

... the **Geochemical Earth Reference Model** initiative is a grass-roots effort to work with the geosciences community towards a chemical characterization of the Earth, its major reservoirs, and the fluxes between them ...

GERM/Margins at the Fall AGU Meeting 2001



Program for 10-11, December 2001

❖ GERM / Margins Subduction Factory Session I

V11B : Monday Morning 8:30 in MC 304

❖ GERM / Margins Subduction Factory Session II

V12E : Monday Afternoon 13:30 in MC 304

❖ GERM / Margins Subduction Factory Session III: Posters

V21C : Tuesday Morning 8:30 in MC Hall D

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Session Summary

Trench-To-Subarc: Diagenetic and Metamorphic Mass Flux in Subduction Zones GERM/MARGINS Subduction Factory Session

Recent study has indicated that profound chemical alteration of subducting materials and related mass flux in fluids occur in forearc regions, beginning with diagenesis at extremely shallow levels, and continuing during prograde, high-P/T metamorphism and perhaps even partial melting of some lithologies in some subduction zones. In this session, we hope to comprehensively consider forearc diagenetic and metamorphic mass flux and its significance for the cycling of materials through convergent margins. We invite abstracts dealing with any and all aspects of this flux and the ways in which its global significance can be evaluated. Topics to be addressed include, but need not be limited to: fluid- flow and chemical alteration accompanying diagenesis during fluid expulsion in accretionary prisms; effects of prograde metamorphic devolatilization on the compositions of subducting materials and the production and mobility of metamorphic fluids; chemical processing in subducting slabs and sediments as recorded in serpentinite seamounts, mud volcanoes, and arc lavas (including across-arc suites); and the potential significance of forearc chemical alteration of subducting rocks for deep-mantle chemical heterogeneity. We encourage both abstracts presenting examples from individual modern or ancient convergent margins and abstracts presenting broader synthesis views. We hope to attract not only geochemical studies, but also studies attacking these problems from geophysical and theoretical approaches.

Conveners:

Gray E. Bebout, Lehigh University, Email: geb0@lehigh.edu
Jonathan B. Martin, University of Florida, Email: mjmartin@geology.ufl.edu
Tim Elliott, University of Bristol, Email: Tim.Elliott@bristol.ac.uk

GERM Information

Free GERM Beer at the VGP reception

Tuesday, 11 December, 5:30 - 7:00 P.M. in Moscone Center, Room 304.

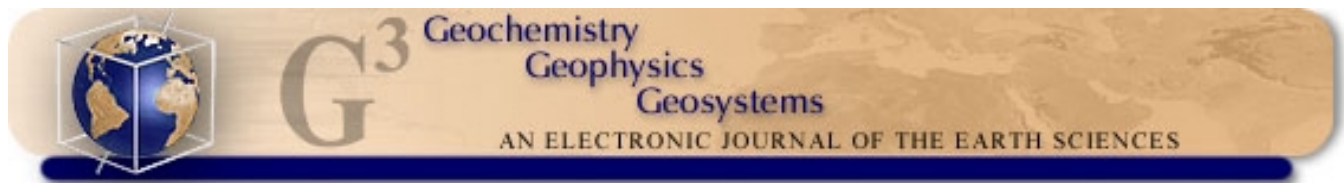
The next GERM Workshop

will be hosted by F. Albarede and J. Blichert-Toft in Lyon, May 20-23, 2003.

Sign up for the mailing list at <http://earthref.org/events/GERM/2003/>

Field trip reservation at http://www.bocuse.com/services/rese_aub.html

Call for Papers



The editors of Geochemistry, Geophysics and Geosystems solicit papers from this year's GERM/MARGINS Subduction Factory Session for the most recent **theme** volume of **G³**.

Trench-To-Subarc: Diagenetic and Metamorphic Mass Flux in Subduction Zones

Recent study has indicated that profound chemical alteration of subducting materials and related mass flux in fluids occur in forearc regions, beginning with diagenesis at extremely shallow levels, and continuing during prograde, high-P/T metamorphism and perhaps even partial melting of some lithologies in some subduction zones. In this multidisciplinary theme, we hope to comprehensively consider forearc (and subarc) diagenetic and metamorphic mass flux and its significance for the cycling of materials through convergent margins. We invite papers dealing with any and all aspects of this flux and the ways in which its global significance can be evaluated. Guest Editors: G. Bebout, J. Martin, and T. Elliot. Target submission date: March 1, 2002.

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 2001 Fall Meeting program (EOS Transactions, AGU Volume 82, 2001) by P. Keizer, and we acknowledge the support of the AGU, and the program chairs Ray Russo (T), Garrett Ito (T), in particular Don Dingwell (V), who helped put the program together.

Daily Program

❖ GERM / Margins Subduction Factory Session I

Monday Morning 08:30 in MC 304

Time	Session	Title
0835	V11B-01	Mass Flux of Continental Material at Cenozoic Subduction Zones--New Global and Trench-sector Calculations Using New Geological and Geophysical Observations D W Scholl , R von Huene
0850	V11B-02 INVITED	Production and Fluid Flow at Shallow to Intermediate Forearc Depths: An Overview K M Brown
0910	V11B-03	Pore pressure development and progressive sediment compaction at the toe of the Costa Rican margin wedge: Mechanical and hydrologic implications D M Saffer , E J Screaton
0925	V11B-04	Boron and B Isotopes in Mud Volcanoes and Their Significance for Mobilization Depth and Global B Cycling A J Kopf , A Deyhle
0940	V11B-05	Deep Fluids from the Subducting Pacific Plate and Associated Microbial Activity on a Mariana Forearc Serpentine Seamount, ODP Leg 195 M J Mottl , S C Komor, P Fryer, Shipboard Scientific Party ODP Leg 195
0955	V11B-06 INVITED	Chemical Fluxes in Subduction Zones: Implications for Forearc and Ocean Chemistry M Kastner , J Martin, A Deyhle
1035	V11B-07	Clastic Intrusions and Chemosynthetic Communities in the Cretaceous-Paleocene Forearc, Panoche Hills, CA: Structural Context of a Linked Fluid System K D Weberling , J Moore, J Sample, H Schwartz
1050	V11B-08	Snapshots From a Tertiary Subduction Factory: Metamorphic Fluids From Fault Zones of the Low-Grade Shimanto Accretionary Prism of Southwest Japan J C Lewis , T B Byrne
1105	V11B-09	Helium-Carbon Relationships in Geothermal Fluids of Guatemala: Mapping the Subducted Sedimentary Component D R Hilton , A M Shaw, T P Fischer
1120	V11B-10	Carbon and noble gas composition of the Central American Volcanic Arc: Implications on global recycling of subducted carbonates G T Snyder , R Poreda, A Hunt, U Fehn
1135	V11B-11 INVITED	Isotopic and Elemental Signatures of the Forearc, and Impacts on Subduction Recycling: Evidence from the Marianas J G Ryan , L Benton, I P Savov

❖ GERM / Margins Subduction Factory Session II

Monday Afternoon 13:30 in MC 304

Time	Session	Title
1335	V12E-01	Comparative Thermal Structures of Circum-Pacific Subduction Zones S Huang , W P Leeman, V B Sisson
1350	V12E-02	Quantification of Subduction Zone Metamorphic Devolatilization From Computed High Pressure Phase Equilibria INVITED D M Kerrick , J D Connolly
1410	V12E-03	The influence of subduction zone thermal structure on arc magma chemistry: B and fluid-mobile elements W P Leeman
1425	V12E-04	Mineral Solubility in Aqueous Fluids at High Pressure: Implications for Metasomatism in Subduction Zones and the Mantle Wedge C E Manning , H Lin, N Caciagli, R C Newton
1440	V12E-05	Experimental Study of Slab-Mantle Geochemical Exchange in Subduction Zones Y Iizuka , E Nakamura, K Kobayashi
1455	V12E-06	Element Fluxes From Subducted Slabs: Constraints From High-Pressure Metamorphic Rocks INVITED H Becker
1535	V12E-07	Slab-related Boron Isotope Signatures in arc Volcanic Rocks From the Central Volcanic Zone (CVZ) of the Andes M Rosner , J Erzinger, G Franz, R Trumbull
1550	V12E-08	Amount of Sediment-Derived Fluid in Mantle Wedge Beneath Northeast Japan Arc: Comparison Between B and Other Element Contents in Japan Trench Sediments and Those in Iwate Lavas T Sano , T Hasenaka, T Fukuoka
1605	V12E-09	Lithium Isotopic Compositions of South Sandwich Arc and Southwest Washington Cascades: A Comparative Study of Arc Processes INVITED L Chan , W P Leeman, S Tonarini
1625	V12E-10	Lithium Budget and Isotopic Characterization of Materials Entering the Izu-Mariana Subduction Zone R B Valentine , J C Alt, J D Morris, K A Kelley
1640	V12E-11	Light Li Isotopic Composition in Subducting Slabs: Evidence From Alpine Eclogites T Zack , P Tomascak, W F McDonough, C Dalpe, R L Rudnick

❖ GERM / Margins Subduction Factory Session III: Posters

Tuesday Morning 08:30 in MC Hall D

Time	Session	Title
0830	V21C-0980	Physical Properties of Upper Oceanic Crust: ODP Hole 801C and the Waning of Hydrothermal Circulation R D Jarrard , L J Abrams, R A Pockalny, R L Larson, T Hirono
0830	V21C-0981	Petrological Constraints on the Thermal Structure of the Southern Washington Cascades J Lewis , W P Leeman, R C Evarts
0830	V21C-0982	Low Water Contents in the Oxidized, Sub-arc Mantle Wedge: Evidence from Pyroxene FT-IR Analyses of Spinel Peridotite Xenoliths from Mexico and Simcoe (WA, USA) A H Peslier , J Luhr, J Post
0830	V21C-0983	LILE-Signatures of IAB: Phengite Decomposition Within the Slab Versus Fractional Crystallisation of Phlogopite in the Wedge B Wunder , S Melzer
0830	V21C-0984	Using Digital Computer Field Mapping of Outcrops to Examine the Preservation of High-P Rocks During Pervasive, Retrograde Greenschist Fluid Infiltration, Tinos, Cyclades Archipelago, Greece C M Breeding , J J Ague, M Broecker
0830	V21C-0985	The Systematics of Boron Isotopes in Izu Arc Front Volcanic Rocks S M Straub , G D Layne
0830	V21C-0986	Record in Metamorphic Tourmalines of Subduction-Zone Devolatilization and Boron Cycling G E Bebout , E Nakamura
0830	V21C-0987	Boron Isotopic Compositions of Mud Volcano Fluids in Taiwan Accretionary Prism C You , M Li, C Chung, K Huang
0830	V21C-0988	Progress in the GEOROC Database - Fast and Simple Access to Analytical Data by Precompilation B Sarbas , U Nohl, U Busch, P Jaekel, P C Maissenbacher, H Schaefer
0830	V21C-0989	Subduction Zone Fluid Flow and Infiltrative Metasomatism in Franciscan Complex Exotic Ultramafic Blocks R L King , M J Kohn, J Eiler
0830	V21C-0990	Methods of Fluid and Geochemical Flux Measurement and new Insights From Seep Studies at the Eel River Margin M D Tryon , C Mahn, K M Brown, J Gieskes
0830	V21C-0991	Argon Ages of Ba-rich Phengitic Muscovite From Subduction Zone Complexes: Samana Peninsula, Dominican Republic and Franciscan Complex, USA E J Catlos , S S Sorensen
0830	V21C-0992	Nitrogen Geochemistry of Subducting Sediments: New Results from the Western Pacific S J Sadofsky , G E Bebout
0830	V21C-0993	Helium and Carbon Relationships in Geothermal Fluids From the Central American arc in Costa Rica A M Shaw , D R Hilton, T P Fischer, M M Zimmer, G Alvarado
0830	V21C-0994	Volatile Chemistry and Fluxes Along the Costa Rican Segment of the Central American Volcanic Arc M M Zimmer , T P Fischer, D R Hilton, A M Shaw, Z D Sharp, G Alvarado
0830	V21C-0995	Nitrogen-Helium-Argon and Nitrogen Isotope Relationships in Geothermal Fluids from the Central American Volcanic Arc: Mapping Subducted and Crustal Contributions to Volatile Output T Fischer , Z Sharp, D R Hilton

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- 0830 V21C-0996 **Clastic Intrusions and Chemosynthetic Paleocommunities in the Cretaceous-Paleocene Great Valley Forearc, Panoche Hills, CA: Fossil Evidence for Prolonged Subduction-Driven Fluid Expulsion**
H Schwartz, J C Moore, K Weberling, J Sample, P Vrolijk
- 0830 V21C-0997 **Clastic Intrusions and Chemosynthetic Paleocommunities in the Cretaceous-Paleocene Great Valley Forearc Basin, Panoche Hills, CA: Geochemistry of Carbonates Suggests Biogenic and Thermogenic Input During Early Tertiary Subduction**
J Sample, C Moore, K Weberling, H Schwartz, P Vrolijk
- 0830 V21C-0998 **Forearc and Backarc Basalts of the Garibaldi Lake-Cheakamus Valley Areas, Southwestern British Columbia**
N L Green
- 0830 V21C-0999 **Volcanisms of the Backarc Echelon Seamounts along the Enpo Seamount Chain in the Northern Izu-Ogasawara Arc**
S Machida, T Ishii
- 0830 V21C-1000 **Behavior of Subducting Sediments Beneath an arc Under High Geothermal Gradient: Implications for Progressive Continental Growth**
G Shimoda, Y Tastumi, Y Morishita
- 0830 V21C-1001 **Geochemical Characteristics of Sediments Potentially Subducted in Western and Eastern Philippines**
R U Solidum, P R Castillo
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Abstracts

listing in alphabetical order

V21C-0986; EOS, Trans. AGU, 82 (47), 1302 (POSTER)

Record in Metamorphic Tourmalines of Subduction-Zone Devolatilization and Boron Cycling

