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We have examined the major and trace elements, and Os isotopic compositions of a suite of cumulate and spinifex textured komatiitic rocks from the Dundonald Beach area, part of the ~2.7 Ga Abitibi greenstone Belt, Ontario, Canada. This suite of rocks forms a series from peridotitic komatiites (MgO ~ 42 wt.% on a volatile-free basis) to komatiitic basalts (MgO ~8 wt.%). Based on major element oxide ratios (e.g. Al_2O_3/TiO_2 ~21-26 and CaO/Al_2O_3 typically <= 1) and unfractionated HREE characteristics (e.g. $(Gd/Yb)_N$ ~0.9-1.1), these rocks are similar to the spatially associated Al-undepleted komatiites from Alexo and Munro Townships. Also, these rocks are strongly LREE-depleted ($(La/Sm)_N$ = 0.41-0.67; $(Ce/Yb)_N$ = 0.41-0.70)) and have variable total REE (4-22 ppm). A strong negative correlation between Mg# and total REEs suggests that the REE patterns of these rocks are primary features of their mantle source. The Re-Os isotope results for whole-rock komatiites and chromite separates from a single flow yield a model 3 isochron age of 2606 ± 55 Ma. This age is slightly younger (~50 Ma) compared to the U-Pb zircon ages of the associated volcanics reported from the presumed extension of the same Kidd-Munro assemblage in Alexo and Munro Townships. The initial $^{187}Os/^{188}Os$ ratio (0.1090 ± 0.0019) obtained from the regression is essentially chondritic (γ_{Os}(T) = -0.2 ± 1.7). The peridotitic komatiites have the highest Os concentrations and low $^{187}Re/^{188}Os$ ratios (up to ~4.2 ppb and < 0.5, respectively) among the whole rocks, whereas the komatiitic basalts have relatively low Os concentrations (~0.3 ppb) and high $^{187}Re/^{188}Os$ ratios (~3.1-11.9). For these komatiites, Os was compatible with the mantle residue ($D_{Os}^{mantle-melt}$ ~7.6), whereas Re was moderately incompatible (D_{Re} ~0.6), typical of most komatiitic magmas. The absence of a strong correlation between Os and Ni concentrations in the whole-rocks suggests that the distribution of Os in these rocks is not primarily controlled by fractionation of olivine. The apparent $D_{Re}^{ol+chmt/liq.}$ (~0.7), on the other hand, suggests that Re was moderately incompatible in olivine and/or chromite during the differentiation of komatiitic magmas. A chondritic initial Os isotopic composition for the mantle source for these komatiites is consistent with that previously reported for the komatiites from Alexo and Munro Townships. Our Os isotopic results for Dundonald komatiites, combined with those reported for Alexo and Pyke Hill komatiites, therefore, suggest that a major portion of the ~2.7 Ga mantle source for the komatiites in the Abitibi greenstone belt was dominated by Os with chondritic isotopic compositions. Also, the LREE-depleted, yet chondritic Os isotopic composition for the mantle source of these komatiites is indistinguishable from the projected chondritic composition of the contemporaneous depleted convective upper mantle.

V42C-0375 1330h POSTER

Partitioning of Au up to 23 GPa: Implications for core formation of the Earth

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The core formation process (the segregation of metal and silicates) left an excess of siderophile elements in the mantle compared to siderophile element abundances predicted from metal-silicate partitioning experiments conducted at 1 bar (Ringwood, 1979). One hypothesis that explains the mantle abundances of siderophiles is that metal-silicate equilibration occurred at greatly elevated temperatures and pressures, where siderophilic behavior may be decreased. Because there is a paucity of data for highly siderophile element partitioning at mantle relevant conditions (P, T, X), we are investigating Au partitioning between metal-sulfide and silicate liquids. Experiments were carried out in a "Walker-type" 6-8 multi-anvil device in a 1100 ton press. Pressures from 5 to 14 GPa and 14 to 23 GPa have been investigated using an 8 mm or 3mm TEL assembly, respectively. Single crystal MgO capsules were used in both assemblies. We chose the Richardton H-chondrite as starting material because it has an appropriate sulfide fraction (12 wt% S), compared to the possible light element abundance of S in the Earth's core, and the silicate approaches a Bulk Earth composition after reaction with the MgO capsules. Experiment durations at superliquidus temperatures (1700 - 2400 C) were from 4 to 9 minutes. Au in the metal-sulfide quench products was measured using the Cameca SX-50 electron microprobe at the University of Arizona. Secondary ion mass spectrometry (SIMS) was used to measure Au in the quenched silicate liquid in depth profiling mode. The intersection of microblebs (or "nuggets") of Au-rich material during the analysis could be identified and subtracted before calculation of Au contents of the quenched silicate fraction. D(Au)metal-sulfide/silicate ranges from 19000 to 100 The addition of microbleb contributions to the silicate lowers D(Au) by an order of magnitude or less. D(Au) decreases with increasing pressure. A linear fit to the data intersects the D(Au)core/mantle of Earth (300) at 21GPa. This suggests an average equilibration depth of 570 km of descending metal droplets in a silicate magma ocean. This is a slightly lower pressure than suggested by Righter and Drake (1999) but still within their uncertainty.. Although the contribution of Au-bearing microblebs to D(Au) is less than expected, dissemination of such microblebs in a magma ocean could represent a physical mechanism of inefficient core formation.

