

the use of a dimensionless parameter,  $\Psi_D$ .  $\Psi_D$  defines a sequence of four flow morphologies (spiny, lobate, leaved, and no-crust), associated with progressively higher effusion rates, lower cooling rates, and lower yield strengths. In this study, a new series of 100 experiments was conducted to determine how slope affects the morphology of lava domes. Adding slope allows us to better constrain the range of  $\Psi_D$  values that could have produced a particular morphology, thus leading to more accurate estimates of emplacement conditions. Once a range of  $\Psi_D$  values for a dome is determined, its yield strength or effusion rate can be calculated based on other available information. In the case of active domes, the effusion rate can be used to calculate yield strength, while for prehistoric domes an assumption of yield strength is used to determine the effusion rate. For active domes we estimate yield strengths from 0.8 to  $5.0 \times 10^5$  Pa; effusion rates for prehistoric domes are estimated to range from 0.1 to  $300 \text{ m}^3 \text{ s}^{-1}$ . These estimates compare well with measured yield strength values of 1.0 to  $2.0 \times 10^5$  Pa and effusion rates of 0.1 to  $40 \text{ m}^3 \text{ s}^{-1}$  from historically active domes. Having more precise field-based estimates of the range of yield strengths and effusion rates of silicic lava domes can help constrain their advance rates and potential for explosive collapse.

V21B-0976 0830h POSTER

**Experimental Constraints on Degassing and Permeability in Volcanic Conduit Flow**

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An often-used assumption in modeling of volcanic conduit flow is that equilibrium degassing occurs throughout magma ascent, causing a rapid increase of the decompression rate shortly before the magma becomes permeable or fragments. This increase occurs because volatile exsolution increases melt viscosity, which causes flow pressure to vary. The highest decompression rates are predicted when equilibrium bubble growth occurs. If equilibrium is not maintained, the density decrease and viscosity increase caused by bubble growth are diminished, hence reducing decompression rates and minimizing flow acceleration. A second limit on possible ascent rates is if the bubbly liquid becomes permeable and loses gas from its bubbles, thus reducing porosity.

To assess the maximum decompression rates that guarantee equilibrium degassing, we have conducted experiments on hydrated natural rhyolitic glass at high pressure and temperature, which were then decompressed isothermally following various time-variant rates. After an initial pressure drop, which ensured the presence of a bubble population to avoid problems related to nucleation kinetics, we decompressed the samples at rates that increased with lower pressure. For each increment, the highest rate that maintained equilibrium was determined. We find that equilibrium degassing can only be maintained at decompression rates much lower than those predicted theoretically.

We also conducted experiments on the same hydrated natural glass to determine the onset of permeability. Using our previous results, we decompressed the samples from high pressure at a rate that ensures equilibrium degassing and quenched them at various lower pressures. Deviation of the porosity value of the quenched samples from the expected equilibrium value indicates the onset of permeability. Initial results show that permeability occurs between 55 and 64% porosity when the decompression rate is 0.025 MPa/s. At this porosity range, the projection of experimental decompression rates is 20 times lower than the theoretical rates. Both this significant difference and the porosity range in which permeability occurs suggest that bubble growth and permeability laws must be included in conduit flow models.

V21B-0977 0830h POSTER

**Directly Linking Magma Chamber Dynamics and Crystal Zoning: The Wavelet Based Correlation (WBC) of Crystal Populations**

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Igneous rocks often show evidence for repeated mixing of distinctive magmas and/or redistribution of within-chamber chemical domains. This is expressed by hybridization trends and changes in isotope ratios at the outcrop and crystal scale, composite dikes, crystal transfer fabrics, and flow structures. We will demonstrate the use of Wavelet Based Correlation (WBC) of crystal zoning populations as a means of 'inverting' for the schedule of magma generation, mixing, crystal growth, and eruption in a structured time-stratigraphic framework. WBC is a new tool that uses the Continuous Wavelet Transform (CWT) to characterize zoning profiles, correlation coefficients of select sets of zoning features to describe crystal similarity, and cluster analysis of correlation coefficients to group crystals into populations. The integrating concepts are the notions of spatial proximity, both within and between samples, of statistical groupings of crystals (clusters) that have experienced a similar thermo-chemo environment at some previous time, and their dispersal and gathering to form new families of clusters. This allows for the construction of a crystal-based phylogeny for the magmatic system where mixing and fractionation events can be ordered and recognized as acting in sequence or in parallel, and the vigor and duration of a mixing event can be inferred from particle dispersal, gathering and zoning.