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Boron partitioning among fluids, tourmaline, and micas may dictate the extent and location, and isotopic composition, of B loss in subducting slabs, but the scarcity of information regarding mineral-fluid fractionation has limited efforts to understand deep B cycling. To clarify tourmaline's role in B redistribution during devolatilization of subducting sediments, we have analyzed tourmaline $\delta^{11}\text{B}$ in HP (Catalina, Sambagawa; peak <1.2 GPa) and UHP (Lago di Cignana; peak 2.7-2.9 GPa) metasedimentary rocks employing high-precision ($2\sigma = 0.5\text{-}0.8\text{‰}$) ion microprobe methods. Sambagawa metasediments show relatively uniform whole-rock B across grade, but an increasing proportion of B in tourmaline and a decreasing proportion in micas at higher grades. In contrast, Catalina Schist metasediments contain less tourmaline, and at higher grades show up to 75 percent decrease in whole-rock B with correlated decreased mica B. In both suites, some higher-grade (~epidote-amphibolite) rocks contain abundant, zoned, dravitic tourmaline. Tourmaline cores have lower $\text{Mg}/(\text{Mg}+\text{Fe}^{+2})$ and $\text{Ca}/(\text{Ca}+\text{Na})$ and higher $\delta^{11}\text{B}_{\text{SRM951}}$ (up to +1.6 ‰, mostly -6 to -2 ‰), and tourmalines show increased $\text{Mg}/(\text{Mg}+\text{Fe}^{+2})$ and $\text{Ca}/(\text{Ca}+\text{Na})$ and decreased $\delta^{11}\text{B}$ (approaching -15 ‰) toward rims. These variations are consistent with significant prograde tourmaline growth. Some grains have thin outermost zones compositionally similar to cores and attributed to retrogradation. The $\delta^{11}\text{B}$ of less-abundant tourmaline in lower-grade rocks (-7 to +4.5 ‰) overlaps with, or is higher than, that of tourmaline cores in higher-grade rocks, and some cores in low- and high-grade rocks are regarded as detrital. For tourmaline in Lago di Cignana metasediments, we associate cores with garnet and rutile inclusions, $\text{Mg}/(\text{Mg}+\text{Fe}^{+2})$ up to 0.95, and $\delta^{11}\text{B}$ as low as -16 ‰ with prograde, high-P/T metamorphism, and rims with clinozoisite and quartz inclusions, lower $\text{Mg}/(\text{Mg}+\text{Fe}^{+2})$, and higher $\delta^{11}\text{B}$ up to +4.3 ‰ with overprinting during exhumation. In the absence of tourmaline, devolatilization can reduce whole-rock B (Catalina), whereas tourmaline growth may retain whole-rock B lost from micas and minimize change in whole-rock $\delta^{11}\text{B}$ (Sambagawa). At Lago di Cignana, tourmaline (with $\delta^{11}\text{B} = -16$ to -9‰ somewhat lower than that of the initially subducted structurally bound B component in sediment) was stable to depths of ~90 km. Based on our results, and results of other recent studies of B isotope fractionation, it appears that B lost during devolatilization of subducting sedimentary rocks (and mica-bearing altered oceanic crust) is isotopically heavier than residual B in micas in the devolatilizing rocks. This heavier B could be sequestered by tourmaline (particularly in sediments), in which it could be subducted to greater depths, or could be released into and mobilized in metamorphic fluids. Fluids containing B released from micas in subducting, progressively devolatilizing sediment and altered oceanic crust appear capable of imparting relatively high- $\delta^{11}\text{B}$ signatures in arc lavas and producing across-arc trends of decreasing $\delta^{11}\text{B}$ observed in several arcs.

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V12E-06; INVITED; EOS, Trans. AGU, 82 (47), 1293

Element Fluxes From Subducted Slabs: Constraints From High-Pressure Metamorphic Rocks

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High-pressure metamorphic rocks in paleo-subduction and collision zones are the exhumed equivalent of subducted crust in modern subduction zones. The variable maximum P-T conditions of high-P terranes represent an opportunity to study kinetics, fluid flow, element partitioning and element fluxes during dehydration or melting reactions at various depth levels in subduction zones. Several conclusions from many metamorphic and stable isotope studies of high-P terranes are important for the study of element fluxes in subduction zones: (1) disequilibrium between phases is prevalent to temperatures of 600-700°C, (2) metabasites and metasediments in most terranes show

evidence for dehydration and fluid flow, however no evidence for partial melting at high P, (3) fluid flow appears to be focused in fractures. Quantitative studies of the major and trace element budget and element mobility in high-P rocks are still scarce. Particularly scarce are data for key elements that are important to model the long-term isotopic evolution of mantle and crust (K, Rb-Sr, U-Th-Pb, Sm-Nd). It has been shown that quantitative constraints on the efficiency of removal of fluid-mobile elements can be obtained by normalizing the abundances of such elements to abundances of elements that are much less soluble in fluids (e. g., Nb, Ta, Zr, HREE, Be). This seems to work well in metabasites in which the protolith chemistry can be reasonably well constrained from major element and Sr-Nd isotopic compositions. The data on eclogites can be used to construct a preliminary model for the composition of dehydrated altered MORB in mantle recycling models. This composition agrees well with predictions based on the composition of HIMU ocean island basalts. Similar approaches for high-P metasediments may work for specific elements but are problematic for others because protolith compositions are much more variable. Smartly designed experimental studies may fill these gaps. Future trace element studies of eclogites from moderate- to high-temperature terranes should help to improve existing model compositions for dehydrated altered MORB. A major limitation on any flux model is the uncertainty on the significance of unaltered oceanic crust for the water and element flux into arcs.

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V21C-0984; EOS, Trans. AGU, 82 (47), 1301 (POSTER)

Using Digital Computer Field Mapping of Outcrops to Examine the Preservation of High-P Rocks During Pervasive, Retrograde Greenschist Fluid Infiltration, Tinos, Cyclades Archipelago, Greece

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Digital field mapping of outcrops on the island of Tinos, Greece, was undertaken to investigate the nature of retrograde fluid infiltration during exhumation of high-P metamorphic rocks of the Attic-Cycladic blueschist belt. High-resolution digital photographs of outcrops were taken and loaded into graphics editing software on a portable, belt-mounted computer in the field. Geologic features from outcrops were drawn and labeled on the digital images using the software in real-time. The ability to simultaneously identify geologic features in outcrops and digitize those features onto digital photographs in the field allows the creation of detailed, field-verified, outcrop-scale maps that aid in geologic interpretation. During Cretaceous-Eocene subduction in the Cyclades, downgoing crustal material was metamorphosed to eclogite and blueschist facies. Subsequent Oligocene-Miocene exhumation of the high-P rocks was accompanied by pervasive, retrograde fluid infiltration resulting in nearly complete greenschist facies overprinting. On Tinos, most high-P rocks have undergone intense retrogression; however, adjacent to thick marble horizons with completely retrograded contact zones, small (sub km-scale) enclaves of high-P rocks (blueschist and minor eclogite facies) were preserved. Field observations suggest that the remnant high-P zones consist mostly of massive metabasic rocks and minor adjacent metasediments. Within the enclaves, detailed digital outcrop maps reveal that greenschist retrogression increases in intensity outward from the center, implying interaction with a fluid flowing along enclave perimeters. Permeability contrasts could not have been solely responsible for preservation of the high-P rocks, as similar rock suites distal to marble contacts were completely overprinted. We conclude that the retrograded contacts of the marble units served as high-permeability conduits for regional retrograde fluid flow. Pervasive, layer-parallel flow through metasediments would have been drawn into these more permeable flow channels. Deflections in fluid flow paths toward the high flux contacts likely caused retrograde fluids to flow around the enclaves, preserving the zones of "dry," unretrograded high-P rocks near marble horizons. Digital mapping of outcrops is a unique method for direct examination of the relationships between geologic structure, lithology, and mineral assemblage variation in the field. Outcrop mapping in the Attic-Cycladic blueschist belt has revealed that regional fluid flow along contacts can have important implications for the large-scale distribution of mineral assemblages in metamorphic terranes.

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V11B-02; INVITED; EOS, Trans. AGU, 82 (47), 1273

Production and Fluid Flow at Shallow to Intermediate Forearc Depths: An Overview

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A variety of physical and chemical processes lead to the production and eventual expulsion of fluids from subduction forearc regions at shallow to intermediate depths. Many processes, such as compaction and some of the stress (in the case of smectite) and thermally induced dehydration reactions, are relatively well understood, at least at a general level. However, much remains uncertain about the depth and temperatures at which water comes to be released, expulsion mechanisms, and pathways to the surface. For example, because most/all systems have a highly heterogeneous permeability distribution it is not known what proportion of the input fluids come to be expelled laterally either along the subduction thrust or through the oceanic basement, or by more vertical pathways through the forearc itself (via faults, diapirs, and diffuse flow). Indeed, a recent benthic flux meter study of the Costa Rican forearc suggests that diffuse flow may account for a significant proportion of the expulsion flux, with the potential that there is only limited lateral focused expulsion along the decollement. Predicting the depth at which fluids originate is also difficult because even though the consolidation behavior of sediments can be determined experimentally, the development of overpressures in low permeability systems can result in a considerable extension of the depth range over which consolidation proceeds. Another factor that has to be considered in predictions of fluid origination and expulsion patterns is that even where mechanical compaction proceeds to near completion, a significant residual fluid volume (~5-20 %) can remain trapped within sediment pores and in the fractured but still relatively ridged upper oceanic basement. Ultimately, however, studies of exhumed materials do suggest, that the bulk of the remaining pore fluids in sediments do come to be expelled (at least into local fracture systems) during the onset of late stage diagenesis and as pressure solution reactions pick up at seismogenic depths. The fate of pore fluids trapped within basement is less clear, however, and this region may not be a significant net source of fluids at shallow to intermediate depths. Indeed, there is the potential that much fluid remains trapped in the basement until temperatures have risen sufficiently for it to lead to the additional development of hydrous minerals such as chlorite. Thus, while fluid production/expulsion within the sediments is probably intimately associated with aseismic/seismogenic processes it seems reasonable to assume that it is the basement that forms the principal source of H₂O involved in magma generation.

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V21C-0991; EOS, Trans. AGU, 82 (47), 1303 (POSTER)

Argon Ages of Ba-rich Phengitic Muscovite From Subduction Zone Complexes: Samana Peninsula, Dominican Republic and Franciscan Complex, USA

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Deciphering processes by which volatile components are released during metamorphism in subduction zone settings is essential for understanding mass transfer from slabs to arc magmas. Because phengitic muscovite is stable to >750°C and >7 GPa, it can transport alkali and alkaline-earth elements to great depths. Phengite dehydration may facilitate material transfer from the subducted slab to the overlying mantle wedge at higher pressures than those at which the slab melts. Sorensen et al (1997) showed that some phengite grains in eclogites from the Franciscan Complex of California and from the Samana Peninsula, Dominican Republic, formed from metasomatic fluids produced by phengite decomposition found at greater depths and temperatures. These phengites have the potential to show timing relationships for the expulsion of K-rich metasomatic fluids from the two paleosubduction zones. Large (500µ- to 4mm-sized) Ba-rich phengite grains are present in eclogites and associated metamatites from both the Samana Peninsula and the Franciscan Complex. Many grains display patchy variation in Ba, likely related to different compositions of metasomatic fluids present during phengite crystallization or alteration. For example, a Samana grain (SS8527B1) contains 0.4-1.1 wt% BaO and a Franciscan grain (T902Ablue) has 0.5-0.9 wt% BaO. Higher BaO contents correlate with brighter regions in BSE images. A total of 19 grains from 7 Samana rocks and 23 grains from 11 Franciscan rocks were dated using the laser ⁴⁰Ar/³⁹Ar method to discern age discrepancies between the compositionally variable areas seen in the BSE images. Ages of Samana samples vary from 25±4 Ma (SS8527B2) to 50±4 Ma (SS8527B1). Some show little age variation within a single grain (SS8424D, 11 spots, 39±3 Ma, MSWD=1.2), whereas others appear age zoned (SS8424C, 4 spots, 36±1 Ma to 42±1 Ma, MSWD=7). These results are similar to mica ⁴⁰Ar/³⁹Ar ages from eclogites in northern Venezuela (Smith and Sisson, 1999), and may

indicate the initial stages of the regional tectonic reorganization from subduction to transcurrent uplift along both the northern and southern margins of the Caribbean plate. A large range of ages is also seen with the Franciscan phengites, which range from 114 ± 8 Ma (GL1604) to 161 ± 3 Ma (T902B). Individual spots on Franciscan grain MH9011C range from 134 ± 3 Ma to 149 ± 1 Ma (4 spots, MSWD=7), whereas sample T902A host shows 153 ± 2 Ma (6 spots, MSWD=1.2). The latter values resemble 160 ± 3 Ma (Ross and Sharp, 1988) and 160-170 Ma (Baldwin and Harrison, 1992) dates for hornblendes from Franciscan and Baja California amphibolite mélange blocks, which have been interpreted as 'initiation of subduction' ages, whereas the younger dates resemble values these authors attributed to the continuation of subduction at lower P-T conditions. Phengite grains, which record ~ 50 Ma of fluid-rock interaction in Franciscan, and ~ 25 Ma in the Samana eclogites, thus may prove to be a powerful tool that links fluid-rock interactions to broader tectonic events.

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V12E-09; INVITED; EOS, Trans. AGU, 82 (47), 1293

Lithium Isotopic Compositions of South Sandwich Arc and Southwest Washington Cascades: A Comparative Study of Arc Processes

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Lithium isotopes constitute a relatively new tracer for island arc processes. Published results show that arc lavas are generally enriched in Li and isotopically heavier compared to mid-ocean ridge and ocean island basalts. This enrichment is attributed to addition of Li from subducted oceanic crust and sediments to the mantle source. We report new data from the South Sandwich (SS) and Southwest Washington Cascades (SWC) arcs, which demonstrate greater diversity of Li isotope systematics among arc lavas. SS basaltic lavas are moderately enriched in Li (Li/Y = 0.29 to 0.37) with $\delta^7\text{Li}$ ranging from (1.3 to 7.6‰). Local diatomaceous ooze and clay-rich sediments (ODP Site 701) have largely constant $\delta^7\text{Li}$ (2.7 to 4.8‰) that closely resemble MORB (3.4 to 4.7‰). On the other hand, oceanic crust altered by seawater can have $\delta^7\text{Li}$ as high as 20‰. $\delta^{11}\text{B}$ of the lavas are distinctly higher than local sediments. These observations suggest that the subduction component is mainly derived from altered oceanic crust with little contribution from the sediment. The low $\delta^7\text{Li}$ may indicate addition of light Li from hydrothermally altered crust or some isotopic fractionation process in the subduction environment. The Cascades arc is characterized by the subduction of young and hot oceanic crust. Li/Y of the forearc and the volcanic front including Mt. St. Helens and Indian Heaven are elevated (up to 0.60) but $\delta^7\text{Li}$ of the enriched lavas are remarkably constant (2.5 to 4.0‰). This suggests that the subduction component has an isotopic composition of about 3‰. The MORB-like signature of the enriched lavas may be explained by (1) a relatively weak isotopic signal of the subducted oceanic crust due to its young age, and (2) sediment compositions that are indistinct from the mantle, much like those near the South Sandwich Trench. The latter will be verified by analyses of sediments on the Juan de Fuca plate. Normalized B/Li ratios decrease from forearc eastward, indicating early loss of B by slab dehydration. Behind the front at Mt. Adams and Simcoe, there is little enrichment in Li and the isotopic composition is mantle like. Apparently Li is also stripped from the deeper slab. Because of high temperatures of this subduction zone, fluid plays a relatively unimportant role in magma generation under the Cascades arc. The main implication of this comparative study is that Li-rich subduction components can exhibit a range of isotopic compositions from arc to arc and the cause of this variability is in part related to the thermal structure of the subducting lithosphere.