V42C-0376 1330h POSTER

Towards a Precise and Accurate Estimate of the Platinum Group Element Composition of the Primitive Upper Mantle

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Determining precise and accurate platinum group element (PGE) abundances in peridotites is key for the detection of primordial and secondary (i.e., magmatic) heterogeneities of the PGE in the mantle, and may be used to establish model PGE compositions of the primitive upper mantle (PUM). In conjunction with $^{187}Os/^{188}Os$ (reflecting the Re/Os of PUM), the PGE model composition of PUM, in particular its Pd/Ir, may help in tracing the source of the late siderophile element influx at 1 AU by comparison with data for chondrites (Horan et al. 2003). We have determined Os, Ir, Ru, Pt, Pd and Re abundances in samples from continental peridotite massifs and peridotite xenoliths. The new approach uses isotope dilution and high-pressure, high-temperature digestion in Carius tubes at 345° C, as most other techniques are either not precise enough, or do not access the complete PGE budget during the digestion of peridotites (Meisel et al. 2003, and in press). Reproducibility and accuracy are controlled by multiple analysis of the peridotite standard UB-N, for which the PGE content is now well constrained through high-T-P digestion and Na2O2-NaOH fusion. New data for peridotites from the Pyrenees and Lanzo indicate that, in some cases, Ir and Ru contents may have been underestimated by up to 50-80% by older techniques using NiS-fire assay, resulting in overestimates of Pd/Ir. The new data also show a good correlation of Pd/Ir with Al, suggesting a Pd/Ir of PUM between 1.5 and 2.0, comparable to or higher than EH chondrites. Data for peridotite xenoliths from Hannuoba (China), while also correlating with Al, show larger scatter in Pd/Ir than the European samples. This could be an analytical artifact, because most of the Chinese samples were digested in standard Carius tubes at 220° C. High-T-P digestions will be performed to test this hypothesis and data on other peridotites are being obtained to constrain the composition of PUM.

V42D MCC: Level 1 Thursday 1330h

Isotope Geochemistry Posters

Presiding: **K H Rubin,** University of Hawaii

V42D-0377 1330h POSTER

^{234}U-^{238}U in volcanic rocks

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New and literature ($^{234}U/^{238}U$) data on standards and rocks erupted from volcanoes in each of the major tectonic environments are analyzed to evaluate the significance, magnitudes and causes of ($^{234}U/^{238}U$) variations within the global data set. The data set is limited to high precision mass spectrometric (MS) data, which are required to resolve small disequilibria differences (0.2-0.3%) and to distinguish them from secular equilibrium. The principle finding is that statistically significant ^{234}U-^{238}U disequilibrium exists in 10-15% of volcanic rocks (413 total samples) and it varies systematically by tectonic setting. This disequilibria causes the mean ($^{234}U/^{238}U$) of all volcanic rock data to be >1 outside of standard error ($2\sigma_m$) and outside of the limitations imposed by U standards data. This is true regardless of ^{234}U decay constant (λ234U) used to convert MS atomic abundance ratio data to activity ratios. A subset of this data set also allows for an independent test of 4 different λ234U used in the literature: ($^{234}U/^{238}U$) =1.000 in intraplate subaerial volcanic (SV) rocks using the most recent λ234U (Cheng et al., Chem. Geo., 169, 2000) indicating that this decay constant is preferable to older, more commonly employed values. The SV data also indicate a closed melt system for U exchange in volcanoes of this tectonic setting. ($^{234}U/^{238}U$) >1 in many convergent margin lavas and mid-ocean ridge basalts (MORB) indicate addition of U with a marine isotopic fingerprint during or after petrogenesis (i.e., as alteration). ^{234}U-^{238}U disequilibrium and ^{238}U- ^{230}Th disequilibrium are strongly correlated in convergent zone data but not in MORB, indicating different controls on both ratios in the two environments. This and other major and trace element covariations with ($^{234}U/^{238}U$) are perhaps best interpreted as predominantly reflecting AFC of young altered crust at ocean ridges, and a combination of crustal AFC and deeper marine-derived fluid addition to the convergent zone lavas when ($^{234}U/^{238}U$) >1.

