of water depleted in deuterium from the base of the sediments into the crust. The cause of this flux is probably hydrogen and/or methane released directly from the mantle, which are oxidized in the basalt underlying the sediment. This flux can be used to estimate the long-term evolution of deuterium content of seawater, with competition between subduction of deuterium-depleted water in altered oceanic crust, release of hydrogen from a primitive source, and escape of hydrogen from thermal escape in the upper atmosphere. While there are large error bars, these estimates may be of some use in estimating the long-term evolution of water in the hydrosphere.

[ back to program schedule ]

V31E-10; EOS 80(46): 1,144

## Birth, Death, and Resurrection: The Life Cycle of Supra-Subduction Zone Ophiolites

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Suprasubduction zone (SSZ) ophiolites display a consistent sequence of events during their formation and evolution which suggests that they form in response to processes that are common to all such ophiolites. This sequence of events may be summarized as follows: (1) Birth: Formation of the ophiolite above a nascent subduction zone with the initiation of subduction-related volcanism and plutonism, or in response to changes in plate geometry or convergence rates; (2) Youth: Continued melting of refractory asthenosphere (depleted during birth) in response to fluid flux from the subducting slab; (3) Maturity: onset of semi-stable arc volcanism, often calc-alkaline in character, as the subduction zone matures and stablizes; (4) Death: The sudden demise of active spreading and ophiolite-related volcanism, which in many (but not all) cases is linked to subduction of an active spreading center and the onset of shallow underthrusting of the bouyant spreading axis; (5) Resurrection: Emplacement or exposure of the ophiolite by obduction (Tethyan ophiolites), or by "accretionary uplift" (Cordilleran ophiolites). Stage 1 is characterized by the eruption of arc tholeiite lavas and the formation of layered gabbros and sheeted dike complex; the parent magmas are MORB-like with an arc overprint, and are often referred to the "axis" series. Stage 2 features extensional deformation of the older plutonic suite, the eruption of lavas with refractory major element compositions and enriched trace elements, e.g., boninites or tholeiitic ankaramites, and the intrusion of refractory wehrlite-cpxite. These enriched refractory magmas result from fluid flux into the stage 1 melt zone from the subducting slab. Stage 3 encompasses the transition toward stable calc-alkaline arc activity, with eruption of more silicic lavas, volcaniclastic eruptions, and the intrusion of hornblende and quartz diorite dikes, sills, and stocks. Stage 4 is expressed as dikes and lavas with oceanic basalt compositions (MORB, OIB) that crosscut or overlie rocks of the older suites; this stage is not seen in all ophiolites. Stage 5 represents emplacement of the ophiolite, and includes obduction (if a passive margin

is encountered) or accretionary uplift (if active subduction continues). These stages are observed in a range of Tethyan (Oman, Troodos, Pindos) and Cordilleran (CRO) ophiolites that formed in SSZ settings, and occur in the same relative order, even if some stages are missing; they are not seen in Alpine ophiolite complexes that apparently formed at true oceanic spreading centers. The existence of this consistent progression implies that ophiolite formation is not a stochastic event, but is a natural consequence of the SSZ tectonic setting. This includes all ophiolites with the classic ophiolite stratigraphy. The progression described here is not consistent with models of ophiolite formation that call on unusual circumstances, or non-uniformitarian interpretations of ocean crust formation.

[ back to program schedule ]