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V21C-0995; EOS, Trans. AGU, 82 (47), 1304 (POSTER)

Nitrogen-Helium-Argon and Nitrogen Isotope Relationships in Geothermal Fluids from the Central American Volcanic Arc: Mapping Subducted and Crustal Contributions to Volatile Output

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Volcanic arcs are locations where elements are recycled from the subducted slab, the mantle wedge and the overlying arc crust to the atmosphere and hydrosphere. A fundamental aim of arc-related studies and the MARGINS initiative is to quantify this flux and compare it with subduction zone parameters, such as sediment compositions and subduction rates. As part of the Central American arc study, we report N₂, He, and Ar abundance relationships and N-isotope ratios for 7 volcanic centers in Guatemala to complement on-going studies in Costa Rica (see previous abstract). In Guatemala, the arc crust is thicker and older than in Costa Rica and the entire sedimentary sequence on the down-going plate is likely to contribute to the slab flux. The Guatemalan volcanic centers of Amatitlan-Pacaya, Fuego, Moyuta, Tecuamburro, Amatitlan, Zunil and San Marcos have N₂/He ratios ranging from 2200 to 8100, typical for arc-related fluids. N₂/Ar ratios (40 - 500) and the high N₂/He indicate addition of N₂ from subducted sediments or arc crust to a mantle derived component (N₂/He < 200). The high N₂/He ratios of Guatemala, are in contrast to the mantle-derived N₂/He ratios measured at Poas, Costa Rica. Nitrogen isotope ratios for the Guatemalan volcanic centers range from $\delta^{15}\text{N} = +1.0\text{‰}$ for San Marcos to $+5.8\text{‰}$ for Fuego ($\delta^{15}\text{N}_{\text{air}} = 0.0\text{‰}$), indicating a sedimentary nitrogen signature. The mantle-derived N₂/He ratio for Poas is consistent with a more mantle-like $\delta^{15}\text{N}$ of -1.0‰ . In Guatemala, the highest ³He/⁴He ratios (7.6 for Pacaya and 7.3 RA for Fuego) correlate with the lowest N₂/He ratios (1500 and 2100) and high $\delta^{15}\text{N}$ values ($+3.8\text{‰}$ and $+5.8\text{‰}$). Lower ³He/⁴He ratios for Zunil (4.7 RA) and San Marcos (2.2 RA) correlate with N₂/He of 5000 and 6600, and lower $\delta^{15}\text{N}$ values of $+2.3\text{‰}$ and $+1.0\text{‰}$, respectively. These N-He relationships suggest that the nitrogen at Pacaya and Fuego is primarily of subducted organic sedimentary origin, with only minor crustal contributions. Additional nitrogen is supplied by the arc crust at Zunil and San Marcos, resulting in elevated N₂/He ratios. This is in contrast to the situation in Costa Rica, where lower N₂/He ratios and lower $\delta^{15}\text{N}$ values suggest possible loss of sediment by underplating and where higher ³He/⁴He indicate only minor crustal contributions to the discharging volatiles.

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Forearc and Backarc Basalts of the Garibaldi Lake-Cheakamus Valley Areas, Southwestern British Columbia

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The Cenozoic Garibaldi belt of the northern Cascadia subduction system is a NNW-trending chain of andesite/dacite eruptive centers that are distributed within three 5-15 km wide, 20-50 km long segments displaced successively northwestward along the volcanic arc. Contemporaneous basaltic volcanism is generally restricted to the forearc region along the volcanic front. In the Garibaldi Lake area, the forearc Cheakamus Valley basalts are transitional to mildly alkalic lavas with phenocrysts of olivine, plagioclase, and relatively Ti- and Na-rich aluminous clinopyroxene set in a matrix of glass, olivine, clinopyroxene, plagioclase, magnetite, and ilmenite. These moderately Fe- and Mg-rich basalts possess relatively low K, Rb, Ba, B, Hf, Th, Zr, Y, Sc, Co, Cr, Ni and total REE abundances, show modest LREE-enrichment, and lack normalized Nb-Ta anomalies. Intrasuite compositional variations apparently reflect shallow-level fractional crystallization involving the observed phenocrysts. A composite basalt-mugearite lava that erupted from The Cinder Cone, about 7 km east of the Cheakamus Valley, represents the only known backarc basalt in the Garibaldi belt. Mineralogically, the Helm Creek basalt contains chromian ulvospinel/chromite, and more magnesian clinopyroxene and olivine phenocrysts than Cheakamus Valley lavas; the mugearite, which lacks plagioclase phenocrysts, also contains sector-zoned Al- and Ti-rich clinopyroxene phenocrysts and resorbed F-bearing, Ti- and K-rich pargasite. Compared to the forearc lavas, the backarc basalt has similar Fe, Zr, Y, Sc, Cr, Ni, and Hf contents, but is enriched in Al, Na, K, P, Rb, Ba, Sr, Th, total REE, LREE, and HREE and depleted in Mg, Ti, Co, Ni, Cr, U and Ta. The Ne-normative Helm Creek mugearite exhibits significantly higher Na, K, P, Hf, Th, Zr, LREE, Sr and Ba but lower Al, Fe, Mg, Ti, Sc, Co, Y, and Yb contents than

the basalts; all backarc lavas exhibits negative Nb-Ta anomalies. Differences between the backarc and forearc basalts appear to reflect varied amounts of slab-derived fluxes and degrees of melting within a common subarc mantle source and locally, MASH-type processes within a lower crust possibly exemplified by rare mafic granulite xenoliths in Helm Creek mugearites.

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V11B-09; EOS, Trans. AGU, 82 (47), 1275

Helium-Carbon Relationships in Geothermal Fluids of Guatemala: Mapping the Subducted Sedimentary Component

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As part of the Central America MARGINS initiative, we report a comprehensive study of helium isotope ($^3\text{He}/^4\text{He}$), carbon isotope $\delta^{13}\text{C}(\text{CO}_2)$ and He-C abundance relationships of geothermal fluids from 7 volcanic centres of Guatemala. Guatemala was selected to provide a contrast to on-going studies in Costa Rica (see next abstract) as the arc crust in this region is thicker and older, and (unlike Costa Rica) the entire sedimentary sequence on the down-going plate (both hemipelagic muds and underlying pelagic carbonates) likely contributes to the slab flux. The Guatemalan volcanic centres of Amatitlan-Pacaya, Tecuamburro, Moyuta, Zunil and V. Fuego have $^3\text{He}/^4\text{He}$ values which fall within the range normally associated with subduction zones ($5 - 8 R_A$ where $R_A = ^3\text{He}/^4\text{He}$ of air). Slightly lower $^3\text{He}/^4\text{He}$ values $< 3 R_A$ are found at San Marcos and L. Atitlan but sampling in these regions was less extensive. $\text{CO}_2/^3\text{He}$ ratios vary between 5 and 81 ($\times 10^9$) with $\delta^{13}\text{C}$ values scattering between -1.4 and -5.5 ‰. Although the helium in Guatemala is overwhelmingly of mantle wedge derivation, He-C results are consistent with the bulk of the CO_2 having a slab origin. Using the approach of Sano and Marty (Chem. Geol., 1995) i.e. volcanic gases can be approximated by a 3-component mixture of MORB (M: $\delta^{13}\text{C} = -6.5$ ‰, slab-derived marine carbonate/limestone (L: $\delta^{13}\text{C} = 0$ ‰) and (organic) sedimentary (S) endmember components, the calculated L/S ratio for Guatemala is 8 and 5 for sedimentary endmember values of -30 and -20 ‰ respectively. These values are higher than worldwide arc averages and imply preferential incorporation of carbonate into the slab flux compared to the hemipelagic muds. However, both values are lower than those found for Costa Rica which indicates that possible loss of subducting sediments (e.g. by underplating) is less pronounced in Guatemala compared with contiguous arc segments to the south.

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V12E-01; EOS, Trans. AGU, 82 (47), 1292

Comparative Thermal Structures of Circum-Pacific Subduction Zones

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Subduction zone thermal structure influences Benioff Zone (BZ) seismicity, slab dehydration/metamorphism, geochemical fluxes, and arc magma production. To evaluate effects of relative differences in slab-surface temperature (SST), we have simulated thermal structures of ten circum-Pacific cross-arc transects (Andean, Central American, Cascades, E Aleutian, Kurile, NE Japan, and Mariana arcs) showing large variations in slab age (9-134 Ma), convergence rate (2-10 cm/yr), duration (40-226 Ma), slab length (200-1200 km), and slab geometry. A finite-element method was used to simulate mantle convection and a finite-difference solver used to compute heat transfer. A staggered grid for discretization enhanced accurate modeling of mantle convection. All models assume realistic curved slab geometries as constrained by BZ earthquake hypocenters. Shear-heating is evaluated using rheology of wet quartzite to simulate the presence of a veneer of subducted sediment near upper slab surfaces. Error propagation analysis indicates that the major uncertainty in SST profile is associated with (1) uncertainty in thickness of the overriding lithospheric plate, which determines the size of the convecting wedge domain, and (2) shear-heating contributions. Assuming constant lithosphere thickness (100 km), we estimate a nearly two-fold range in SST (~ 300 to 600°C) at BZ depths below the respective volcanic fronts. Moreover, for most transects similar SSTs ($\sim 800 \pm 50^\circ\text{C}$) are predicted at depths of the deepest BZ earthquakes. Even where slow subduction of young slabs occur, Ts approaching the wet solidus of oceanic crust or sediments are predicted only if the lithospheric lid is relatively thin or there is very strong shear-heating. Thus, we consider direct melting of subducted materials unlikely in any of the model transects. Assuming that highly fluid-mobile B is derived largely from subducted slabs,

B-enrichment data help constrain our thermal models. We show that B-enrichment (e.g., B/Zr ratios) in arc volcanic rocks is anti-correlated with SSTs at 100 km depth. This relation is consistent with progressive loss of fluids and fluid-mobile elements as descending slabs warm, and with variation in slab thermal structure from arc to arc.

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V12E-05; EOS, Trans. AGU, 82 (47), 1292-1293

Experimental Study of Slab-Mantle Geochemical Exchange in Subduction Zones

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Aqueous fluids derived from subducting oceanic crust play an important role in the material transport leading to the production of arc lavas, and in the long-term chemical evolution of the Earth's mantle and crust. In order to determine the geochemical evolution of both the subducting slab and the overlying mantle wedge, a series of dehydration/hydration experiments was carried out at conditions of 0.8-4.0 GPa and 650-900°C appropriate for subduction zones. Blueschist facies rocks/minerals, and olivine (Fo⁹⁰) were used for starting materials, as analogue materials of slab and mantle, respectively. Finely ground metabasalt (H₂O = 5.9 wt%) and glaucophane (H₂O = 2.3 wt%) were separately sealed in gold capsules with an olivine grain (1mm diameter), and then run in a piston-cylinder apparatus. Polished sections of run products were observed and analyzed for major element compositions with an electron micro-probe. Trace elements of selected run-products were determined using an ion probe (Cameca-5f). At subsolidus conditions, the metabasalt was transformed into amphibolite-facies mineral assemblages containing Mg-ilmenite at <1.5 GPa, and eclogite-facies assemblages containing rutile at >1.5 GPa. Glaucophane was transformed into the mineral assemblage of Na-Cpx, Opx ± garnet. Garnets formed in the slab portion show low-LREE/HREE and higher-HREE contents when compared with the starting materials. In all subsolidus experiments, Al-rich silicate glasses, which could be quenched aqueous fluids, were observed between mineral grain boundaries in the slab portions. The *fluids* at 3.0 GPa show high-LREE/HREE, and higher-LILE and lower-HREE contents. In contrast, the quenched fluids for <1.5 GPa, which did not coexist with garnet, do not show strong depletion in HREE. Negative Nb anomalies were observed in the quenched fluids in the metabasalt experiments, but this anomaly does not appear to exist in the glaucophane experiments. The behavior of the HREE and HFSE is consistent with the existence of garnet and Ti-oxides (rutile and ilmenite) in the slab portion of the experiments. The *fluids* should therefore be enriched in SiO₂, LILE and LREE. Mineral zones were observed on olivine grains near the initial olivine-slab interface. These reaction zones consisted of talc and enstatite layers at >800°C, and an enstatite layer only at >800°C. Because the enstatite layers are strongly LILE and LREE-enriched compared with the primary olivine, the reacted layers are thought to have been formed by chemical interaction between olivine and SiO₂-riched aqueous fluids which were capable of also delivering these other trace elements. As a consequence of this transfer, the chemical compositions of the descending slab and the overlying mantle could be considerably depleted and enriched, respectively, in SiO₂, LILE and LREE during the process of subduction.