V42D-0378 1330h POSTER

Improving the Sensitivity of Uranium Isotope Ratio Measurements

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Accurate and precise measurements of natural and anthropogenic 235/238 U isotope ratios are important for a range of investigations where the amount of sample is extremely restricted and/or the analyte is only present in ultra-trace quantities. Examples include biological, cosmochemical, environmental, geological, and radiological studies. We have developed and validated a novel method using our Nu Instruments Nu Plasma Multi Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) and a 233U, 236U mixed double spike for the measurement of 235U/238U ratios. Our multi-dynamic technique employs the installed quadrupole zoom optics and fixed positioning of the ion counting detectors such that rather than the commonly used mass dispersion of 1 or 2, we utilize a mass dispersion of 1.5. Using this configuration, we can simultaneously monitor the 235U and 238U ion beams in the first cycle followed by a second cycle that simultaneously monitors the 233U and 236U beams. This innovative approach allows us to correct for the considerable, but consistent, instrumental mass fractionation and ion-counter amplification bias within each sequence. Since we were hesitant to use a U500 (235U, 238U equal atom) solution for spike calibration because of possible enriched U laboratory and instrumentation contamination, we used a U960 (terrestrial 235U/238U) solution for isotopic calibration of the spike. This standardization corrected for the small amounts of 235U and 238U in the spike solution by using a U960 standard solution. With a mean intraday 2-sigma precision of 1.5 permil and an overall 2-sigma precision of 2.25 permil using individual sample sizes of 350 pg (8.8 × 10 E11 atoms), we are confident our technique will be useful for identifying U isotopic anomalies present in many sample types.

V42D-0379 1330h POSTER

^{15}N Enriched Archean Crust, or ^{15}N Depleted Crust Recycled into -6 $^{o}/_{oo}$ Upper Mantle?

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V

Nitrogen concentrations and isotopic compositions have been measured on 2.7 to 1.0 Ga Precambrian metasedimentary rocks from Botswana, Canada and Ghana; pre-metamorphic 2.7 Ga VMS deposits in Canada; and on post-metamorphic hydrothermal micas from 2.7 to 1.8 Ga quartz vein systems in Zimbabwe, Canada, and Ghana, to investigate the origin and evolution of nitrogen in the atmosphere, crust, and mantle systems during Earth's early history. Archean sedimentary kerogens, in K-silicates in VMS deposits, and K-micas in hydrothermal systems that sample average crust, yield δ^{15}N values of 15-24$^{o}/_{oo}$, compared to 2 to 6$^{o}/_{oo}$ in Phanerozoic counterparts. Paleoproterozoic equivalents have intermediate δ^{15}N of 7 to 12$^{o}/_{oo}$, implying a secular decrease in crustal δ^{15}N. In parallel, N contents increase from tens to hundreds ppm in the Archean to hundreds up to thousands ppm since the Paleoproterozoic. The ^{15}N-enriched nitrogen in both Archean sedimentary rocks and hydrothermal vein systems cannot be caused either by long-term diffusional loss of ^{14}N, or by N-isotopic shifts due to metamorphism; such fractionations are <2$^{o}/_{oo}$ as established from empirical studies of Phanerozoic terranes with progressive metamorphism, and experiments. Moreover, pre- and post-metamorphic Archean samples have ^{15}N enriched values in common. Retention of near-primary ^{15}N-enriched values is endorsed by the lack of covariation of C/N with δ^{13}C or δ^{15}N, or with metamorphic grade. It is possible that the ^{15}N-enriched values stem from a different N-cycle in the Archean, with large biologically mediated fractionations, yet the magnitude of the fractionations observed exceeds any presently known. The ^{15}N-enriched nitrogen does not robustly constrain Archean redox-state. We attribute the ^{15}N-enrichment to a secondary atmosphere derived from CI-chondrite-like material and comets with δ^{15}N of +30 to +42$^{o}/_{oo}$. Shifts of atmospheric δ^{15}N to its present values of 0$^{o}/_{oo}$ can be accounted for by a combination of early growth of the continents, and sequestering of atmospheric N_2 into crustal rocks; recycling into the mantle; and mantle degassing. Consequently, these shifts are tracked by the secular change of δ^{15}N in continental crust. If Earth's surface environment became oxygenated at 2 Ga, then there were no associated large N-isotope excursions. Based on a few ^{15}N depleted Archean cherts Marty and Dauphas (2003) proposed that recycling of ^{15}N depleted Archean crust could shift the upper mantle from a primordial value of +6 to +8 $^{o}/_{oo}$ to the observed value of -5$^{o}/_{oo}$G85. The new data rule out this model.