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V42D-03; EOS 80(46): 1,183

## Does the "Gabbroic" Component in Hawaiian Lavas Come From Oceanic Lower Crust?

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It has previously been suggested that certain trace element characteristics of Mauna Loa and Mauna Kea basalts are derived from a source characterized by the widespread presence of recycled oceanic gabbro (Hofmann and Jochum 1996). One difficulty with this hypothesis is the paucity of trace element measurements of oceanic gabbros. The critical ratios (e.g., chondrite-normalized Th/La) have been measured in only a few rocks from ophiolites and none from the present-day oceanic crust. For this reason we have conducted a study of trace element compositions of a long continuous section of oceanic gabbros from the SW Indian Ridge at the Atlantis II Fracture Zone, ODP Hole 735B. Previous work on the upper 500m of the hole (Hart, Pers. Comm.) did not show a significant difference of the bulk hole from the prevailing MORB value of $(Th/La)_N$ of about 0.4. This would not serve as a viable source for the Hawaiian signature that ranges down to $(Th/La)_N$ of 0.15. We have determined the bulk $(Th/La)_N$ of the lower 1000m based on sediment trap samples from the shipboard core splitting table of 0.15. Many individual point samples of the core fall substantially below this. This value falls at the extreme lower end of the Hawaiian array and thus can very plausibly represent a source for the Hawaiian array. It is also in agreement with, if not as extreme as results from ophiolitic gabbros at Oman, Gabal Gerf and Agardagh. The apparent lack of bulk fractionation near the top of the hole is probably the result of mixing of a cumulate (low $(Th/La)_N$) component with an evolved residual liquid (high $(Th/La)_N$) during the evolution of the crystal pile. Nearer the base of the pile as sampled in the lower 1000m, the cumulate component becomes more and more prominent. The total bulk lower crustal $(Th/La)_N$, including levels not sampled by Hole 735B, is thus probably consistent with the Hawaiian source. Hofmann, A.W. and K.P. Jochum (1996) J. Geophys. Res., 101, 11,831-11,839.

[ back to program schedule ]

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V41E-03; EOS 80(46): 1,171

## Preservation of Local Source Heterogeneities Trough Convection and Remelting

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The idea of recycling of oceanic lithosphere through the sources of mantle plumes [1] has been supported in many recent contributions reporting crustal fingerprints in oceanic basalts [2,3]. Some evidence has been reported for specific rock types being recycled. For example [2,3], have found evidence for a "gabbroic signature" in Hawaiian basalts. However the geological meaning of this gabbro signature is not immediately obvious, because mantle magmas may come in contact with (former or present) oceanic lithosphere at least twice: first in the deep plume source (i.e. if the gabbro is recycled and the recycled gabbroic component melts) and then on their way to the surface (if the primary melt assimilates present day crust). We report the discovery of highly exotic, Sr-rich (and Th-poor) melt inclusions in olivines from Mauna Loa lavas, which resolve this ambiguity. These anomalous melts have not only exceptionally high Sr, but also very significant negative anomalies in Th, Nb and Zr contents. Compared with the majority of melt inclusions and Mauna Loa lavas, "Sr-rich" melts are also severely depleted in the most incompatible elements (Ba, Th, Nb, B, K, La, Ce) and are characterized by different isotopic ratios of $^{206}$Pb/$^{207}$Pb/$^{208}$Pb, $^{7}$Li/$^{6}$Li and $^{11}$B/$^{10}$B. Lead in Sr-rich inclusions is less radiogenic and Li and B are significantly enriched in light isotope compared to lavas and common inclusions. These trace element abundance patterns and isotope signatures strongly resemble those of typical old, layered gabbros from ophiolites (4) which are enriched in cumulus plagioclase. However, major element compositions of the melts show no evidence for equilibrium with, or significant resorption of, actual plagioclase. Therefore gabbro is not involved in magma production directly by assimilation of present-day oceanic crust, but occurs as a "ghost" which has been transformed to an eclogitic (high-pressure) mineral assemblage by subduction and recycling. Furthermore, the "ghost" plagioclase trace element signature demonstrates that the former gabbro can occasionally retain its (trace-element) chemical identity through the convective cycle without mixing with other portions of the former crust. 1.Hofmann, A. W. & White, W. M. Earth Planet. Sci. Lett. 57, 421-436 (1982). 2.Eiler, J. M., Farley, K. A., Valley, J. W., Hofmann, A. W. & Stolper, E. M. Earth Planet. Sci. Lett. 144, 453-468 (1996). 3. Hofmann, A. W. & Jochum, K. P. J. Geophys. Res. 101, 11,831-811,839 (1996). 4. Zimmer, M., Kr?ner, A., Jochum, K. P., Reischmann, T. & Todt, W. Chem. Geol. 123, 29-51 (1995).