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Physical Properties of Upper Oceanic Crust: ODP Hole 801C and the Waning of Hydrothermal Circulation

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The hydrologic evolution of oceanic crust, from vigorous hydrothermal circulation in young, permeable volcanic crust to reduced circulation in old, cooler crust, is thought to cause a corresponding evolution of geophysical properties such as velocity, density, and resistivity. Ocean Drilling Program (ODP) Hole 801C, which obtained the world's oldest section of in situ, normal oceanic crust, provides

the opportunity to examine relationships among hydrologic properties (porosity, permeability, fluid flow), crustal alteration, and geophysical properties, at both core-plug and downhole-log scales. Within these upper crustal basalts, fluid flux in zones with high porosity and associated high permeability fosters alteration, particularly hydration to smectite. Consequently, porosity is well correlated with both permeability and a variety of hydration indicators. Porosity-dependent alteration is also seen at the log scale: potassium enrichment is strongly proportional to porosity. At Hole 801C, intergranular-scale patterns detectable with core plugs are generally similar to log-scale patterns, despite the fact that log responses are also sensitive to large-scale fractures and voids, or macroporosity. We extend the crustal alteration patterns observed at Hole 801C to a global examination of how the physical properties of upper oceanic crust change as a function of age, based on global datasets of Deep Sea Drilling Project (DSDP) and ODP core physical properties and downhole logs. These core and log data indicate that crustal aging is accompanied by increased hydration, increased velocity, and decreased macroporosity. The suite of logged DSDP and ODP sites confirms that macroporosity is reduced with increasing crustal age, due to hydrothermal alteration. The velocity increase that results from this macroporosity reduction dominates the competing intergranular-scale velocity decrease from crustal alteration. The changes in macroporosity and velocity are large for pillows, but subtle for flows. Off-axis hydrothermal circulation and associated ongoing crustal alteration are not confined to high-permeability channels measured by packers; fluid flow and attendant alteration can proceed even at the exceedingly low permeabilities that characterize pillows and flow margins. Matrix densities provide the strongest demonstration of systematic increase in hydration (decrease in matrix density). Based on observed decreases in matrix density that are proportional to the logarithm of age, approximately half of all intergranular-scale crustal alteration occurs after the first 10-15 Ma. Apparently, crustal alteration continues, at a decreasing rate, throughout the lifetime of oceanic crust.

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V11B-06; INVITED; EOS, Trans. AGU, 82 (47), 1274

Chemical Fluxes in Subduction Zones: Implications for Forearc and Ocean Chemistry

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Subduction zone pore fluid chemical and isotopic profiles and recent modeling of the fluid flow regimes and solute fluxes indicate rapid and intense alteration of the accreted and subducted sediments and mostly episodic expulsion of considerably altered seawater (pore water) into the ocean. Fluid flow is along higher permeability conduits. The extent of alteration and the fluid fluxes involved vary, they depend on the type of sediments involved, the ratio of accreted to subducted sediments, the subduction rate, the thermal regime, and the geophysical properties of the subduction zone. The important diagenetic and low-grade metamorphic reactions which modify the fluid compositions, and concurrently the physical and thermal properties of the solids through which they flow are: bacterial and thermal degradation of organic matter; carbonate precipitation and recrystallization; formation and dissociation of gas hydrates; dehydration and transformation of hydrous minerals, especially of clay minerals and opal-A; volcanic ash hydration and alteration, principally zeolitization and smectite formation; and higher temperatures hydrous silicates formation. These fluid-sediment diagenetic and low-grade metamorphic reactions alter the sediment properties of the subduction system. The degree to which these fluid regimes influence the global chemical and isotopic systems, for example the seawater and mantle Cl isotopic compositions, are significant for some components and insignificant for others. An evaluation of the fluid fluxes and associated Li, Cl, Sr, Ca, and Mg chemical and or isotopic budgets will be considered, assuming that the ocean is circulating through the global subduction zones once in 200 to 300 million years. The fluid-sediment reactions and fluid and solutes expelled may alter the bulk chemical composition of the underthrust sediments. If so, it would alter the original concentrations of some typical sediment signatures in volcanic arcs.

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V12E-02; INVITED; EOS, Trans. AGU, 82 (47), 1292

Quantification of Subduction Zone Metamorphic Devolatilization From Computed High Pressure Phase Equilibria

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Devolatilization in subduction zones is essential to arc magmatism, seismicity and volatile recycling. A premise of our research is that realistic modeling of metamorphic devolatilization of subducted lithologies is only possible with phase equilibria for chemical systems that closely approximate actual bulk compositions. Volatile components are introduced into subduction zones by three contrasting lithologies: marine sediments, and hydrothermally altered mantle ultramafic rocks and oceanic metabasalts. Using free energy minimization (Perplex programs - web address: erdw.ethz.ch/~jamie/perplex), phase equilibria were computed to 6 GPa (~160 km) to quantify the evolution of CO₂ and H₂O by prograde metamorphism of these lithologies. Geotherms for NW and SE Japan [1] were adopted as thermal extremes along the tops of subducted slabs. The following summarizes our conclusions regarding the correlation between the depth of devolatilization, bulk rock composition and P-T locations geotherms. Serpentinites: for carbonate-bearing serpentinites (ophicarbonates) little CO₂ is released; for high-temperature (high-T) geotherms complete dehydration occurs under forearcs, and for low-temperature (low-T) geotherms major dehydration occurs under subarcs. Siliceous limestones: little devolatilization for all geotherms. Marls: with high-T geotherms devolatilization is complete under subarcs; in contrast, little devolatilization occurs with low-T geotherms. Carbonate-free pelites and turbidites: with high-T geotherms most dehydration occurs under forearcs, whereas along low-T geotherms substantial H₂O is released under subarcs. Carbonate-bearing oceanic metabasalts: decarbonation is negligible along low-T and intermediate-T geotherms and is limited along high-T geotherms; dehydration is complete under forearcs for high-T geotherms, significant under subarcs for intermediate-T geotherms, and very limited along low-T geotherms. Carbonate-free oceanic metabasalts: dehydration is complete under forearcs for high-T geotherms, and widespread under subarcs for intermediate-T and low-T geotherms. Metamorphic devolatilization of subducted metabasalts and metasediments is continuous; thus, we do not expect pulses of fluid release (corresponding to univariant devolatilization) for these lithologies. Our study emphasizes that because of differences in the bulk compositions of volatile-bearing lithologies and in the P-T location of geotherms, generalized modeling of subduction zone volatile recycling is questionable. References: [1] Peacock, S.M. and Wang, K. (1999) Science, 268, 937-939.

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V21C-0989; EOS, Trans. AGU, 82 (47), 1302 (POSTER)

Subduction Zone Fluid Flow and Infiltrative Metasomatism in Franciscan Complex Exotic Ultramafic Blocks

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Exotic ultramafic blocks within mud-matrix mantle of the Franciscan Complex, CA, preserve a series of metasomatic mineral zones due to the infiltration of SiO₂-rich fluids during subduction. These blocks have experienced extremely large fluid fluxes during metamorphism within the Franciscan subduction channel and appear to have recorded the composition of the fluids present within the Franciscan subduction zone. Chemical constituents dissolved in this fluid include many elements expected to be mobile in high-T aqueous fluids (e.g. SiO₂, but also include elements generally believed to be immobile in fluids liberated during the devolatilization of subducted material (e.g. TiO₂). We examined the petrology, whole-rock geochemistry, and oxygen isotope composition of these mineral zones to place further constraints on the petrologic structure of the forearc mantle wedge. The ultramafic blocks preserve the relict peridotite mineralogy Ol + Opx + Cpx + Cr-Spl. Fluid flow forms serpentinite (Srp + Mgt + Chl ± relict Cr-Spl) after peridotite. Additional infiltration formed Tlc (Tlc + Chl ± relict Cr-Spl) and is the strongest evidence for fluid-mediated addition of SiO₂. A fourth mineral zone, outside the scope of the models presented by Manning [1995, 1997], was created by metasomatism of Tlc-bearing rocks, and is composed of Tr + barroisite + Chl + Czo + Ttn + Ap + Zrc ± relict Cr-Spl. The amphiboles appear to buffer SiO₂ at higher activities, stabilizing this diverse group of minerals. Whole-rock geochemical changes occurring during metasomatism include wholesale removal of approximately 6-8 wt% of CaO by through-going fluids during serpentinization. During the production of Tlc from Srp, minor amounts of Al₂O₃ were added to the rock in

addition to the requisite SiO₂. At the final stage of metasomatism preserved, Tr-rich rocks show increases in SiO₂, TiO₂, Al₂O₃, P₂O₅, and especially CaO. Separates of Srp from synmetamorphic Srp + Cal veins give Srp δ¹⁸O of 8.23 ‰, which suggests Srp in equilibrium with metasomatic fluids has this approximate value. Values of Srp δ¹⁸O from the ultramafic blocks range from 6.37 to 8.18 ‰. This range of values probably reflects the progressive equilibration of oxygen between the rock and fluid as higher values correspond to greater extents of serpentinization. This result implies that the rock closely approached equilibrium with the fluid during serpentinization. Supporting this interpretation, Tlc, Tr, and vein Srp have isotopic compositions corresponding to equilibration at approximately 500°C. Intermineral fractionations between vein Cal and vein Srp give slightly lower temperature estimates of 420-480°C. These temperature estimates exceed values for the Dodson closure temperature for the Cal in these veins, which implies that the Cal in these veins may have been isotopically reset to some extent. Taken as a whole, the blocks may preserve the metamorphic structure of the mantle wedge in contact with subducted material. If so, these metasomatic layers have the potential to modify substantially the chemistry of fluids as they pass through this evolving mineralogic filter forming between the subducted slab and "deeper" regions of the mantle. These results suggest that the primary composition of subduction zone fluids is not reflected by arc magmas; that is, they are instead derived from regions of the mantle fluxed by fluids residual to the metasomatic processes we observe.

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V11B-04; EOS, Trans. AGU, 82 (47), 1274

Boron and B Isotopes in Mud Volcanoes and Their Significance for Mobilization Depth and Global B Cycling

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Mud volcanism is a global phenomenon in mostly convergent margin settings, whose nature has long been subject to scientific investigation. However, only recently its significance has been unravelled by quantitative studies in well-investigated submarine environments, like large accretionary complexes. The fluid flux through active mud volcanoes has been estimated to exceed that of the frontal accretionary prism (Kopf et al. 2001, EPSL 189, p295-313), and may have done so in earlier Earth's history. Pore fluids as well as muds and clasts of onshore and offshore mud volcanoes all over the world have undergone a systematic geochemical study using contents and stable isotopes of the mobile element boron. When tied into results from hydrothermal geochemical experiments in the laboratory (You et al. 1996, EPSL 140, p41-52), the B geochemistry proves to be a powerful tracer to estimate the depth of fluid and mud mobilization below ground. Boron adsorbed to clay minerals is preferably donated to the fluid when either tectonic stress (vertical and/or lateral compaction) or temperature increase. Here, we report variations in B content and B isotope ratios in mud volcano deposits as a result of different history of the material prior to extrusion. Results reflect the regional geology of the study areas, ranging from dewatering of undercompacted marine sediment in accretionary prisms (Barbados, Makran, Mediterranean Sea) to diagenetic reactions in mud volcanoes of orogenic belts (Malaysia, Pakistan, Georgia, Taman Peninsula, Western Alps). Boron shows maximum enrichment in the fluid phase (owing to desorption in the mud) when faulting roots deepest and deformation is strongest. Mud domes juxtaposing out-of-sequence faults in the Caucasus orogenic wedge show mud B contents 8x marine sediment, and fluid B contents up to 25x seawater. Deep-seated, B-rich fluids liquefy clay-bearing strata to facilitate mud extrusion, allowing the clay to re-adsorb B in the process. B isotopic composition of the mud decreases with incipient stress and mobilization depth. Given the abundance and high discharge rates of mud volcanoes along subduction zones, this process generally affects chemical and fluid budgets in the subduction factory. Also, it clearly has to be considered a major backflux mechanism in global B cycling from the lithosphere to the hydrosphere.

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V12E-03; EOS, Trans. AGU, 82 (47), 1292

The influence of subduction zone thermal structure on arc magma chemistry: B and fluid-mobile elements

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It is postulated that contents of B and other highly fluid-mobile elements (HFMs) in primitive arc lavas are sensitive to thermal structures of subducting slabs (*sensu lato*), which are the principal sources for these elements in subduction zones. Initial slab HFM inventories may be variably depleted in proportion to progressive fluid release as a consequence of gradual warming and metamorphism of descending

slabs. Also, some variation in the rate of slab heating is expected from arc to arc due to differences in subduction rate, slab age, Benioff Zone (BZ) geometry, etc. Thus, a greater fraction of the initial slab HFM inventory will be available to modify subarc mantle domains in relatively cool subduction zones, and vice versa. Nearly 100-fold variation in B-enrichment (e.g., as monitored by B/Zr or similar ratios normalized to constant B content) is observed for volcanic front (VF) basalts from arcs worldwide. B-enrichment is highly correlated with the above measurable subduction parameters and with other temperature-sensitive parameters such as 'slab length' (= down-dip extent of BZ seismicity). B-enrichment is also well correlated with slab-surface temperatures (SSTs) below the VF, as determined from numerical models (Huang et al., this volume). These relations suggest that slab HFM fluxes are strongly influenced by slab thermal history, and probably controlled by stability of HFM host minerals as well as the availability of fluid transport media. Different behavior is expected for various elements depending on their fluid-solubility and/or P-T stability of relevant host phases - in which case geochemical fractionations are readily feasible and may explain some of the geochemical variability among arc magma suites. Moreover, B/Zr and similar ratios potentially can be used to infer aspects of slab thermal structure. However, care must be taken that the ratios are representative of the most primitive mafic magmas and not modified by shallow crust-level processes. For example, interaction with lower crust rocks can lower normalized B/Zr values for relatively evolved lavas.