V42D-0380 1330h POSTER

Oxygen isotopic signature of mantle xenoliths from the Patagonia region, Argentina

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In order to provide petrological information about the continental lithospheric mantle in the Patagonian region, a series of oxygen isotopic analyses were performed in mantle xenoliths. Hosted by Miocene-Pleistocene alkaline basalts erupted in the Andean back-arc setting, the studied mantle xenoliths are represented by anhydrous spinel-bearing lherzolites to harzburgites, and subordinately websterites and olivine websterites. Using a conventional vacuum extraction line employing BrF_5, oxygen isotopic analyses were conducted in whole-rock, olivine, clinopyroxene and orthopyroxene at the Department of Geological Sciences, Indiana University, Bloomington - USA. Isotopic ratios were measured on a Finnigan MAT 252 stable isotope mass spectrometer. Values of NBS-28 quartz are δ^{18}O = +9.6 $\pm$ 0.2 $^{o}/_{oo}$. Errors obtained were better than $\pm$ 0.1 $^{o}/_{oo}$ (2SD). Whole-rock data suggests a wide range of δ^{18}O from +5.5 to +10.1 $^{o}/_{oo}$, whereas mantle rocks, in general, presented values ranging around 5.5 $\pm$ 0.2 $^{o}/_{oo}$. Olivines showed two distinct isotopic ranges, with values of +5.0 to +5.9 $^{o}/_{oo}$, similar to values for upper mantle olivines, but also low δ^{18}O values, around 3.2 $^{o}/_{oo}$. Pyroxenes demonstrated a wide range of values, between +4.5 and +6.3 $^{o}/_{oo}$ similar to upper mantle pyroxenes. The discrepancy of some whole-rock and olivine values in relation to mantle compositions could be interpreted as an inter-mineral disequilibrium, mineral zonation reflecting or not, metasomatic interaction, or even crust participation during subduction

V42D-0381 1330h POSTER

Pre-BIF, Negative Ce-Anomaly in Mid-Archean Shales From the Eastern Indian Craton.