[ back to program schedule ]

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V31E-12; EOS 80(46): 1,145

# A Next-Generation Model for Computing the Geochemical Evolution of Magma Undergoing Concurrent Recharge, Wallrock Partial Melt Assimilation, and Fractional Crystallization With Self-Consistent Energy Conservation (EC-RAFC)

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Geochemical data for igneous rocks provide definitive evidence for the occurrence of open-system processes in evolving magma bodies, including **R**echarge by intrusion of primitive magma, **A**ssimilation of anatectic wallrock partial melt, **F**ractional **C**rystallization, and fluid-mediated chemical **E**xchange. Existing methods that quantify trace element and isotopic trends associated with these processes account for total mass and species conservation but almost invariably neglect the First Law of Thermodynamics **E**nergy **C**onservation. When energy conservation and wallrock partial melting are taken into account, the manifold of possible geochemical solutions describing a particular data set decreases significantly; indeed, many "classical" (defined as mass and species conservation models) AFC solutions violate energy conservation and therefore are of limited value in petrological reconstruction. Our models (EC-RAFC and EC-REFC), which express conservation of mass, species and energy, generate geochemical trends for a homogeneous magma body undergoing simultaneous recharge, assimilation, fractional crystallization, and fluid-mediated trace element exchange. The general problem is formulated as a set of 3+k+j coupled nonlinear ordinary differential equations, where the number of trace elements and isotope ratios are k and j, respectively. Partial melting of wallrock, modeled as fractional melting, is incorporated as are sensible and latent heat effects. Temperature-dependent partition coefficients are used to describe partitioning of trace elements between crystals, melt, and fluid, if present. RAFC events require *a priori* specification of the cumulative mass of recharge magma, its temperature, and its composition as a function of magma temperature. Solution of the set of differential equations, with magma temperature as the independent variable, provides information regarding the average temperature of wallrock (Ta), fraction of melt within the magma body (Mm), concentration of k trace elements (Cm), and j isotopic ratios (εm) (e.g., Pb, Nd, Sr) in the melt portion of the magma body. The parameters needed to run a simulation include the final magma temperature, denoted as the equilibration temperature (Teq), the initial temperature and composition of original magma, recharge magma, and wallrock, values for all distribution coefficients and their temperature dependencies (if applicable), heats of fusion and crystallization, and isobaric specific heat capacities of the various constituents. For *a priori* defined magma recharge mass and Teq, the mass of wallrock heated to Teq can be calculated and the geochemical evolution of melt within the magma body computed as the magma body temperature decreases from its initial value to Teq. The effects of imperfect extraction of anatectic wallrock melt are accounted for by use of an extraction efficiency factor. Our energy constrained models have the advantage of linking thermal and chemical properties of magma chambers. Compared to classical models, they therefore represent more complete assessments of the complex physiochemical dynamics that govern open-system magma bodies. Results of EC-RAFC simulations demonstrate that geochemical trends and mass balance considerations can differ greatly from those of classical RAFC because incorporation of energy conservation and partial melting enables previously forbidden nonlinearities to play the role nature intended.

[ back to program schedule ]

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V42A-07; EOS 80(46): 1,174

# The Evolution of Palagonite and its Effect on Element Budgets of Alteration Processes

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The structure, composition and evolution of palagonite, the first stable low-temperature alteration product of mafic glass, have a major influence on the overall alteration process. The chemical and structural evolution of palagonite have been studied analytically and experimentally as a function of glass composition, alteration environment and time. Application of bulk (XRF and XRD) and high resolution analytical methods (EM, SYRFA, FTIR and AFM) reveal that palagonitization of volcanic glass is a two-step process, each step being characterized by contrasting element mobilities. The first step is characterized by congruent dissolution of glass and contemporaneous precipitation of "fresh", gel-like, amorphous, isotropic, brown to yellow palagonite. This step is accompanied by the loss of $SiO_2$, $Al_2O_3$, MgO, CaO, $Na_2O$ and $K_2O$, the active enrichment of $H_2O$ and the passive enrichment of $TiO_2$ and $Fe_{tot}$. The second step is an ageing process during which the thermodynamically unstable, amorphous, gel-like palagonite crystallizes, in reaction with the surrounding fluid, to smectite. This step is accompanied by uptake of $SiO_2$, $Al_2O_3$, MgO and $K_2O$ from solution and loss of $TiO_2$ and $H_2O$. The behavior of CaO and $Na_2O$ remains unchanged, whereas Fetot reacts less consistently. The chemical composition of palagonite and thus the degree and direction of element mobility varies as a function of fluid properties and palagonite ageing stage. This is indicated, for example, by less depleted major element concentrations of palagonite formed during meteoric alteration compared to palagonite derived from submarine alteration and by the general decrease of element loss with increasing palagonite crystallinity. Nonetheless palagonite formation is governed by complex kinetic controls as suggested by the extensive loss of CaO, Na2O and K2O to a solution being saturated in those elements.