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V11B-08; EOS, Trans. AGU, 82 (47), 1274-1275

Snapshots From a Tertiary Subduction Factory: Metamorphic Fluids From Fault Zones of the Low-Grade Shimanto Accretionary Prism of Southwest Japan

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We characterize the physico-chemical conditions in the Shimanto accretionary wedge by examining fluids trapped synkinematically in euhedral quartz crystals associated with late-stage reverse faults. The samples come from three areas that span the Paleogene exposures on the Muroto Peninsula of Shikoku Island. Applying microthermometric and laser Raman microsampling techniques to coeval water-rich and carbonic fluid inclusions, we constrain the fluid chemistry, pressure and temperature conditions during a widespread and kinematically distinct phase of deformation. Crosscutting relations between the faults that host the fluid inclusions and pressure solution cleavage suggest that these conditions postdate peak heating. At Cape Oyama the carbonic phase appears to be pure methane, and this enables us to constrain geothermal gradients between 24 and 77 degrees Celsius per kilometer, depending on assumptions regarding overburden. The occurrence of the fluid inclusions along faults of mm- to cm-scale thickness suggests that these structures facilitated transient and very localized fluid flow during thickening of the prism. The evolution of the thermal structure of this low-grade accretionary wedge is revealed by comparing peak temperatures inferred from organic phases such as vitrinite to fluid trapping temperatures. The former show a prominent southeastward increase that has been interpreted to reflect landward tilting of the Paleogene portion of the wedge after peak heating. In contrast, the latter indicate consistent temperatures during late-stage faulting across all three locations investigated. Although this result suggests minimal modification of the thermal structure that is recorded by the trapped fluids, the fluids reveal a southeastward decrease in molar proportion of methane relative to carbon dioxide that may reflect tilting adequate to differentially expose this metamorphic gradient. In total we document thermally-driven oxidation of methane relatively late (i.e., post-cleavage) in the deformation history of the Shimanto accretionary wedge.

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V21C-0981; EOS, Trans. AGU, 82 (47), 1301 (POSTER)

Petrological Constraints on the Thermal Structure of the Southern Washington Cascades

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Slow descent (3-4cm/yr) of a young (<10Ma) lithospheric slab in the Cascadia subduction zone results in (1) a relatively steep thermal gradient along the slab/mantle interface compared to typical volcanic arcs worldwide, and (2) accelerated (shallow) dehydration of the slab. Quaternary olivine basalts erupted over an unusually wide (~160 km) E-W transect across the arc in S. Washington (from west of Mt. St. Helens to the Simcoe field); many display primitive (MgO up to ~10%, Mg# up to ~0.68, Ni up to 150-200 ppm, Cr up to 200-400 ppm) OIB-like compositions atypical of most arc lavas. Locally, these lavas are calcalkalic (CA) and display coherent fractionation trends consistent with removal of olivine & clinopyroxene phenocrysts. Distinctive ol- and plag-phyric basalts of low-K₂O tholeiitic affinity occur sporadically across much of the arc; these have distinctive trace element patterns inherited from relatively depleted sources. In some areas (Indian Heaven, Simcoe) compositions define two or more subgroups with distinctive major and trace element characteristics. Overall, bulk compositions generally become more fractionated, poorer in SiO₂, and more alkalic with distance eastward from the trench. However, in many respects the easternmost lavas (Simcoe) more closely reflect OIB-like sources with negligible slab contributions. B/Zr ratios are very low across most of the arc, but increase slightly in the frontal arc region (west of Mt. St. Helens) signifying small slab-derived contributions there. Mineral chemistry and compositions of the most chemically primitive basalts, determined through electron microprobe analysis (EMP), will be used to constrain the temperature and depth of magma generation and/or segregation through use of various geobarometers and geothermometers. Changes in depth and temperature of magma formation of across the transect can then be correlated to the subducting slab profile as determined by seismologic studies as well as compared to thermal models of the Cascade arc.

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V21C-0999; EOS, Trans. AGU, 82 (47), 1304-1305 (POSTER)

Volcanisms of the Backarc Echelon Seamounts along the Enpo Seamount Chain in the Northern Izu-Ogasawara Arc

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Echelon seamount chains trending ENE-WSW exist in the backarc region of the northern Izu-Ogasawara Arc. The Kan'ei, Manji, Enpo and Genroku seamount chains (from north to south) constitute four especially well documented and investigated example. These seamount chains formed between 17 Ma and 3 Ma (Ishizuka, 1999). The eastern sections of each seamount chain are over-printed by many small knolls formed by intra arc rifting volcanism after 2.5 Ma (e.g. Hochstetter et al., 2000; Morita, 1999). We report results of detail petrological analysis of basalts from two different seamounts and andesites from four different seamounts of the Enpo seamount chain. The Ar-Ar age of these volcanic rocks range from 5.8 Ma to 3.9 Ma (Ishizuka, 1999). Bulk chemistry of trace element and composition of chrome spinel included in olivine phenocrysts indicate that there are two kinds of primitive basalts in the Enpo seamount chain. These were produced from different mantle sources each other. One type of basalt has 'enriched' composition similar to enriched mid-ocean ridge basalt (E-MORB). Trace element signatures indicate that the other type of basalt is produced by 'subduction-related' magmatism. It is defined that there are two mantle sources, enriched (E-MORB-like) and subduction related, for the volcanic rocks constituting the Enpo seamount chain. Enriched basalts exhibit reverse zoning and resorptive rims of olivine crystals, which may indicate magma mixing. We use mineralogical and geochemical studies, to conclude that most andesites from this region are produced mainly by fractionation of 'subduction related' basalts, and that fractionation occurs along with magma mixing and/or interaction with crustal materials. Andesites, which cannot be explained by fractionation, require either different mechanisms for magma genesis and/or the presence of a different primary basalt with a different petrological characteristics. Volcanism on the Enpo seamount chain is characterized by complex relationships between enriched (E-MORB-like) basalt, subduction-related basalt, fractionation-related andesites, and other apparently unrelated andesites.

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V12E-04; EOS, Trans. AGU, 82 (47), 1292

Mineral Solubility in Aqueous Fluids at High Pressure: Implications for Metasomatism in Subduction Zones and the Mantle Wedge

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Subduction zones are regions of profound fluid-controlled mass transfer (metasomatism). However, the physical chemistry of fluid-rock interaction in this environment remains poorly understood because there are few measurements of mineral solubility at the relevant pressures and temperatures. We have carried out a program of experimental and theoretical studies of mineral solubility in H₂O-NaCl-HCl-H₂S fluids at 5-20 kbar and 350-900°C. Experiments are performed in a piston-cylinder apparatus; mineral solubilities are determined based on weight changes of encapsulated minerals or analysis of extracted quench fluids. When combined with theoretical predictions, these studies provide a basis for modeling metasomatism in subduction zones and the mantle wedge. Experimental studies on quartz, diaspore, corundum, albite-paragonite-quartz, calcite, forsterite and enstatite show that, as a general rule, mineral solubility increases strongly with pressure at constant temperature in pure H₂O. In some cases solubility is 3-4 orders of magnitude higher at subduction zone conditions than in shallow crustal environments. Silica, alkalis, and Al dominate the solute load relative to alkaline earths and transition metals. NaCl profoundly enhances the solubility of calcite and Al and other metal oxides, but decreases SiO₂ solubility significantly. Studies of HCl dissociation show it to be a weaker acid at >5 kbar than anticipated from low-pressure experiments. H₂S does not strongly influence the solubilities of Si, Al, and Na, but is expected to enhance metal solubility. Experimental results agree well with theoretical predictions of solubility based on the observation that the quantity $\delta V_r / \beta_{H_2O} RT$ is isothermally constant with increasing pressure. This gives a foundation for predicting thermodynamic properties of aqueous species that have not been studied experimentally. Results of our studies confirm that aqueous subduction-zone fluids will be rich in alkalis, Al, and Si. Metal contents will be low, unless additional components (NaCl, HCl, H₂S) are present.

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V11B-05; EOS, Trans. AGU, 82 (47), 1274

Deep Fluids from the Subducting Pacific Plate and Associated Microbial Activity on a Mariana Forearc Serpentine Seamount, ODP Leg 195

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As the Pacific plate subducts beneath the non-accretionary Mariana forearc its crust emits water and other volatiles that hydrate the mantle of the overriding plate. The resulting serpentinite rises through faults to the seafloor, along with partially altered harzburgite and the excess volatiles, to form a belt of serpentine mud volcanoes in the outer half of the forearc that have cold springs at their summits. This mass flux through the forearc represents one of the earliest returns of subducted material to the oceans. To assess this flux, Ocean Drilling Program Site 1200 was drilled on the summit of one of these mud volcanoes. South Chamorro seamount lies near 14°N, 85 km landward of the Mariana trench and 27 km above the top of the subducting plate. Cold springs at its summit, discovered on Dive 351 of the Shinkai-6500 in 1996, are populated by mussels, small tubeworms, whelks, and galatheid crabs. We recovered pore waters from three holes drilled on a transect <10, 20, and 80 m from one of these springs. Composition-depth profiles for these pore waters, to a maximum depth of 71 mbsf, verify that water is upwelling through serpentinite to feed the springs. Like the upwelling water sampled on another serpentine mud volcano, Conical seamount, at ODP Site 780 (Leg 125) near 20°N, the ascending water at Site 1200 has a clear chemical signature of a deep-slab origin. It is highly enriched in a suite of elements that are virtually absent in the partially serpentinized, depleted harzburgite matrix, including (mainly carbonate) alkalinity (60; all units in mmol/kg), Na (610), Na/Cl (1.2), K (19), B (3.2), ammonia (0.22), methane (2), and C2 through C6 hydrocarbons. The fluids have a pH of 12.5, similar to the 12.6 at Conical Seamount. They are highly depleted in Mg, Ca, Sr, and Li, and have low concentrations of Si, Mn, Fe, Ba, and phosphate. They are slightly depleted in chloride (510 vs. 545 in seawater) and enriched in sulfate (by 7% relative to chloride). This chloride depletion is much smaller than that in the deep fluid from Conical Seamount, suggesting that the conduit at Conical is more heavily serpentinized and less reactive, allowing more of the H₂O from the deep source to arrive at the seafloor without being lost to serpentinization along the way. Pore water composition-depth profiles reveal

that these deep fluids feed an active microbial community within the upper 20 mbsf that is oxidizing light hydrocarbons from the fluid while reducing sulfate. At pH 12.5, this is a true extremophile community. Sulfate reduction is most active at two levels. Microbes within the upper level at 3 mbsf reduce seawater sulfate that diffuses downward against the ascending flow. Those within the lower level at 13 mbsf reduce sulfate that is supplied from the subducting slab by the upwelling fluid. As organic carbon is virtually absent within the depleted harzburgite, the microbes rely on methane and the C₂ through C₆ thermogenic hydrocarbons for their source of organic carbon, and ammonia for their source of nitrogen. Both are supplied by the upwelling fluid. The microbial community intercepts these nutrients and traps them within the ecosystem, where they can be recycled and continually enriched. This process may explain the enrichment in organic carbon in the uppermost sediment. Iron sulfides, and CaCO₃ in the form of aragonite needles and chimneys, are also enriched there, by reaction between the ascending fluid, the microbial community, and the overlying seawater.

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V21C-0982; EOS, Trans. AGU, 82 (47), 1301 (POSTER)

Low Water Contents in the Oxidized, Sub-arc Mantle Wedge: Evidence from Pyroxene FT-IR Analyses of Spinel Peridotite Xenoliths from Mexico and Simcoe (WA, USA)

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The pyroxenes of spinel-peridotite mantle xenoliths from Mexico and Simcoe (WA, USA) were analyzed for water content by Fourier-transform infrared spectrometry (FTIR). The locations selected span large geographical distances to the Pacific subducting margin (175 to 610 km) and the xenoliths represent a wide range of melt extraction amount and oxygen fugacities (δFMQ from minus 2.2 to 0.9). Pyroxene water contents range from 140 to 528 ppm in clinopyroxenes and 39 to 265 ppm in orthopyroxenes. Cpx water contents correlate positively with those of Opx. Correlations between these water contents and major-element compositional data for the pyroxenes, associated spinels, and whole-rock xenoliths demonstrate that these water contents record mantle values that have not been perturbed since the xenoliths were brought to the surface by their host magmas. Broad correlations between Opx and Cpx water contents with indices of fusion of the bulk xenoliths such as MgO (negative), Al₂O₃, TiO₂, CaO, and Na₂O (positive) contents also confirm that water is incompatible during melting of peridotite. The main control on the range of pyroxene water contents, however, appears to be the redox state of the peridotite, because estimates of oxygen fugacity from Mössbauer (Simcoe) and microprobe data (Mexico) on spinels are negatively correlated with water contents. This is consistent with the dominant mechanism of H incorporation into pyroxene, which is dependent on the oxidation-reduction of iron. The oxidation of the mantle-wedge peridotites by subduction related fluids or melts thus significantly lowers the solubility of water in their pyroxenes, causing more than half of the water originally housed in the mantle wedge to be expelled. That water is likely incorporated into the ascending hydrous partial melts that feed the overlying magmatic arc. The nominally anhydrous minerals in the mantle-wedge are consequently not an important storage reservoir for subducted water. Instead the mantle wedge appears to be capable of efficiently transporting slab-derived water to the upper crustal magmatic arc, to which it may contribute up to 5 % of the total arc magma water. The relatively dry nature of oxidized sub-arc mantle-wedge peridotites can be viewed as the complement to the hydrous and oxidized magmas whose common explosive eruptions characterize subduction-related volcanoes.

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V12E-07; EOS, Trans. AGU, 82 (47), 1293

Slab-related Boron Isotope Signatures in arc Volcanic Rocks From the Central Volcanic Zone (CVZ) of the Andes

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This study uses the geochemical and isotopic behavior of boron as a tracer for mass transfer and the generation of arc magmas in the southern part of the CVZ. Investigations were made on andesitic to dacitic arc lavas between 20 and 26°S. B isotopic ratios were measured

using the Cs_2BO_2^+ -graphite method and are reported as $\delta^{11}\text{B}$ values in ‰ relative to NBS 951. The total B concentrations of investigated rocks range from 10 to 54 ppm and $\delta^{11}\text{B}$ values vary between +4 and -7 ‰, whereby the trench-side locations show systematically higher $\delta^{11}\text{B}$ values and B contents. The wide range of $\delta^{11}\text{B}$ values and B contents is the most striking feature of the presented dataset. Potential source reservoirs for B and their assumed compositions in this setting include: Altered oceanic crust (5ppm; $\delta^{11}\text{B}$: + 4 ‰), marine sediments (100ppm; $\delta^{11}\text{B}$: -10 ‰), mantle (1ppm; $\delta^{11}\text{B}$: -3 ‰) and continental crust (15ppm; $\delta^{11}\text{B}$: -10 ‰). The contribution of subducted marine sediments in the CVZ is negligible. Assuming these compositions, positive $\delta^{11}\text{B}$ values can neither be explained by incorporation of mantle-derived B nor by B from the crust. For these samples, a ^{11}B rich slab-derived component dominated by altered oceanic crust must be the major source. This implies that B and possibly other mobile elements were effectively transferred via fluids from the subducted slab into the mantle wedge where generation of arc magmas took place. Various experiments indicate a temperature dependent fractionation of B isotopes between rock and fluid. Using published fractionation factors, $\delta^{11}\text{B}$ values of the subduction zone fluids would decrease from ca. +12 ‰ at 150°C to ca. -6 ‰ at 750°C with increasing depth to the slab. The range of observed $\delta^{11}\text{B}$ values can be explained with the fractionation effect. The correlation of decreasing $\delta^{11}\text{B}$ values and B contents with distance to the trench and depths of the subducted plate suggests that the total boron budget is dominantly controlled by slab-derived B. If this is true, decreasing B contents toward the back-arc indicate a decrease in the mass flux of B and perhaps other fluid mobile elements with increasing depths of the slab. Deviations from the general across-arc variation may be due to locally variable degrees of crustal contamination. Two component mixing models of $\delta^{11}\text{B}$ with Sr and Nd isotopic compositions indicate an addition of 15 to 35% crustal material to the initial magma.