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We report preliminary geochemical data for the Iron Ore Group (IOG) of rocks from the Eastern Indian Craton. These rocks have been intruded by 3.0-3.1 Ga old phases of the Singhbhum and Bonai granites and thus have been assigned a Mid-Archean age (3.2Ga). The IOG rocks represent a sequence of volcano-sedimentary litho-units starting with a 1km thick basal lava flow (lower lava) followed successively upward by a shale (lower shale), Banded Iron Formation (BIF), a banded shale (upper shale) with associated lava flow (upper lava). The occurrence of pillow lava in the lower part of the IOG indicates that the lavas erupted under submarine conditions. The Chondrite-normalized Rare Earth Element (REE) patterns of both the Lower and Upper lava samples show a near-uniform fractionation pattern. However, the lower lavas show a smaller degree of fractionation (LaN/LuN = 4-6) than the upper lavas (LaN/LuN = 8-10), suggesting an evolved and already fractionated source for the Upper Lava rocks. The negative Eu-anomaly in all the lavas is due to separation of plagioclase in the magma chamber beneath the sea floor. The REE patterns of the Lower Shale samples are very similar to those of the underlying lavas indicating their affinities with those lavas. The lower shale samples exhibit a large negative Ce-anomaly (Ce/Ce* = 0.3-0.45). A smaller degree of negative Ce-anomaly (Ce/Ce* = 0.8-0.9) is also seen in the Lower Lava samples. Oxidative scavenging of cerium by Fe-Mn oxyhydroxides in the marine environment is believed to result in a negative Ce-anomaly in the seawater and in the phases precipitating in equilibrium with seawater. Hydrous minerals in basalts forming in equilibrium with seawater can impart a mild negative Ce-anomaly as observed in the Lower Lava samples. A more pronounced Ce-anomaly in the shales is a result of further subaqueous, hydrothermal disintegration of the basalts. Ce-anomaly in such ancient rocks, suggest oxygenation of the deeper waters as early as 3.1 Ga, much earlier than the precipitation of the overlying Banded Iron Formation. This has important implications regarding the oxygen budget in the early Earth and the rise of oxygen. Positive Ce-anomaly in an Upper Shale sample is due to the associated occurrence of Manganese deposits in these shales.

V42D-0382 1330h POSTER

Hf-Nd Isotope Geochemistry of Contrasting Global Sedimentary Columns in Subduction Zones

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Most terrestrial Hf-Nd isotopic compositions lie along a positively correlated Hf-Nd array [1]. However, some abyssal sediments (e.g., ferromanganese nodules, crusts, and metalliferous clays; [1, 2]) have strongly decoupled Hf-Nd isotopic compositions. In order to evaluate the range of Hf-Nd isotopic compositions in subducting sediments on a global scale, we have selected contrasting drill sites outboard of active subduction systems. The selected sections differ in characteristics such as age, thickness and type of sediment, convergence rate and accretionary prism development. An example of one endmember is the metalliferous clay-rich Tonga section (DSDP sites 595 and 596). These compositions show large deviations from the Hf-Nd array by having a higher ϵHf relative to ϵNd, and have highly elevated REE concentrations and Lu/Hf ratios compared to normal terrigenous samples. These systems have moderately negative Hf and Nd isotopic compositions that are (at least in the case of Nd) similar to seawater. This type of signature may be seen in other slowly accumulating systems dominated by metalliferous sediments, such as the Philippine (DSDP site 291) and Ryukyu (DSDP site 294/295) sections. The Central America (ODP site 844 and DSDP site 495) subduction system has a bimodal sediment input, consisting of carbonates overlain by hemipelagic diatomaceous muds. The muds are dominated by volcanic arc input and show little variation on the Hf-Nd array (ϵHf $^{+}$10 to $^{+}$11 and ϵNd $^{+}$2 to $^{+}$6). Volumetrically the largest flux of sediments into subduction zones worldwide, however, are terrigenous sediments derived from active continental margins. An example of this is the Cascadia system (DSDP site 174). The Cascadia sediments all plot on the crustal portion of the Hf-Nd array, but show large variation (ϵHf $^{-}$6.5 to $^{-}$20 and ϵNd $^{-}$5.5 to $^{-}$14) reflecting changing sediment sources. Nd and Hf model ages for these sediments range from 0.4 Ga to 1.3 Ga. These negative epsilon values and dominantly Precambrian model ages conflict with exposed crust in the Pacific NW proximal to site 174. Instead, these sediments may be the result of Pleistocene glaciation with pulses of catastrophic flooding, which brought older cratonic material from distal sources to the site. This illustrates that Hf-Nd isotopic composition is useful not only for applications such as mantle composition and arc petrogenesis, but also for sediment provenance. [1] Vervoort et al., 1999, EPSL, Vol 168: 79-99. [2] Albarède et al., 1998, GRL, Vol 25: 3895-3898. [3] Vervoort and Plank, 2002, EOS, Vol 83.