CWT decomposition allows direct comparison of specific components of crystal zoning patterns because the locations of individual spectral features are preserved. For example, boundary layer diffusion growth effects, rapid mixing events and pressure changes tend to have small scales. Using WBC, the data can be windowed in scale space to isolate small-scale details in the profile independent of all other scales of features in the profile. Conversely, large-scale features such as fractional crystallization trends can be isolated in the zoning signal. WBC can provide a statistical binding point between geochemical and dynamic studies of igneous systems.

V21B-0978 0830h POSTER

**Melt Viscosity at the Glass Transition During Volcanic Processes: Predictions From Calorimetric Studies**

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The viscosity of volcanic melts at the glass transition has been determined for 11 compositions ranging from basanite to rhyolite. The temperature-dependence of viscosity, together with the cooling rate dependence of the glass transition, permits the calibration of the value of the viscosity at the glass transition at a given cooling rate for each melt.

We have applied micropenetration techniques to determine viscosities of supercooled melts. In addition, glass transition temperatures have been obtained by rate heating glass samples to supercooled liquid conditions using differential scanning calorimetry. The activation energies obtained from calorimetry and viscometry are identical for each melt composition investigated. This confirms that a simple shift factor can be used for each in order to determine the viscosity at the glass transition for a given cooling rate in nature.

The results of this study indicate that there is a subtle but significant compositional dependence of the shift factor by a factor of 10 (in log terms) from 10.8 for rhyolites to 9.6 for basanites. The composition-dependence of the shift factor is presented here in terms of a compositional parameter, the mol% of excess oxides. Using this parameterisation, we obtain a non-linear dependence of the shift factor upon composition that matches all 11 observed values within error. The resulting model permits the prediction of viscosity at the glass transition, during the cooling of glassy volcanic rocks to within 0.1 log units.

The resultant shear viscosities vary over five orders of magnitude for published cooling rates in the literature between tens of Kelvins per second and few Kelvins per day across the glass transition.

V21B-0979 0830h POSTER

**Inferring Volcanic Degassing Processes From Vesicle Size Distributions**

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Both power law and exponential vesicle size distributions (VSDs) have been observed in many different types of volcanic rocks. We present results of laboratory analogue experiments, of the type pioneered by Brad Sturtevant, which reproduce these observations, and use experimental results and computer simulations to show that the distributions can be interpreted as the product of continuous bubble nucleation resulting from non-equilibrium degassing. This ongoing nucleation causes the bubbles to evolve through an exponential size distribution into a power law size distribution as nucleation and growth progress. The process of continuous nucleation is a mechanism whereby the volcanic system maintains near-equilibrium in the case of rapid depressurisation and slow volatile diffusion.

V21C MC: Hall D Tuesday 0830h

**Trench to Subarc: Diagenetic and Metamorphic Mass Flux in Subduction Zones (GERM/MARGINS Subduction Factory Session) III (joint with OS, T, MR)**

**Presiding:** G E Bebout, Lehigh University; J B Martin, University of Florida; T Elliott, University of Bristol

V21C-0980 0830h POSTER

**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 worlds 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.

## V21C-0981 0830h 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 plagiophyric basalts of low-K<sub>2</sub>O 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 SiO<sub>2</sub>, 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.

## V21C-0982 0830h 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 ( $\Delta$ FMQ 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), Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO, and Na<sub>2</sub>O (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 Mssbauer (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.

## V21C-0983 0830h 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):  $1.62 \pm 0.10$  at 2 GPa/600°C and  $1.84 \pm 0.15$  at 4 GPa/700°C and  $K_D$ (Cs-K):  $0.22 \pm 0.06$  at 2 GPa/600°C and  $0.37 \pm 0.10$  at 4 GPa/700°C), and between phlogopite and fluid by Melzer and Wunder (2001) ( $K_D$ (Rb-K) (all at 800°C):  $1.71 \pm 0.06$  at 0.2 GPa,  $2.73 \pm 0.10$  at 2 GPa and  $2.76 \pm 0.15$  at 4 GPa and  $K_D$ (Cs-K) (all at 800°C):  $0.57 \pm 0.05$  at 0.2 GPa,  $0.73 \pm 0.09$  at 2 GPa and  $0.93 \pm 0.26$  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).