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V11B-11; INVITED; EOS, Trans. AGU, 82 (47), 1275

Isotopic and Elemental Signatures of the Forearc, and Impacts on Subduction Recycling: Evidence from the Marianas

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Trace element and B and Li isotope systematics of serpentinites from the Conical Seamount in the Mariana forearc indicate significant geochemical changes occur in the slab and mantle wedge in the earliest stages of subduction. Elevated K, Rb, Cs, B, Li and possibly Pb and As contents in fluids, clasts, and/or muds from Conical indicate transport of H_2O -soluble species off the slab at <30 km depths. Boron contents in Conical clasts correlate broadly with LOI, suggesting continuous inputs of B with progressive hydration. Abundances of Li, Rb and Cs covary mutually, but do not correlate with LOI or other elemental concentrations in Conical clasts. The alkalis may thus reflect a different (later?) stage of slab inputs in which a broader menu of species are mobilized. Boron isotopic systematics of Conical serpentines point to additions of fluid with uniform $\delta^{11}\text{B}$, irrespective of fluid-rock ratio. This fluid, at $\delta^{11}\text{B}$ of +13‰, is >10‰ heavier than any subducted component, indicating fractionation of B isotopes during slab fluid releases beneath forearcs. The temperatures of shallow slabs must be cool enough for B isotope fractionations to occur, which is consistent with the observed, low T serpentine mineralogy in Conical samples. The fraction of slab B recycled in the forearc depends on the model for developing high $\delta^{11}\text{B}$ arc lavas: either slab fluids with elevated $\delta^{11}\text{B}$ are released beneath arcs, or a hotter (and presumably lower $\delta^{11}\text{B}$) fluids from the slab mix with some portion of hydrated, high $\delta^{11}\text{B}$ mantle convected in from shallower depths. Li isotopes in Conical serpentinites indicate more modest, if variable, slab inputs. $\delta^7\text{Li}$ variations in these samples (from -0.5 to +11 ‰) are greater than those observed in probable slab materials, or in most arc lavas, and may indicate the development of Li isotopic heterogeneities in the Mariana forearc mantle, like those suggested by Li isotope variations in "hot" arcs (Tomascak et al., 2000). $\delta^7\text{Li}$ in Mariana arc lavas (at +1 to +8.5 ‰), are more diverse than observed in other arcs, but show less variation than Mariana forearc rocks, supporting contentions that Li from the mantle wedge dilutes the slab input during arc melting.

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V21C-0992; EOS, Trans. AGU, 82 (47), 1303 (POSTER)

Nitrogen Geochemistry of Subducting Sediments: New Results from the Western Pacific

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Recent study of nitrogen concentration and isotopic composition of subduction-zone metamorphic rocks (Franciscan complex, Western Baja Terrane, Catalina Schist) has shown that most low-grade metaclastic rocks contain 100 to 500 ppm nitrogen with $\delta^{15}\text{N}_{\text{Air}}$ from +0.3 to $\sim +3.4$ ‰. Modern surface sediments have highly variable $\delta^{15}\text{N}_{\text{Air}}$, but most tend to be in the range of +5 to +12 per mil. Metamorphic devolatilization would likely drive $\delta^{15}\text{N}$ to higher values as we have documented at several localities (Catalina Schist, California; Skiddaw Aureole, UK; Townshend Dam, Vermont). To try and reconcile the difference in $\delta^{15}\text{N}$ between low-grade metasedimentary rocks and modern surface sediments we have analyzed N geochemistry of sediments outboard of the Izu-Bonin and Marianas subduction zones. Forty bulk-sediment samples from ODP sites 1149, 800, 801, and 802 contain 5 to 661 ppm N with $\delta^{15}\text{N}_{\text{Air}}$ of -0.2 to +8.2 per mil. $\delta^{15}\text{N}$ varies within the uppermost 120 m of site 1149A from +8.2 per mil at 1.4 mbsf to +4.7 at 113 mbsf. Nitrogen and reduced-C concentrations and reduced-C- $\delta^{13}\text{C}$ also decrease somewhat with increasing depth in the upper 150 mbsf of site 1149. Analyzed samples from greater depth at site 1149 (silica- and carbonate-rich horizons) contain less N (18 - 26 ppm) with lower $\delta^{15}\text{N}$ (+2.5 to +4.0 per mil). A smaller data set for sediments from sites 800, 801 and 802 also shows higher N content in volcanoclastic and clay-rich units relative to silica and carbonate horizons, and decreasing $\delta^{15}\text{N}$ with depth. From 0 to 100 mbsf at ODP site 1149, sediment $\delta^{15}\text{N}$ varies systematically with depth, from +8.2 per mil, values like those of modern surface sediments (cf. Peters et al., 1978; Mizuka et al., 1991; Minorwa et al., 1997) to +4.7 per mil (similar to the Franciscan complex, Western Baja Terrane, and low-grade subunits of the Catalina Schist). This sharp gradient suggests that most of the difference in $\delta^{15}\text{N}$ between modern sediments and low-grade, high-P/T metasedimentary suites (peak metamorphism at 5-40 km) is produced at very shallow depths during early stages of diagenesis.

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V11B-03; EOS, Trans. AGU, 82 (47), 1273

Pore pressure development and progressive sediment compaction at the toe of the Costa Rican margin wedge: Mechanical and hydrologic implications

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At subduction zones, the fate of pore fluids within underthrust sediments has important effects on the evolution of mechanical strength and structural development. Results from Ocean Drilling Program (ODP) Leg 170, offshore Costa Rica, documented the complete underthrusting of a regionally uniform sediment section, with the important implication that observed changes in sediment thickness and void ratio directly reflect the evolution of effective stress. Combining logging-while-drilling (LWD) data, down-hole physical properties data, and laboratory consolidation tests, we track the development of effective stress and pore pressure within underthrust sediments with progressive loading beneath the margin wedge. High-quality drilling data, combined with numerous laboratory consolidation tests, allows a spatially detailed investigation of down-section pore pressure evolution with progressive loading. Effective stresses inferred from laboratory experiments and those projected from observed reductions in void ratio are in excellent agreement. In both cases, the results indicate essentially undrained conditions at site 1043 (located ~ 0.5 km landward of the trench). At site 1040 (located ~ 1.6 km from the trench), our results suggest that the lower, pelagic underthrust sediments remain nearly undrained, whereas the upper, hemipelagic sediments are partially drained. An inferred minimum in effective stress developed near the base of the hemipelagic section between sites 1043 and 1040 is consistent with observed down-stepping of the decollement at $\sim 2-3$ km from the trench, and illustrates the important

effects of pore pressure distribution on structural development. In comparison, pore pressures within underthrust sediments at the Nankai and Barbados subduction zones inferred from porosity data indicate that dewatering at these locations occurs more slowly than at Costa Rica. These differences can be attributed to the higher permeability and larger compressibility of near-surface sediments underthrust at Costa Rica.

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V21C-0997; EOS, Trans. AGU, 82 (47), 1304 (POSTER)

Clastic Intrusions and Chemosynthetic Paleocommunities in the Cretaceous-Paleocene Great Valley Forearc Basin, Panoche Hills, CA: Geochemistry of Carbonates Suggests Biogenic and Thermogenic Input During Early Tertiary Subduction

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A Paleocene seep system is remarkably well preserved in the Panoche Hills of central California. The seep horizons lie within a 45-m-thick interval in the Dos Palos Shale Member of the Moreno Formation, which contains chemosynthetic fauna. Extensive sandstone dikes in the underlying Cretaceous to Paleocene units presumably acted as conduits to replenish the seep organisms with the methane-enriched fluids required for chemosynthesis. We investigated the geochemistry of the carbonate cements and veins within the seep horizons and sandstone dikes to determine the nature of the fluid sources. Carbonate occurs as pore-filling cement, infill of tubes, shell material, veins, and possible replacement of tubeworm walls. The preserved carbonate textures, including fibrous, syntaxial vein minerals and radial, fibrous fills of tubes (fluid pipes?), indicate that many of the samples have not undergone extensive recrystallization during diagenesis. Isotopic values of 33 seep samples are $\delta^{13}\text{C}_{\text{PDB}} = -42.56\text{‰}$ to 0.55‰ and $\delta^{18}\text{O}_{\text{PDB}} = -5.81\text{‰}$ to 3.78‰ . These carbon isotope values are consistent with a fluid source during seep formation containing a mixture of oxidized thermogenic methane from marine organic matter, seawater bicarbonate, and a component of biogenic methane. Three dike samples have carbonate with $\delta^{13}\text{C}_{\text{PDB}} = -21.12\text{‰}$ to -5.54‰ , and $\delta^{18}\text{O}_{\text{PDB}} = -8.45\text{‰}$ to -6.26‰ . The low dike oxygen values suggest that fluids retained some of the elevated temperature of the source region during migration, or later diagenesis recrystallized the cement. Given that the source of sandstone dikes was at most a few hundred metres below the seeps at the time of their formation, a significant component of thermogenic methane preserved in the carbonates requires some westward lateral migration of fluids from beneath the Great Valley forearc basin before expulsion at the Paleocene seafloor. The migration pathways probably developed as a consequence of early Tertiary subduction and deformation in the forearc.

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V12E-08; EOS, Trans. AGU, 82 (47), 1293

Amount of Sediment-Derived Fluid in Mantle Wedge Beneath Northeast Japan Arc: Comparison Between B and Other Element Contents in Japan Trench Sediments and Those in Iwate Lavas

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From the Japan Trench, the Pacific Plate descends to the deep mantle. Parts of the plate, the altered oceanic crust (AOC) and overlying sediments, release hydrous fluids at the deep mantle, and these slab-derived fluids would be added to the mantle wedge beneath Northeast Japan arc. In order to estimate the weight percent of the fluid in the mantle wedge, we determine boron and other element contents of 42

sediments from Japan Trench and 29 lavas from Iwate volcano on Northeast Japan volcanic front. The Japan Trench sediments are typical trench-fill sediments mainly consisting of pelagic clay. 15 Iwate lavas belong to the tholeiite series and 4 Iwate lavas belong to the calc-alkali series. The tholeiite lavas have uniform B/K, indicating these lavas were formed by melting of a single magma source. B/K of the calc-alkali lavas is lower than that of the tholeiite lavas. Also, B/K ratios are distinctly more variable in the calc-alkali lavas, suggesting we have to consider more than two magma source. Trace element contents of the trench sediments are used to estimate those of the sediment-derived fluid, and previously reported trace element contents of the AOC (Smith et al., 1995, Chem. Geol., 126, 119-135) are used to estimate those of the AOC-derived fluid. Examination of mobile/immobile element ratios (B/Sm, Ba/Sm, K/Sm, B/Zr, Ba/Zr, K/Zr) of the two slab-derived fluids and Iwate tholeiite lavas, indicates a mixing ratio between the AOC-derived fluid and the sediment-derived fluid is 90 : 10 in the mantle wedge beneath the Northeastern Japan arc. Based on the element ratio diagrams, weight fraction of the total slab-derived fluid in the mantle wedge is estimated to be less than 1 wt %. When we combine the above two estimations, the amount of the sediment-derived fluid in the mantle wedge is estimated to be less than 0.1 wt %.

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V21C-0988; EOS, Trans. AGU, 82 (47), 1302 (POSTER)

Progress in the GEOROC Database - Fast and Simple Access to Analytical Data by Precompilation

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The geochemical database GEOROC of the Max-Planck-Institut fuer Chemie in Mainz <http://georoc.mpch-mainz.gwdg.de> includes the published chemical analyses of samples from Oceanic Islands, Convergent Margins, and Large Igneous Provinces. As a whole, the database comprises about 77,000 whole-rock, 35,000 mineral and 3,000 inclusion analyses published in about 2,800 papers (status Sept. 2001). For the individual tectonic settings, the following numbers of analyses are available: Oceanic Islands - 25,000 whole rocks, 14,000 minerals, 1,500 inclusions Convergent Margins - 20,000 whole rocks, 9,000 minerals, 500 inclusions Large Igneous Provinces - 32,000 whole rocks, 12,000 minerals, 1500 inclusions. Data entry is complete for samples from Oceanic Islands and Oceanic Large Igneous Provinces. Newly published papers are added regularly. Among the Continental Flood Basalts, which comprise 25,000 whole-rock and 12,000 mineral analyses, large and nearly complete datasets are available for the Columbia River, Deccan, Karoo, Paran, and Siberian Plateau Basalts. Data for Convergent Margins have been added to the database most recently. The database includes, for instance, for the Honshu Arc 3,300, for the Izu-Bonin Arc 1,550, for the Mariana Arc 1,800, for the Kurile Arc 1,400, for the Aleutian Arc 1,500, for the Cascades 500, for the Andes 1,600, for the Lesser Antilles 1,100, and for the Tonga Arc 1,400 whole-rock analyses. For many localities, huge numbers of analyses (more than 2000) are included in the GEOROC database. The selection and compilation of such substantial datasets proved to be difficult and time-consuming when using the web interface of the database. Therefore, we are building precompiled datasets that include all published whole-rock analyses and a fixed set of location and sample metadata for the respective locations. These precompiled datasets are stored as Excel files and can be downloaded easily and rapidly. If multiple element analyses exist for a sample, these are compiled according to specific rules. These rules consider the method of analysis as well as the year of publication.