V42D-0383 1330h POSTER

In-situ Hf isotope analysis of early Archean zircons in the Acasta Gneisses from the Slave province, Northwestern Canada

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Lu-Hf and Sm-Nd isotopic systems of early Archean rocks provide insights into the early crustal evolution and early mantle differentiation of the Earth. The Acasta Gneisses have been established as the oldest known intact terrestrial rocks (Bowring et al., 1999). The Acasta Gneiss Complex comprises mainly of Gray Gneiss (granodioritic gneiss), White Gneiss (tonalitic to granitic gneiss), and Foliated Granite, with many aplite and basaltic intrusions, and the relation between these rocks is very complex. Bowring et al. (1989) carried out the whole-rock Sm-Nd isotopic system measurement of the Acasta gneisses, and demonstrated that the gneisses exhibit a wide range of initial ϵ(Nd) (+3.5 to -4 at 4.0 Ga and +4 to -7 at 3.6 Ga). However, because most of the Acasta gneisses have experienced amphibolite facies metamorphism, it is difficult that the whole-rock isotopic system remains closed. Zircon, which is extremely resistant against erosion and/or metamorphic events, and it can be also dated precisely by U-Pb chronometer. Because of high Hf content (ca. 1 wt%) and low Lu/Hf ratio, zircon has been widely used for the isotopic study using Lu-Hf system, too. Recent Lu-Hf isotopic studies were carried out using a multiplecollector inductively coupled plasma mass spectrometer (MC-ICPMS). Amelin et al. (2000) carried out the Hf isotope analyses of some zircon grains from the Acasta Gneisses using MC-ICPMS. The zircon grains exhibit enriched initial ϵ(Hf) (+0.16 to -4.1 at ca. 3.6 Ga), while other early Archean zircon grains from the Amitsoq gneisses and the Barberton gneisses indicate depleted signature (Amelin et al., 2000). One possible reason is that the zircon grains from the Acasta Gneisses are grown at partial melting of the gneisses and/or underwent isotopic disturbance caused by intrusion of younger granites. Therefore, it is very important to reveal the growth features of zircon, such as oscillatory zoning, in order to derive inherent information of the early Archean rocks, because zircon grains in the rocks usually have complex internal structures. Moreover, precise in-situ Hf isotope microanalysis is required in order to avoid the disturbance of inclusions and cracks in the zircon grain. In this study, we separated many zircon grains from rock samples, and carefully observed the internal texture using cathodluminescence. In addition, we carried out in-situ U-Pb analysis and in-situ Hf isotope analysis from ablation crater size of <20 μm and 30 $\sim$ 60 μm diameter, respectively, using laser ablation-MC-ICPMS. We established to estimate the original isotopic signature of protoliths of the Acasta Gneisses from comprehensive analyses of zircon.

URL: http://www.agu.org/rb33ti

V42D-0384 1330h POSTER

Lead Paradoxes as a Result of the Secular Evolution of Crustal Recycling Processes

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The positioning of both the upper mantle and upper crust to the right of the Geochron, and the inconsistency between the Th/U ratio of depleted mantle and their time-integrated values calculated from Pb-isotope compositions, constitute the two terrestrial Pb-isotope paradoxes. Based on estimates of present-day continental uranium added to oceanic crust, several authors have attempted to explain the paradoxes by oxygenation at $\sim$ 2.2 Ga and consequent uranium fluxing to the mantle, via subduction of U enriched oceanic crust. However, reasoning founded in trace element ratios involving U in several types of oceanic basalts is consistent with significant loss of U from the slab to arc magmas, such that little U is recycled to the mantle. This constraint on U recycling requires an alternative explanation for the long-term mantle evolution characterized by U/Pb increase and Th/U decrease. We propose that this evolution, inferred from the lead isotopic signatures, can be accounted for secular variations in subduction zone trace element fractionation, where the upper mantle composition is constrained by the mixing of recycled oceanic crust and harzburgite. Archean continental crust formed at convergent margins dominantly from high Al, high La/Yb_n tonalitic liquids generated by slab melting under higher geothermal gradients, whereas post-Archean arc magmatism is characteristically generated by slab dehydration-peridotite wedge melting under relatively lower geothermal gradients. We consider Th/U decrease in the mantle to have started through magmatic processes associated with Archean partial melting of subducting slabs, governed by garnet, and recycling of a complementary low Th/U residue. This explains evolution of the Th/U from the primordial value of $\sim$ 4.2 to $\sim$ 3.8 at 2.6 Ga. This decrease continued subsequently as a result of the Th/U fractionation associated with the generation of MORB and consequent recycling of the complementary depleted harzburgitic residue. In contrast, the U/Pb increase, which explains the positioning of oceanic basalts to the right of the Geochron, is thought to be produced by non-magmatic processes through the recycling of dehydrated, lead depleted, oceanic crust in post-Archean times. However, the ante-2.6 Ga μ decrease from the primitive mantle value of $\sim$ 9.2 to $<$ 8, inferred from the two stages model for recent oceanic basalts, is considered the result of $D_U < D_{Pb}$ during slab melting induced by the high Archean geathermal gradients. This model also explains the time-integrated Nd/Sm and Rb/Sr mantle ratios inferred from isotopic signatures of modern basalts. The depleted $^{143}Nd/^{144}Nd$ signature is considered a consequence of mantle depletion tendency initiated during Archean crustal-forming events, whereas the low $^{87}Sr/^{86}Sr$ reflects essentially the recycling of a low Rb/Sr residue stemming from the high Rb mobility at Phanerozoic subduction zones.