[ back to program schedule ]

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V42D-01; EOS 80(46): 1,182

# Trace element compositions of ocean ridge basalts: evidence from a global compilation

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In order to investigate trace element signatures of global ocean basins and the evolution of mid-ocean ridge systems, we have carried out the analysis of a large suite of mid-ocean basalts by ICP-MS at Lamont over the last three years. Over 350 analyses have been accumulated thus far, and about one third of them have radiogenic isotopic data. These samples are primarily from the northern mid-Atlantic Ridge, the East Pacific Rise, the Juan de Fuca Ridge, the Central Indian Ridge and the Australian Antarctic Discordance. These data can now be combined with a large quantity of literature data by making use of the RIDGE Petrological database (Lehnert et al, 1998, 1999) which enables the assembly of a large amount of petrological data from the literature. We query the database from the web and can access an additional 700 samples with trace element data (of varying quality) from all over the world with MgO over 5.0wt%. Altogether there are over a thousand samples, half of which have high quality ICP-MS data. These data allow the construction of far more rigorous and documented values for average MORB than currently exist, the elucidation of trace element systematics and their consistency from one ocean basin to another, an evaluation of the processes involved in creating the heterogeneity of MORB sources, and an evaluation of the statistical distribution of sample types from one ocean basin to another. There are significant contrasts among some ocean basins, both in terms of trace element systematics and in terms of distribution of sample types. For example, relative to other ridges, much of the northern MAR is dominated by a unique trace element pattern. Compared with the EPR and other portions of the MAR, NMORBs from this region have the same level of highly incompatible elements (Rb, Ba, Th, U), but about half the concentration of moderately incompatible elements (Ce, Pr, Nd, Zr etc), and 85% for less incompatible elements (Yb, Lu etc). Investigation of water contents (Michael, EPSL, 1995) and isotopes(Dosso et al, EPSL, 1999) also revealed that this region is exceptional when compared with other ridges. A combination of mantle source and complex plume-ridge interactions are necessary to account for the data. In addition to providing rigorous reference values for MORB, the systematics and distribution of the data will provide new constraints on mantle sources and processes for the global system of ocean ridges.

[ back to program schedule ]

V42A-02; EOS 80(46): 1,173

# Oxygen-Isotope Fractionation Between Al-Hydroxides and Water: Decade-long Synthesis Experiments at < 60˚C

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Oxygen-isotope data have been gathered for synthetic aluminum hydroxides precipitated over 65 to 125 months. These data are compared to earlier experimental results obtained over much shorter periods, to $\alpha_{gibbsite-water}$ values deduced previously using samples from soils and bauxite deposits, and to fractionation factors calculated using bond type and modified increment methods. All three $Al(OH)_3$ polymorphs, gibbsite, nordstrandite and bayerite, were generated during the synthesis, but gibbsite was dominant in most samples, and commonly the only phase present. Using pure gibbsite samples, the following values for $1000\ln\alpha_{gibbsite-water}$ were obtained: 1.0167±0.0003 (9±1˚C), 1.0147±0.0007 (24±2˚C), 1.0120±0.0003 (51±2˚C). In the resulting geothermometer: $1000\ln\alpha_{gibbsite-water} = 2.04\times10^6/T^2 - 3.61\times10^3/T + 3.65$ (T in ˚K), $\alpha_{gibbsite-water}$ ranges from 1.018 at 0˚C to 1.0113 at 60˚C for gibbsite crystallized directly from solution. These results are not significantly different from those obtained during the earlier experiments of much shorter duration. This behavior, and the good agreement with $\alpha_{gibbsite-water}$ values obtained for well-constrained natural systems, suggests that the experimentally determined fractionation factors describe equilibrium conditions for gibbsite that has precipitated directly from solution. The experimental data for nordstrandite and bayerite also lend support to the prediction of Zheng (1998) that oxygen-isotope fractionation in aluminum hydroxides may be polymorph-dependent, with variations of 1 to 2‰ occurring at 20- 25˚C. Ref. Zheng, Y.F. (1998) Oxygen isotope fractionation between hydroxide minerals and water. Phys. Chem. Minerals, 25, 213-221.