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V11B-01; EOS, Trans. AGU, 82 (47), 1273

Mass Flux of Continental Material at Cenozoic Subduction Zones--New Global and Trench-sector Calculations Using New Geological and Geophysical Observations

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INTRODUCTION: A decade ago, then available geophysical and geological data implied that more than 65 percent of ocean floor sediment entering most subduction zones (SZ) accompanied the oceanic crust to the mantle (= sediment subduction or SS). The underthrusting slab also eroded the margin's crustal framework and conveyed this material to the mantle (= subduction erosion or SE). Globally, the mass of continental material recycled to the mantle was estimated at 1.3-1.8 km³/yr (SS. = 0.7 km³ + SE = 0.6-1.1 km³).

SEDIMENT SUBDUCTION: New and enhanced seismic reflection data, new drilling observations, and reevaluation of older information stress that the efficacy of SS is higher than earlier assessed. In detail, it appears that 100 percent SS occurs at non-accreting margins (19,000 km), at least 80 percent at accreting margins (16,000 km) where small to moderate size accretionary prisms (width=5-40 km) are forming, and 40-45 percent where larger prisms are accumulating (8,000 km). At Cenozoic SZs (~43,000 km), it is now estimated that the long-term (i.e., >10 Myr) rate of SS is at least 1.0 km³/yr (solid volume). SUBDUCTION EROSION: New and reassessed seismic, drilling, submersible, coastal mapping and arc-retreat observations suggest a higher long-term rate of SE than formerly estimated at 30 km³/Myr / km of trench. We now estimate that, except perhaps where large accretionary bodies are forming, the long-term rate of forearc erosion averages at least 40 km³/Myr (range = 28-62), which corresponds to a global recycling rate of 1.4 km³/yr. The matching average rate of landward truncation of the submerged forearc is 2.5 km / Myr (range = 1.8-4.2). SUMMARY: The late Cenozoic rate at which continental crust is recycled at SZs is currently estimated at 2.4 km³/yr (ss=1+ se=1.4) ± 25 percent, which is basically that now approximated for arc magmatic additions. It can thus be inferred that at Cenozoic SZs rates of crustal addition and recycling have been in general balance. This quasi-stasis may be applicable to the Phanerozoic.

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V21C-0996; EOS, Trans. AGU, 82 (47), 1304 (POSTER)

Clastic Intrusions and Chemosynthetic Paleocommunities in the Cretaceous-Paleocene Great Valley Forearc, Panoche Hills, CA: Fossil Evidence for Prolonged Subduction-Driven Fluid Expulsion

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Fossiliferous 'calcareous layers' are well known but hitherto poorly understood components of the dominantly siliceous Dos Palos Shale Member of the Moreno Fm. in the western San Joaquin Basin. Our preliminary reevaluation of macrofossils in the southern Panoche Hills suggests that the anomalous carbonates are authigenic remnants of a Paleocene fluid seep system. Three principal paleontologic features support this interpretation: 1) isolated carbonate mounds and lenses comprise a volumetrically insignificant portion of the Dos Palos Shale but contain virtually all of its macrofossils, 2) macrofossils are clearly autochthonous, and 3) the low diversity 'core macrobiota' in the carbonates consists of infaunal and epifaunal invertebrates characteristic of chemosynthetic communities; vestimentiferan? and serpulid tube worms, solemyid and lucinid bivalves (including *Lucina sp.*), and cerithiacean gastropods are key faunal elements. Similar taxa are reported from other paleoseep localities, including several in the Great Valley. Additional seep indicators in the carbonates include intensive bioturbation, microbial mats, fluid vents, faunal zonation, and geochemistry consistent with biogenic and thermogenic methane sources. Also, sandstone intrusions below the carbonate horizon appear to delineate the subsurface plumbing of the seep system. Seep carbonates are irregularly distributed over at least 45 vertical meters of section in the upper Dos Palos Shale, first appearing approximately 100m above the K/T boundary. They are abundant in this stratigraphic interval along at least 5km of exposure, signifying a prolonged episode of vigorous early Tertiary seep activity. This episode significantly extends the record of subduction-driven fluid expulsion and chemosynthetic paleocommunities in the Great Valley forearc basin. Its timing also makes it tempting to speculate that the paleoseeps functioned as important ecological oases in the forearc region following the terminal Cretaceous extinction.

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V21C-0993; EOS, Trans. AGU, 82 (47), 1303 (POSTER)

Helium and Carbon Relationships in Geothermal Fluids From the Central American arc in Costa Rica

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A fundamental aim of arc-related studies is to quantify the flux of elements from the various subduction zone reservoirs: a) the mantle wedge, b) the overlying arc crust through which the magmas erupt and c) both the oceanic basement and sedimentary veneer of the subducting slab. In the case of estimating the CO₂ mass balance at convergent margins, one approach has been to couple CO₂ and He measurements (isotopes and relative abundances) which allows both identification and quantitative assessment of the various contributors to the magmatic output. The Central American arc presents a unique opportunity to consider the He-C approach given prior studies which show dramatic variations in the angle of subduction, the amount and type of sediments subducted and the crustal thickness. The Costa Rica subduction zone is particularly intriguing due to the pronounced steepening of the down-going slab to the north and the occurrence of carbonate rich sediments on the down-going plate. Here, we report ³He/⁴He ratios, He, Ne, and CO₂ abundances as well as δ¹³C values for volatiles from the volcanic output along the Costa Rican segment utilising fumaroles, geothermal wells, water springs and bubbling hot springs. The results from our study show the following: 1) ³He/⁴He ratios of the southern volcanoes (Turrialba, Irazu and Poas) are slightly higher (6.9-8.1 R_A) than those of Miravalles and Rincon de la Vieja in the north (5.1-6.8 R_A), 2) water spring samples show poor preservation of magmatic gases (low ³He/⁴He; very high CO₂/³He) relative to other sampling media, 3) CO₂/³He ratios range from 9.9-27 x 10⁹ in the south to 13-78 x 10⁹ in the north, and 4) δ¹³C values trend from isotopically heavier values in the north ~ -1.0 ‰ at Rincon de la Vieja) to lighter more MORB-like values in the south ~ -6.1 ‰ at Poas volcano). The He-CO₂ relationships are consistent with a large input of marine carbonate/limestone carbon to magma sources in Costa Rica. The average ratio of CO₂ derived from carbonate/limestone vs. subducted sediment is 11 vs. 8 for Guatemala (see previous abstract) and 5 for arcs worldwide. Our results therefore support geochemical and geophysical evidence which suggests that most of the uppermost (organic-rich) sediments on the slab subducting beneath Costa Rica are scraped off in the forearc region of the subduction zone or are underplated before reaching the magma generation zone.

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V21C-1000; EOS, Trans. AGU, 82 (47), 1305 (POSTER)

Behavior of Subducting Sediments Beneath an arc Under High Geothermal Gradient: Implications for Progressive Continental Growth

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In order to evaluate the role of sediment subduction in the magma genesis in the Setouchi volcanic belt, SW Japan, the bulk rock compositions of both pelagic sediments from the Philippine Sea (GDP 15-12) and trench-filled sediments from the Nankai Trough (DSDP site 582) were determined. The incompatible element concentrations, particularly Pb, Ba and Th, of these pelagic sediments are much higher than those of terrigenous sediments. Mixing calculations for Pb/Sr, Ba/Sr and Th/Zr ratios indicate that terrigenous rather than pelagic sediments played a major role in producing the magmas in the Setouchi volcanic belt. Further, if a reaction between slab-derived melt and mantle was taken into account, Pb/K₂O and Pb/Rb ratios on the MgO variation diagrams also suggest a similar contribution. The

relatively minor presence of pelagic sediment would not only suggest that the small amounts of pelagic sediment on the young slab but also suggest that crustal material can not recycle back into the upper mantle because higher K₂O concentration of the pelagic sediments facilitate the production of large quantities of hydrous phases (mica) indicating higher degree of partial melting of pelagic sediments. Thus, most of sediments, especially incompatible elements, will be consumed to produce new continental crust via arc magmatism.

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V11B-10; EOS, Trans. AGU, 82 (47), 1275

Carbon and noble gas composition of the Central American Volcanic Arc: Implications on global recycling of subducted carbonates.

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Four geothermal fields in Central America were sampled for gas composition in order to determine the degree to which mantle and subducted components contribute to the present CO₂ flux. Subducted marine carbonates contribute 86% to 98% of the carbon dioxide emitted by volcanoes of the Central American arc system, based upon $\delta^{13}\text{C}$ values and CO₂/³He ratios. Previous investigations from active arc systems around the world report similar proportions of recycled carbon dioxide. The highest proportion of carbonate recycling in Central America occurs in the Costa Rican segment of arc, presumably due to higher temperatures of the subducting slab. Although the subducted sediment column along the Middle America Trench system is rich in carbonate lithologies, carbon-helium relationships require that only 0.3% to 3.3% of the subducted carbon is released through devolatilization beneath the arc, roughly an order of magnitude less than other arc systems which generally contain a higher water content and lower carbon content. The lack of extensive decarbonation along the subducting Central American slab is due to insufficient mineral-bound water in the subducted sediments, as well as insufficient temperatures beneath the volcanic axis. When differences between Central America and other arc systems are accounted for, the total global flux of carbon from island arcs is only 0.18×10^{12} mol/a. This is much less than previous estimates, yet balances the flux of carbon dioxide gas at mid-ocean ridges and the return of subducted carbon to the mantle. Given the low flux of subducted carbon from active arc volcanoes, global models which consider arc volcanism as a substantial source of exospheric carbon should be reconsidered.

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V21C-1001; EOS, Trans. AGU, 82 (47), 1305 (POSTER)

Geochemical Characteristics of Sediments Potentially Subducted in Western and Eastern Philippines

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One key ingredient in the subduction factory is the composition of sediment input. Here we present new major/trace element and Sr, Nd and Pb isotopic composition of sediment columns being subducted at the western (Celebes Sea Basin - ODP767 and SE Sulu Sea Basin - ODP768) and eastern (West Philippine Sea Basin - DSDP291) margins of the Philippines. Combined with previous major and trace element analyses (Brass et al., Sci. Res. ODP 124, 1991), the new data were used to estimate mass-weighted averages for major lithostratigraphic units and whole sediment columns following the procedure of Plank and Langmuir (Chem. Geol. 145, 1998). Results indicate that the basin sediments have different trace element and isotopic characteristics consistent with the nature of their respective lithologies. Sediments at ODP767 (787 m) and 768 (~1047 m) are dominantly continental and volcanoclastic whereas those at DSDP291 (~118 m) are mainly pelagic. The bulk sediments at all sites have trace element patterns almost similar to arc lavas. These are enriched in Rb, Ba, K, Pb and LREE relative to HFSE and HREE. However, Sr is not enriched at ODP767 and 768 and only slightly enriched at DSDP291. The compositions of bulk sediments at the western basins are similar. Compared with that at the eastern basin, these have higher Rb, K, Nb, Zr and Ti but lower Ba, Sr, Pb and P and Y. All bulk sediments display a small negative Eu anomaly. DSDP291 bulk sediment, however, is more enriched in REE than its western counterparts except for Ce, which shows a distinct negative anomaly similar to other sediments subducted in Tonga and the Marianas. The isotopic ratios of pelagic samples from DSDP291 exhibit a narrower and distinct range (e.g., ⁸⁷Sr/⁸⁶Sr = 0.707413-0.709090) compared with data from ODP767 and 768, which reflect volcanoclastic and continental end

member values (0.704986-0.715278). The eastern margin of the Philippines is non-accreting, hence, it could be assumed that the whole sediment section similar to that at DSDP291 is subducted. In contrast, the presence of accretionary prisms at the western margin suggests that part of the incoming sediments is not subducted. If only the basal section of the sediment columns at ODP767 and 768 gets subducted, the chemical characteristics of sediment inputs at the western margin will differ. Although the two sites are dominated by the same lithological types, basal sediments at ODP767 are continental whereas those at ODP768 are volcanoclastic.

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V21C-0985; EOS, Trans. AGU, 82 (47), 1301-1302 (POSTER)

The Systematics of Boron Isotopes in Izu Arc Front Volcanic Rocks

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We studied the processes of fluid release from the subducting slab beneath the Izu arc volcanic front (Izu VF) by measuring B concentrations and B isotope ratios of the Neogene fallout tephra (ODP Site 782A). The B isotopes were measured by secondary ion mass spectrometry (SIMS) of matrix glasses and plagioclase-hosted melt inclusions (=glasses) on samples that have been previously analysed for major and trace elements as well as radiogenic isotopes. The tephra glasses have high B abundances (~10-60 ppm) and high $\delta^{11}\text{B}$ values, ranging from +4.5 ‰ to +12.0 ‰, extending the previously reported range for Izu arc front volcanic rocks ($\delta^{11}\text{B} = +7.0$ to 7.3 ‰). The glasses show strikingly negative correlations of $\delta^{11}\text{B}$ with Nb-normalized large ion lithophile elements (LILE). These correlations cannot be explained by mixing of two separate slab fluids that originate from the subducting sediment and the subducting basaltic crust, respectively (model A). Two alternative models (model B and model C) are presented. Model B suggests that the inverse correlations are inherited from the altered oceanic crust since the crust shows a systematic decrease of B and LILE with increasing depth (from layer 2A to layer 3) that is paralleled by an increase in $\delta^{11}\text{B}$ (from ~ 1 ‰ to >10 to +24 ‰). Model C explains the correlations by mixing of variable amounts of a low- $\delta^{11}\text{B}$ (~ +1 ‰) slab-derived fluid with a high- $\delta^{11}\text{B}$ (~ +14 ‰), B-rich (1-2 ppm) mantle wedge. The infiltration of the wedge with heavy ^{11}B mostly likely occurred during slab dehydration beneath the forearc, and reflects the preferred partitioning of $\delta^{11}\text{B}$ into fluids. A decreasing flux of high- $\delta^{11}\text{B}$, wedge-derived B with increasing depth could explain the decreasing B and $\delta^{11}\text{B}$ observed in across-arc transects, without requiring a general decrease of fluid flux from the subducting slab. Cyclic, short-term fluctuations on the scale of a few million years predominate at the Izu VF since 15 million years. This suggests that fluctuations of the slab fluids are a natural background 'noise' of slab dehydration rather than a driving force for the well-known global periodicity of arc volcanism during the Neogene.