## V21C-0984 0830h 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 metabasaltic 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.

## V21C-0985 0830h 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  $\sim 1\text{‰}$  to  $>10$  to  $+24\text{‰}$ ). Model C explains the correlations by mixing of variable amounts of a low- $\delta^{11}\text{B}$  ( $\sim +1\text{‰}$ ) slab-derived fluid with a high- $\delta^{11}\text{B}$  ( $\sim +14\text{‰}$ ), B-rich (1-2 ppm) mantle wedge. The infiltration of the wedge with heavy  $^{11}\text{B}$  mostly likely occurred during slab dehydration beneath the forearc, and reflects the preferred partitioning of  $^{11}\text{B}$  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.

V21C-0986 0830h 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  $<1.2\text{ GPa}$ ) and UHP (Lago di Cignana; peak 2.7-2.9 GPa) metasedimentary rocks employing high-precision ( $\sigma_{\text{mean}} = 0.5\text{--}0.8\text{‰}$ ) 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, dravite 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  $+1.6\text{‰}$ , mostly  $-6$  to  $-2\text{‰}$ ), 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  $-15\text{‰}$ ) 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  $+4.5\text{‰}$ ) 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  $-16\text{‰}$  with prograde, high-P/T metamorphism, and rims with clinzoisite and quartz inclusions, lower  $\text{Mg}/(\text{Mg}+\text{Fe}^{+2})$ , and higher  $\delta^{11}\text{B}$  up to  $+4.3\text{‰}$  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  $-9\text{‰}$ ) somewhat lower than that of the initially subducted structurally bound B component in sediment) was stable to depths of  $\sim 90\text{ km}$ . 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 pro-

ducing across-arc trends of decreasing  $\delta^{11}\text{B}$  observed in several arcs.

V21C-0987 0830h 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  $\text{NH}_4$ , but low  $\text{SO}_4$  concentrations. In contrast, the CHF fluids are much less saline (100 mM) with anomalously heavy oxygen isotopic compositions (up to 6.5 permils). 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 permils), 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.

V21C-0988 0830h 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.

V21C-0989 0830h POSTER

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

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Exotic ultramafic blocks within mud-matrix mélange of the Franciscan Complex, CA, preserve a series of metasomatic mineral zones due to the infiltration of  $\text{SiO}_2$ -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.  $\text{SiO}_2$ ), but also include elements generally believed to be immobile in fluids liberated during the devolatilization of subducted material (e.g.  $\text{TiO}_2$ ). 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 serpentine (Srp + Mgt + Chl  $\pm$  relict Cr-Spl) after peridotite. Additional infiltration formed Tlc (Tlc + Chl  $\pm$  relict Cr-Spl) and is the strongest evidence for fluid-mediated addition of  $\text{SiO}_2$ . 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  $\pm$  relict Cr-Spl. The amphiboles appear to buffer  $\text{SiO}_2$  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  $\text{Al}_2\text{O}_3$  were added to the rock in addition to the requisite  $\text{SiO}_2$ . At the final stage of metasomatism preserved, Tr-rich rocks show increases in  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and especially CaO. Separates of Srp from synmetamorphic Srp + Cal veins give Srp  $\delta^{18}\text{O}$  of  $8.23\text{‰}$ , which suggests Srp in equilibrium with metasomatic fluids has this approximate value. Values of Srp  $\delta^{18}\text{O}$  from the ultramafic blocks range from 6.37 to  $8.18\text{‰}$ . 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  $500^\circ\text{C}$ . Intermineral fractionations between vein Cal and vein Srp give slightly lower temperature estimates of  $420\text{--}480^\circ\text{C}$ . 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 mineralogical 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.

V21C-0990 0830h 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 m<sup>2</sup> 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.

#### V21C-0991 0830h 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 (500µm- 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 <sup>40</sup>Ar/<sup>39</sup>Ar 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 <sup>40</sup>Ar/<sup>39</sup>Ar 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 T902Ahost 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.