[ back to program schedule ]

V41E-01; EOS 80(46): 1,171

# Convection and the Formation of the Principal Reservoirs of the Earth's Silicate Mantle

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Mantle convection tends to diminish and to annihilate chemical reservoirs by blend. However, the chemical differentiation generates new geochemical reservoirs. It takes place in partially molten areas of the asthenosphere. If this partially molten regions are rich in incompatible elements,i.e., if this region is fed by plumes from deeper parts of the mantle, oceanic plateaus develop which will be carried by the normal oceanic lithosphere up to the continent where they will be accreted. The solved main problem is to show by computation, why we observe two spatially divided chemical main reservoirs of the mantle, i.e., a depleted upper part of the mantle and a lower part rich in incompatible elements, in spite of the mantle convection that is active since more than 4.49 billion years. The problem has been solved by computation of a convection-fractionation model that differs from the published model K2A [Walzer,U., Hendel,R., PEPI 112 (1999) 211-256] in a new viscosity model. The principal idea is to compute the relative viscosity variations as a function of depth from observable quantities. We developed a self-consistent theory using the Helmholtz free energy, the Ullmann-Pan'kov equation of state,the free-volume Grueneisen parameter and Lindemann's law. In order to get the relative variations of the radial factor of the viscosity, we insert the pressure P , the bulk modulus K , and $\delta K/ \delta P$ from PREM. For calibration, the standard postglacial-uplift viscosity under continental lithosphere was used. Moreover, we took into account the dependence of the viscosity on temperature and on the degree of depletion of volatiles. The convection-fractionation mechanism is based on the solution of the differential equations of a 2D-FD thermal Oberbeck-Boussinesq convection and of the chemical segregation and fractionation. For the latter one, we use a tracer mechanism. The conservation of the four numbers of atoms of the radionuclides $^{238}U$, $^{235}U$, $^{232}Th$, $^{40}K$ plus the corresponding daughter nuclides is guaranteed. Oceanic plateaus develop leaving behind depleted parts of the mantle. Although our model mantle is essentially heated from within, we assume additionally a $20 \sim mW \sim m^{-2}$ heat flow at the CMB. This is necessary because of the dynamo theory of the outer core. The concentrations of the heating radionuclides and the viscosity are functions of the location and time. Although the viscosity distribution is crucial for the

convection patterns, we included also the phase boundaries using conventional values of the Clapeyron slope, the density contrast and the transition width of the olivine-spinel transition and of the spinel-perovskite transition. The evolving inhomogeneity of the heat source concentrations in the mantle and the lateral movability of the growing continent generate a non-steady state. The frequency distribution of the fluctuations of juvenile continent material addition and surface heat flow is similar to the observed world-wide time distribution of mineral dates and the tectonic episodicity. We obtained realistic values for the lateral velocity of the continent, the continental growth rate, the surface heat flow and for the distributions of temperature, viscosity and mantle flow velocity as a function of time, especially for the present time. The following result is insensitive even to strong variations of the Rayleigh number: We arrive at a predominantly depleted upper part of the mantle and at a lower part of the mantle which is rich in incompatible elements, yet. This bipartition corresponds to geochemical expectations.