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V21C-0990; EOS, Trans. AGU, 82 (47), 1302-1303 (POSTER)

Methods of Fluid and Geochemical Flux Measurement and new Insights From Seep Studies at the Eel River Margin

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Improving current estimates of elemental fluxes from sediments into overlying ocean water has been an ongoing goal in geochemistry. Improved estimates of elemental fluxes will provide better constraints on the geochemical cycles of these elements. Although there will always be a large amount of error associated with such calculations, because of the small number of measurements made in such an extensive area (e.g., ocean basins or continental margins), major refinements in current flux estimates are still necessary. The most widely used method to estimate fluxes across the sediment-water interface has been to model porewater geochemical gradients. Although, this method has been widely accepted as an accurate way to calculate such fluxes, the major problems with this method lie in the limited areal extent of appropriate cores and the lack of any information on temporal variability. However, with the development of the Chemical and Aqueous Transport (CAT) meters, a new tool has been developed to analyze both the spatial and temporal variability in aqueous and chemical flux. New measurements at methane seeps on the Eel River margin, northern California, further extend our understanding of the

hydrology and chemistry of seep environments. Time series aqueous and chemical flux measurements were made with the CAT meters on microbial mat, clam, and non-seep sites in an 800 m² area over a seven month period. Chemical profiles were also done on tube core pore fluids both before and after the deployments. In this poster we show comparisons of the flux data obtained from CAT meters and push cores to 1) evaluate the potential usefulness of using flow meters as an easier alternative for obtaining elemental flux estimates, and 2) also to compare the time series fluid flow rates with the steady-state flux estimate obtained from modeling of interstitial water chemical gradients.

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V12E-10; EOS, Trans. AGU, 82 (47), 1293-1294

Lithium Budget and Isotopic Characterization of Materials Entering the Izu-Mariana Subduction Zone

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We present lithium-isotopic data for alteration products entering the Izu-Mariana subduction zone, as part of a larger study of the Li flux balance across the margin. Sediments and altered basaltic crust samples were collected during ODP Leg 185 at Site 801C, Pigafetta Basin outboard of the Mariana arc, and Site 1149, Nadezhda Basin outboard of the Izu arc. Dramatic variability between the two sites has been observed in sediment lithology and basement petrology, architecture and alteration styles. This study will address the extent to which these factors affect the along-strike heterogeneity of the Li-content and isotopic ratios of subducting material. A small, preliminary, data set shows that whole rock samples (altered alkali and tholeiitic basalt, altered basalt rich in smectite, or in early or late stage celadonites etc.) are characterized by Li concentrations ranging from 8 ppm to greater than 30 ppm and $\delta^6\text{Li}$ values of -3‰ to -14‰. Many weathered samples appear to fall on a mixing line first observed by Chan et al. (EPSL, 1992, 108, 151-160) between fresh MORB and authigenic phyllosilicates in equilibrium with seawater. Deviations from this trend are observed for alkalic basalts and late stage celadonitic samples. The alkalic basalts may possess greater initial Li concentrations than tholeiitic basalts, but the intrusive nature of the alkali basalts into sediments must contribute to their enhanced Li content and elevated $\delta^6\text{Li}$ values. Preliminary results suggest that early celadonites are characterized by Li-systematics similar to smectite, while low Li-concentrations and extreme isotopic ratios characterize late-stage celadonites. $\delta^6\text{Li}$ depletions may be the result of higher temperature fluids, but considered in light of low Li concentrations we suggest that this mineral phase formed in equilibrium with previously reacted, relatively low-temperature seawater component.

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V11B-07; EOS, Trans. AGU, 82 (47), 1274

Clastic Intrusions and Chemosynthetic Communities in the Cretaceous-Paleocene Forearc, Panoche Hills, CA: Structural Context of a Linked Fluid System

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Modern cold-seep deposits containing carbonate structures and chemosynthetic organisms are well documented but do not expose the underlying "plumbing" systems. In the Panoche Hills, CA, outstanding exposures of an intact, Cretaceous-Tertiary cold-seep system reveal both subsurface plumbing and the surface seepage system. The Panoche Hills occur along the western margin of the Great Valley forearc basin in central California. Regional dips in the Cretaceous-Tertiary section are basinward 35°-45° east. The base of this seep-system is defined by a network of interconnected sandstone intrusions propagating upward through the shale-rich Moreno Formation as dikes and sills. Previous investigations have indicated that the source of these intruded sands is the underlying Panoche Group sandstones. The sandstone intrusions cut through approximately 500-600 meters of section and are interpreted as being permeable pathways for fluids and gasses that fed the overlying seep-related carbonates and chemosynthetic organisms. Coeval dikes and sills suggest similar magnitudes of

principal stresses. A NW-SE dike maxima suggests NE-SW extension. These carbonate seep-structures contain micro and macrofossils common to cold-seep environments. The seep related organisms and carbonates are present only within a 45 meter-thick stratigraphic horizon near the upper boundary of the Moreno Formation. This stratigraphic horizon begins generally less than 100 meters upsection from the terminous of the sandstone intrusions. These exposures define a fluid system that is, in total, about 800 m thick and that uniquely ties subsurface sandstone intrusions to carbonate-dominated cold seeps, Fluids were probably derived from an underlying overpressured section that thickened eastward towards the center of the forearc basin. Thus, the system was probably driven by subduction-imposed forearc basin architecture.

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V21C-0983; EOS, Trans. AGU, 82 (47), 1301 (POSTER)

LILE-Signatures of IAB: Phengite Decomposition Within the Slab Versus Fractional Crystallisation of Phlogopite in the Wedge

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The large ion lithophile (LIL) elements K, Rb and Cs are important geochemical tracers for subduction zone environments. Phengite is proposed to be the main host of LILE in metasedimentary and metabasaltic blueschists and eclogites. Additionally, it has been proposed that metasomatic phlogopite crystallisation should occur at the base of a mantle wedge overlying the subducting slab as the result of infiltration of slab derived fluid and should therefore play an important role in determining the LILE-characteristics of IAB. Based on recently determined K-Rb- and K-Cs-exchange coefficients between phengite and fluid by Melzer and Wunder (2000) (K_D (Rb-K): 1.62 ± 0.10 at 2 GPa/600°C and 1.84 ± 0.15 at 4 GPa/700°C and K_D (Cs-K): 0.22 ± 0.06 at 2 GPa/600°C and 0.37 ± 0.10 at 4 GPa/700°C), and between phlogopite and fluid by Melzer and Wunder (2001) (K_D (Rb-K) (all at 800°C): 1.71 ± 0.06 at 0.2 GPa, 2.73 ± 0.10 at 2 GPa and 2.76 ± 0.15 at 4 GPa and K_D (Cs-K) (all at 800°C): 0.57 ± 0.05 at 0.2 GPa, 0.73 ± 0.09 at 2 GPa and 0.93 ± 0.26 at 4 GPa), variations of LILE-ratios within IAB are modeled and discussed (i) applying a model of perfect Rayleigh fractionation for continuous breakdown of phengite during subduction and (ii) applying ion exchange processes within an fluid-infiltrated one-dimensional phlogopite-containing chromatographic rock column representing a metasomatised mantle wedge. From these modeling and comparison to IAB LILE signatures it seems obvious, that (i) varying alkali ratios for IAB as a function of slab depth can nicely be explained by the LILE-fractionation between fluids and phengite, however, (ii) assuming significant amounts of metasomatically formed phlogopite within the mantle wedge, would lead to Cs/K-ratios lower than those observed for IAB. The results of this study indicate, that mantle metasomatism combined with phlogopite formation beneath island arcs has only a minor to negligible effect on the LILE-signature of IAB. This would suggest, that the subduction of slabs with high phengite abundance may control the LILE-composition of IAB, rather than a metasomatised mantle wedge. Melzer, S. and Wunder, B. (2000): Island-arc basalt alkali ratios: Constraints from phengite-fluid partitioning experiments. - *Geology*, 28: 583-586. Melzer, S. and Wunder, B. (2001): K-Rb-Cs partitioning between phlogopite and fluid: experiments and consequences on the LILE signatures of island arc basalts. - *Lithos*, (in press).

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V21C-0987; EOS, Trans. AGU, 82 (47), 1302 (POSTER)

Boron Isotopic Compositions of Mud Volcano Fluids in Taiwan Accretionary Prism

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Boron and B isotopes are sensitive diagnostic tracers of sediment de-watering in subduction zones. More than 20 mud volcano fluids collected along two major geological structures, the Chishan fault (CHF) and the Gutingkeng anticline (GTKA), in the southwestern Taiwan were analyzed for B and $\delta^{11}\text{B}$, as well as other geochemical constituents. These fluids are characterized by high chloride contents, up to 420 mM, suggestive of seawater origin. The GTKA fluids show high Cl, Na, K, Ca, Mg and NH_4 , but low SO_4 concentrations. In contrast, the CHF fluids are much less saline (~100 mM) with anomalous heavy oxygen isotopic compositions (up to 6.5 ‰). The results can be understood in terms of mixing between original sedimentary pore waters and fluids affected by clay dehydration released at depth. The Taiwan mud volcano fluids contain high concentration of B, up to ~12x seawater value, and is strongly enriched in heavy

isotope ($\delta^{11}\text{B}$ heavier than 40 ‰), a possible result of smectite illitization at depth. Pore fluids with similar B and $\delta^{11}\text{B}$ characteristics have been recovered during DSDP/ODP drill holes in the Nankai Trough, Japan and the Barbados Ridge complex. The preliminary results indicate that the return flux of B by mud volcano de-watering fluids in convergent margins may have significant implication for B chemical budget in the ocean.

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Light Li Isotopic Composition in Subducting Slabs: Evidence From Alpine Eclogites

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As the Li isotopic compositions of various regions of the Earth become known, a mass balance problem is emerging: the $\delta^7\text{Li}$ value of oceanic mantle-derived basalts is 3-5 ‰, which is thought to be representative of the upper mantle. Oceans and sediments are heavier than this (32 and 9-23 ‰, respectively). Arc lavas have variable $\delta^7\text{Li}$, ranging from 2 to 11 ‰, with the heavier values interpreted as resulting from addition of a heavy, slab-derived component (sediments or sea-water altered oceanic crust). Few rocks have been measured with light $\delta^7\text{Li}$ values. If the heavy $\delta^7\text{Li}$ in arc lavas derive from slab fluids, it is possible that the dehydrated slab is isotopically light, and provides the light Li reservoir needed to balance the heavy surface rocks to make a bulk Earth $\delta^7\text{Li}$ of ~-4. High pressure metamorphic rocks from Trescolmen (Swiss Alps) are an analogue to subducted oceanic crust. Eclogites from this locality have geochemical characteristics of MORB that experienced low temperature hydrothermal alteration (Zack et al., 2001, J. Petrol.). Surrounding eclogite-facies garnet mica schists were once pelitic sediments. Although tectonic reconstructions place these rocks in a passive margin setting, they nevertheless experienced metamorphic conditions similar to those in a subducting slab (ca. 650°C and 2 GPa). Li concentrations in the eclogites are all significantly higher than MORB, implying overprinting by post-magmatic processes (sea-floor alteration, metamorphism and exchange with the surrounding metasediments). Interestingly, $\delta^7\text{Li}$ values range from -10 to 5 ‰, with all but 2 samples having $\delta^7\text{Li}$ values <0. The uniquely light values for these samples cannot be explained by sea-floor alteration or eclogite-sediment exchange and must be related to the dehydration reactions accompanying high pressure metamorphism. These data provide the first evidence that the Li isotopic compositions of subducted slabs may be light, and thus has implications for storage of slabs in the mantle and their subsequent incorporation into mantle plumes.

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Volatile Chemistry and Fluxes Along the Costa Rican Segment of the Central American Volcanic Arc

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A systematic study of magmatic volatile output was undertaken for five volcanic centers in Costa Rica. The study was directed at quantifying the volatile output along this segment of the Central American volcanic arc with the aim of addressing the general question of volatile mass balance at subduction zones. Both direct sampling and remote sensing techniques were utilized. Direct sampling involved collecting gases from fumaroles, bubbling hot springs, and geothermal wells. Remote sensing was performed using the stationary COSPEC technique to measure SO_2 flux. Gas samples have been analyzed for major chemical species, and helium, carbon and nitrogen isotopes. COSPEC measurements were taken at Arenal and Poas volcanoes. SO_2 flux is 180 tons/day and 8 tons/day, respectively. Fumarole and COSPEC data can be combined to determine an annual volatile flux for individual volcanic centers. For example, fluxes for Poas (mol/yr) are: SO_2 : 1.89×10^{10} , H_2S : 3.14×10^8 , He: 3.14×10^8 , ^3He : 1.92, N_2 : 6.62×10^7 , CH_4 : 3.42×10^4 . We will discuss how these figures can be utilized to derive the total volatile flux for the Costa Rican segment making assumptions about the total volume of magma degassing. In addition to total fluxes, it is essential to resolve volcanic output into contributory input sources. N_2/He and N-isotopes can be particularly useful tracers in this respect. For the most part, geothermal samples from Costa Rica display typical subduction zone ratios of N_2/He (1300-25,000); however, Poas and Turrialba have significantly lower values. N_2/He values from Poas (~ 150) and Turrialba (~ 775) are more

typical of mid ocean ridge and ocean island volatiles. Nitrogen isotope evidence corroborates these findings. The $\delta^{15}\text{N}$ of Poas is -1.3‰ , indicating a predominant mantle component with very little sediment addition ($\delta^{15}\text{N}$ in the upper mantle is -3‰ , and $\delta^{15}\text{N}$ in marine sediments is $+7 \pm 4\text{‰}$). $\delta^{15}\text{N}$ of Turrialba is $+0.7\text{‰}$, indicating sediment addition intermediate between that of Poas and other Costa Rican volcanoes, e.g. Irazu which has a $\delta^{15}\text{N}$ of $+2.5\text{‰}$ and an N_2/He ratio of 1400. The coupling of N_2/He ratios and nitrogen isotopes suggests that sedimentary nitrogen from the subducted slab contributes substantially to the nitrogen output at Irazu but to a much lesser extent at Turrialba and Poas. Possible causes for the discrepancies in sediment input along the arc include offscraping from the subducting slab or ponding in the forearc region.

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