#### V21C-0992 0830h 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 ~+3.4 permil. Modern surface sediments have highly variable  $\delta^{15}\text{N}_{\text{air}}$ , but most tend to be in the range of +5 to +12 permil. 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 permil.  $\delta^{15}\text{N}$  varies within the uppermost 120 m of site 1149A from +8.2permil 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 permil). 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, with +8.2 permil, values like those of modern surface sediments (cf. Peters et al., 1978; Mizuka et al., 1991; Minorva et al., 1997) to +4.7 permil (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.

#### V21C-0993 0830h 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 CO<sub>2</sub> mass balance at convergent margins, one approach has been to couple CO<sub>2</sub> 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 <sup>3</sup>He/<sup>4</sup>He ratios, He, Ne, and CO<sub>2</sub> abundances as well as  $\delta^{13}\text{C}$  values for volatiles from the volcanic output along the Costa Rican segment utilizing fumaroles, geothermal wells, water springs and bubbling hot springs.

The results from our study show the following: 1) <sup>3</sup>He/<sup>4</sup>He ratios of the southern volcanoes (Turrialba, Irazu and Poas) are slightly higher (6.9-8.1 R<sub>A</sub>) than those of Miravalles and Rincon de la Vieja in the north (5.1-6.8 R<sub>A</sub>), 2) water spring samples show poor preservation of magmatic gases (low <sup>3</sup>He/<sup>4</sup>He; very high CO<sub>2</sub>/<sup>3</sup>He) relative to other sampling media, 3) CO<sub>2</sub>/<sup>3</sup>He ratios range from 9.9-27 x 10<sup>9</sup> in the south to 13-78 x 10<sup>9</sup> in the north, and 4)  $\delta^{13}\text{C}$  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-CO<sub>2</sub> relationships are consistent with a large input of marine carbonate/limestone carbon to magma sources in Costa Rica. The average ratio of CO<sub>2</sub> 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.

#### V21C-0994 0830h POSTER

##### 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<sub>2</sub> 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<sub>2</sub> 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: CO<sub>2</sub>: 1.89x10<sup>10</sup>, H<sub>2</sub>S: 3.14x10<sup>8</sup>, He: 3.14x10<sup>8</sup>, <sup>3</sup>He: 1.92, N<sub>2</sub>: 6.62x10<sup>7</sup>, CH<sub>4</sub>: 3.42x10<sup>4</sup>. 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<sub>2</sub>/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<sub>2</sub>/He (1300-25,000): however, Poas and Turrialba have significantly lower values. N<sub>2</sub>/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 (the  $\delta^{15}\text{N}$  in the upper mantle is -3‰, and  $\delta^{15}\text{N}$  in marine sediments is +7±4‰).  $\delta^{15}\text{N}$  of Turrialba is +0.7‰, 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‰ and an N<sub>2</sub>/He ratio of 1400. The coupling of N<sub>2</sub>/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.

## V21C-0995 0830h 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 N<sub>2</sub>, He, and Ar abundance relationships and N-isotope ratios for 7 volcanic centers in Guatemala to complement ongoing 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 N<sub>2</sub>/He ratios ranging from 2200 to 8100, typical for arc-related fluids. N<sub>2</sub>/Ar ratios (40 - 500) and the high N<sub>2</sub>/He indicate addition of N<sub>2</sub> from subducted sediments or arc crust to a mantle derived component (N<sub>2</sub>/He < 200). The high N<sub>2</sub>/He ratios of Guatemala, are in contrast to the mantle-derived N<sub>2</sub>/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 N<sub>2</sub>/He ratio for Poas is consistent with a more mantle-like  $\delta^{15}\text{N}$  of  $-1.0\text{‰}$ . In Guatemala, the highest <sup>3</sup>He/<sup>4</sup>He ratios (7.6 for Pacaya and 7.3 RA for Fuego) correlate with the lowest N<sub>2</sub>/He ratios (1500 and 2100) and high  $\delta^{15}\text{N}$  values ( $+3.8\text{‰}$  and  $+5.8\text{‰}$ ). Lower <sup>3</sup>He/<sup>4</sup>He ratios for Zunil (4.7 RA) and San Marcos (2.2 RA) correlate with N<sub>2</sub>/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 N<sub>2</sub>/He ratios. This is in contrast to the situation in Costa Rica, where lower N<sub>2</sub>/He ratios and lower  $\delta^{15}\text{N}$  values suggest possible loss of sediment by underplating and where higher <sup>3</sup>He/<sup>4</sup>He indicate only minor crustal contributions to the discharging volatiles.