[ back to program schedule ]

V41E-05; EOS 80(46): 1,172

## Pb Isotopic Evolution of the Earth

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Suitable models of the isotopic composition of the Earth must reproduce not only the present day radiogenic isotope ratios in each terrestrial reservoir, but also the parent-daughter ratios in those reservoirs. The U-Th-Pb system provides a particularly powerful constraint on such models because three radioactive parents ($^{235}$U, $^{238}$U, and $^{232}$Th) decay to different isotopes of Pb ($^{207}$Pb, $^{206}$Pb, and $^{208}$Pb) with very different half-lives. Galer et al. (1985) observed that $^{230}$Th/$^{232}$Th ratios of mid-ocean ridge basalts (MORB) imply a present $^{232}$Th/$^{238}$U ratio (κ) in the depleted upper mantle (DUM) of < 2.5, while $^{208}$Pb*/$^{206}$Pbratios implied a much higher time-integrated κ of > 3.7. Subsequently, White (1993) concluded that while $^{206}$Pb/$^{204}$Pb ratios in MORB implied a time-integrated $^{238}$U/$^{204}$Pb ratio (μ) in the DUM of > 8, the present μ in the DUM must be < 6. Galer et al. (1985) and White (1993) argued that the contrast between low present κ and μ and high time-integrated κ and μ in the DUM reflected a short residence time (500-1000 Ma) of Pb in the DUM. According to this view, the high time-integrated κ and μ results not from *in situ* U and Th decay in the DUM, but is inherited from earlier residence of Pb in a reservoir with high κ and μ, presumably the lower mantle. To test these ideas, we constructed a simple model of the U-Th-Pb system of the Earth. It consists of 3 reservoirs: crust, upper mantle and lower mantle, with fluxes between them representing mantle plume, oceanic crust production, and subduction. Mantle plume and oceanic crust production vary with time in proportion to radiogenic heat production and are scaled to yield the observed present fluxes. These fluxes, together with subduction fluxes, are further constrained to produce the present day mass of the crust. Relative sizes of the two mantle reservoirs and fractionation of U, Th, and Pb during partial melting and subduction dehydration are adjustable parameters of the model. Mathematically, the model is a series of differential equations representing changing reservoir compositions. These are solved over 4.55 Ga at 10 Ma intervals using the Runge-Kutta method. The model produces a plausible distribution of Pb isotopes and parent daughter ratios in these reservoirs. In particular, our model reproduces the difference in present and time-integrated values of κ and μ in the DUM. One interesting aspect of the results is that reservoir compositions become nearly steady-state within 1 to 1.5 Ga. Using reasonable values for the adjustable parameters, we can approximately reproduce many features of Pb isotope geochemistry of the real Earth. For example, one model run yields present values of μ and κ for the DUM of 3.9 and 2.1 respectively, with corresponding time-integrated μ and κ of 7.9 and 2.1 respectively. This model also produces reasonable compositions for the crust and lower mantle that imitate features of the real Earth. We conclude that rapid cycling of Pb through the upper mantle is indeed responsible for many of the enigmatic features of terrestrial Pb isotope geochemistry.

[ back to program schedule ]

U32B-01; EOS 80(46): 31

## The Composition of the Earth's Core

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The core is “an uncertain mixture of all the elements” whose composition can be partially constrained from plausible models of bulk earth composition based on chondritic meteorites. If we consider those elements which are nonvolatile and siderophile and were hence concentrated into the metal during core formation, then their concentrations in the core are readily derived from the difference between bulk earth and the peridotitic mantle. Thus we obtain, in the core, about 80% Fe, 5% Ni, 0.25% Co, 0.5% Pt, 0.02% Re and so on. Volatile siderophile elements such as C, and S are of uncertain in abundance in the earth, but are important because of their potential contribution to the `light element' content of the core. The low atomic number `light element' which constitutes, from density considerations, about 10% of core mass is most plausibly a mixture of Si, S, C and H. A combination of cosmic abundances and high pressure experiments suggests

around 2% S and 1% each of C and H. Si is an attractive option because its abundance in the bulk earth is reasonably constrained and presence of about 7 wt% Si in the core is easy to reconcile with a meteorite bulk earth model (Allegre et. al., 1995). Si as the dominant light element is, however, only consistent with core segregation at high pressure (about 25Gpa). At the low pressures (1-5 Gpa) favored in some core-formation scenarios, separation of an Fe-Ni-Si metal would also remove elements such as V and Cr, which are moderately abundant in the silicate mantle. Given, however, recent high pressure experiments showing that core-mantle equilibrium is easier to explain if segregation occurred at 25-30 Gpa, the presence of significant Si in the core becomes plausible. Thus, my personal view is that 2-7% Si and lesser amounts of S,C and H make up the light component of the core.

[ back to program schedule ]