V42D-0385 1330h POSTER

LA-ICPMS Measurements of Pb Isotopes and Th/U Ratios of HSDP Glasses from the Submarine Section of Mauna Kea Volcano

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We have developed a LA-ICPMS technique to simultaneously determine Pb isotopes, Th, U and other trace element concentrations in small glass samples. The experiments were done with a New Wave UP-213 laser system and an Element 2 ICP mass spectrometer. The glasses were ablated for 60 s in single spots 120 μm in diameter, applying a laser energy density of $7 mJ/cm^2$ and a pulse repetition rate of 10 Hz. The geological MPI-DING reference glasses (Jochum et al., 2000), for which high precision isotope data are now available, were used to determine the mass bias of Pb isotopes and to calibrate the trace element data. Reproducibility (RSD) of the Pb isotope data for concentrations of about 0.5 - 2 ppm is about 0.2 - 0.7 % (208/206), 0.2 - 0.5 % (207/206) and better than 1.5 % (206/204, 207/204, 208/204), respectively. The quantity of Pb measured for one analysis is about 3 pg for a Pb concentration of 1 ppm. Th/U ratios are determined with a precision of about 1 - 3 %. Overall analytical uncertainties of the trace element concentration data are about 5 - 10 %.
We have applied the technique for the direct analysis of carefully handpicked glass fragments from 19 samples of the submarine section of the Hawaii Scientific Drilling Project 2 (HSDP2). Some samples provided just a few glass chips. Samples cover the depth interval from 1314 to 3060 mbsl. Three to four fresh, 200 - 500 μm large, fragments of each sample were analyzed. In these fragments the results are indistinguishable at each spot implying a homogeneous distribution of trace elements. Our results show that $^{208}Pb/^{206}Pb$ ratios vary significantly along the stratigraphic column of the HSDP2-core ranging between 2.070 and 2.121. The lowest values are found in samples coming from depths around 1400, 2800 and 3000 mbsl whereas the highest ratios are measured in samples of 2100 mbsl depth. These microanalytical data agree with the high-precision TIMS data of Eisele et al. (2003) who found temporal variations of Pb isotopes in the whole HSDP2-core. Attributing varying isotope ratios to source heterogeneities can be confirmed when considering trace element ratios. This is best demonstrated by the correlation of the element ratio of Th and U that are parent nuclides of ^{208}Pb and ^{206}Pb with the $^{208}Pb/^{206}Pb$ ratios measured in the same glass fragments.
Ref.: Jochum et al. (2000), Geostandards Newsletter 24, 87-133; Eisele et al. (2003), Geochem. Geophys. Geosyst. 4 (5), 8710.

V42D-0386 1330h POSTER

High Precision Pb and Tl Isotope Measurements by MC-ICP-MS: Problems and Solutions