## V21C-0996 0830h 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 microfossils 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 microbiota 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.

## V21C-0997 0830h 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  $0.55\text{‰}$  and  $\delta^{18}\text{O}_{\text{PDB}} = -5.81\text{‰}$  to  $3.78\text{‰}$ . 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  $-5.54\text{‰}$ , and  $\delta^{18}\text{O}_{\text{PDB}} = -8.45\text{‰}$  to  $-6.26\text{‰}$ . 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.

## V21C-0998 0830h POSTER

### 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 alkaline 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. Intracrustal 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 ulvöspinel/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 Fe-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 exhibit 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.

## V21C-0999 0830h POSTER

### Volcanisms of the Backarc Echelon Seamounds along the Enpo Seamound Chain in the Northern Izu-Ogasawara Arc

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Echelon seamound chains trending ENE-WSW exist in the backarc region of the northern Izu-Ogasawara Arc. The Kan'ei, Manji, Enpo and Genroku seamound chains (from north to south) constitute four especially well documented and investigated examples. These seamound chains formed between 17 Ma and 3 Ma (Ishizuka, 1999). The eastern sections of each seamound chain are over-printed by many small knolls formed by intra arc rifting volcanism after 2.5 Ma (e.g. Hochstetder et al., 2000; Morita, 1999). We report results of detail petrological analysis of basalts from two different seamounds and andesites from four different seamounds of the Enpo seamound 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 seamound 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 seamound 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.

## V21C-1000 0830h 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/K<sub>2</sub>O 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 K<sub>2</sub>O 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.

## V21C-1001 0830h 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.,  $87\text{Sr}/86\text{Sr} = 0.707413\text{--}0.709090$ ) 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.

## V21D MC: 304 Tuesday 0830h

### Highly Siderophile Element Chemistry of the Earth, Moon, and Planets (honoring John Morgan) I (joint with P, HG)

Presiding: M Horan, Carnegie

Institution of Washington Department of  
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## V21D-01 0830h

### Meteorite - Impact Melt Mixing: PGE and Re-Os Evidence from the Morokweng Impact, South Africa

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Preserved within the 870m thick impact melt sheet of the 144 Ma Morokweng impact structure, South Africa (1.2) are small (mm-cm) inclusions that are interpreted to be remnants of the impactor. Inclusions are disseminated throughout the melt sheet and consist of ultramafic silicate clasts with segregations of Ni-rich sulfides and oxides. The silicate component in the inclusions displays remnant fabric and, where unaltered, has mineral compositions consistent with ordinary chondrites (3). The sulfide-oxide component of the inclusions is Ni-rich, has high PGE contents ( $\text{Ir} = 16.7 \times$  chondrite) and fractionated PGE ratios compared to chondrites and to the bulk impact melt which reflects the signature of the ordinary chondrite impactor (4). Specifically, the oxides show depletion in Pd, while the sulfide is slightly enriched in Rh and Pt and strongly enriched in Pd relative to Ir and Ru. Significantly, Ru and Ir (the high temperature PGE's) are not fractionated from one another. Initial Os isotopic compositions of the inclusion sulfides and oxides (0.1335 - 0.1358) are slightly more radiogenic than found in the melt rock (0.1301 - 0.1324), but both are substantially less radiogenic than a sample of the basement granite (0.259). The 1/Os vs 187Os/188Os correlation displayed by the bulk melt rocks is consistent with the presence of 1-3 wt% chondritic impactor in the crustal melt. The more radiogenic Os found in the inclusion minerals indicates that the inclusions contain a larger crustal PGE component than the melt rock. Though Os concentration is well correlated with Os isotopic composition in the melt rock, Re concentration is not. Thus, simple binary mixing between crustal melt and meteorite cannot explain the Re-Os systematics. The Re-Os and PGE fractionation observed in inclusion minerals suggests that meteorite-impact melt mixing occurred first through chemical exchange between oxidized melt and reduced, metal or sulfur-rich, impactor. Lithophile elements (e.g. Fe, Cr, Co, Re) in the hot, perhaps partially molten, impactor fragments migrated into the impact melt, while highly siderophile elements (e.g. Ni, Ru, Ir, Os) migrated from the melt into the meteorite fragments. (1) Hart, R.J. et al. EPSL 1997, (2) Koeberl et al. Geology, 1997, (3) Cloete et al., MAPS, 2001, (4) McDonald et al., GCA, 2001.

## V21D-02 0845h INVITED

### Highly Siderophile Element Abundances in Martian Meteorites

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Critical evaluation of new and literature data for highly siderophile elements (HSE) in martian (SNC) meteorites allows several first order conclusions to be drawn. (i) Re concentrations in SNC meteorites are nearly constant (within a factor of two) and do not correlate with rock type. Exceptions to this rule are Chassigny and Dar al Gani (DaG) 476, both of which are inferred to have experienced terrestrial Re contamination. (ii) Fractionations between Rh and Pd are small. Excluding Shergotty, the Rh/Pd ratio of the SNC suite is  $0.22 \pm 0.05$ . (iii) Os and Ir contents vary by about four orders of magnitude; and positive correlations with MgO, Cr, and Ni suggest that these variations are not controlled by sulfide fractionation. A possible exception is the orthopyroxenite ALH84001, whose HSEs (including Ni, which is compatible in opx) are very low. (iv) Zagami, Shergotty, and Nakhla have nearly identical HSE signatures. Shergotty and Zagami have experienced assimilation-fractional crystallization (AFC) and have "crustal" Sr and Nd isotopic signatures. Conversely, the Nakhla parent was a small degree partial melt of a depleted mantle that interacted little with the martian crust. These observations suggest that "evolved" HSE signatures can be produced by either fractional crystallization or small degrees of partial melting. (v) Chassigny and other mafic SNCs have HSE signatures that are very distinct from those of Nakhla-Zagami-Shergotty. The HSE elemental ratios of mafic SNCs approach chondritic, implying that the martian mantle has nearly chondritic relative abundances of the HSEs. (vi) This chondritic HSE signature is observed in SNCs of various ages, suggesting that this is an ancient feature that has not evolved over time. (vii) No correlation is observed between HSEs and signatures of crustal contamination (e.g., Sr isotopes), indicating that the HSE signatures of the SNC suite are not derived from the crust. (viii) The Ru/Pd ratio for the SNC suite is about 0.5 chondritic. We attribute this depletion of Ru to the presence of spinel in the SNC source regions. (ix) Assignment of this depletion of Ru to spinel seems to also imply that spinel is not the cause of Os and Ir fractionations, requiring some other mafic phase to account for the observed variations.

## V21D-03 0900h

### A Comparison of Re-Os Isotopes and Abundances of Highly Siderophile Elements in Chondritic Meteorites: Constraints on Terrestrial Late Accretion

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Understanding the distributions of refractory, highly-siderophile elements (HSE) in chondritic meteorites is necessary to better constrain the history and distributions of those elements in terrestrial and planetary mantles. It is now widely, although not unanimously, agreed that the bulk of the highly siderophile elements in the Earth's mantle were added subsequent to terrestrial core segregation, by late accretion of broadly chondritic materials. New, precise abundance data for the HSE in chondrites, coupled with Re-Os isotopic data for the same meteorites, indicate that each of the three major chondrite groups is uniquely defined. Re-Os isotopic data show isotopic evidence for a major difference in long-term Re/Os (as shown in their modern  $^{187}\text{Os}/^{188}\text{Os}$ ) between carbonaceous chondrites relative to and ordinary and enstatite chondrites. Ordinary chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1283 \pm 0.0031$ . Enstatite chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1281 \pm 0.0009$ ; and carbonaceous chondrites have  $^{187}\text{Os}/^{188}\text{Os} = 0.1260 \pm 0.0021$ . These differences reflect 7-8% lower Re/Os ratio in carbonaceous chondrites, compared to enstatite and ordinary chondrites. This fractionation process occurred very early in the history of the solar system, possibly during condensation. It has been long recognized that