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Measurements of NBS 981 Pb mixed with Tl for mass bias corrections were conducted on a MC-ICP-MS (Nu Plasma) during the period of April-August, 2003. During the initial stages of the experiments, Pb and Tl from single concentrated stock solutions were mixed in 2%HNO3 and then measured from 48 hours to 60 days after preparation (mixing). Initial results (n=28) with these solutions revealed relatively poor precision and accuracy with 206Pb/204Pb=16.921 (+/-0.039 2s), 207Pb/204Pb=15.469 (+/-0.052 2s), and 208Pb/204Pb=36.630 (+/-0.160 2s). Similarly, using NBS 981 for mass bias correction of the 205Tl/203Tl yielded large epsilon Tl variations (-4 to +31). Comparison of measured Pb and Tl beam intensities for these solutions over this period showed higher Pb:Tl intensity ratios compared to the known elemental ratios in the original mixtures. In addition, the longer the mixed solutions aged, the greater the Pb:Tl decoupling was, and poorer precision and accuracy in the isotope measurements were observed. To address this problem, we prepared new mixed solutions and analyzed them immediately (< 1 hour) after mixing. Analyses (n=26) showed excellent precision and accuracy with 206Pb/204Pb=16.937 (+/-0.001 2s), 207Pb/204Pb=15.491 (+/-0.001 2s), and 208Pb/204Pb=36.694 (+/-0.004 2s). Measured epsilon Tl in these fresh solutions was 1.5 (+/-0.6 2s). In addition, measured Pb and Tl ion beam intensities always reflected those calculated for the mixtures. Poor precision and accuracy in the isotope measurements and decoupling of Pb and Tl elemental abundances vs. ion beam intensities were observed only when the aged solutions were aspirated through the DSN. The same solutions aspirated in wet plasma mode did not show variations in the measured Pb:Tl ratios, suggesting that precipitation of Tl in the PFA bottles cannot explain the decrease in the Tl signal. Thallium commonly exists as Tl+ in solution, but at low pH-high Eh it can be oxidized to the less soluble form Tl+3. If this oxidation leads to the formation of complex Tl molecules (colloids), then during wet plasma mode the colloids will be introduced into the plasma together with the rest of the analyte, so no decoupling between measured Pb and Tl abundances and intensities is observed. If, however, the colloids behave differently than the rest of the analyte ions in the DSN during the liquid-vapor transition, that may account for the observed elemental fractionations and subsequent inapplicability of Tl isotope ratios for mass bias corrections for Pb. Measured intensities in single Pb and Tl control solutions does not show changes over time suggesting that the reactions occur only in mixed solutions. In addition, experiments currently under way with solutions with different HNO3 concentrations suggest that the interaction between Pb and Tl occurs preferentially at certain pH-Eh range. This study demonstrates that highly precise Pb isotopic measurements can be produced using Tl normalization with MC-ICP-MS. However, significant analytical errors, resulting in poor precision and accuracy in the Pb isotope measurements and up to 30-40 epsilon Tl units variation, can be generated during aging of mixed solutions as a result of complex interactions between the analyte ions. Experiments utilizing thallium for mass bias corrections for Pb, and lead for mass bias corrections for Tl isotope measurements and desolvation are most reproducible when conducted on freshly prepared analyte mixtures.

V42D-0387 1330h POSTER

Pb Isotopic Compositions of Olivine-Hosted Melt Inclusions in Continental Basalt, Eastern Snake River Plain

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Previous studies of melt and mineral inclusions from oceanic island basalts found Pb isotopic variability more than five times than that exhibited by the basalts themselves and values that encompass much of the variability exhibited in mantle products erupted worldwide. In our study, *in situ* Pb isotopic analyses of olivine-hosted melt inclusions from an intracontinental basalt from the eastern Snake River Plain (SRP) of southern Idaho were obtained using a Cameca IMS 1270 ion microprobe in order to investigate the role of diverse magma sources in the genesis of these magmas. Analyses of 14 melt inclusions in zoned olivines (Fo = 78-83) in a magnesian Pleistocene SRP basalt yield an average isotopic composition of $^{208}Pb/^{206}Pb = 2.121$ and $^{207}Pb/^{206}Pb = 0.8671$, essentially identical to that of the whole rock. However, duplicate analyses of one melt inclusion yield distinctly lower ratios ($^{208}Pb/^{206}Pb = 2.052$; $^{207}Pb/^{206}Pb = 0.8424$), outside all published SRP fields. The dominant phases contained within the melt inclusions are silicate glass, clinopyroxene (cpx) and trace amounts of plagioclase and Fe-Ti oxides. Most cpx associated with these melt inclusions are more calcic (Wo = 48-53) than other SRP cpx (Wo = 35-45, including both phenocrystic and groundmass cpx). The Mg# of the less radiogenic melt inclusion is higher (37-48) than that of the other included cpx (23-38). Our preliminary results for an intracontinental basalt find less heterogeneity than that obtained in previous studies which focused on oceanic basalts, even though the basalts are equally magnesian. Either the source is more uniform in composition or homogenization of disparate melt fractions occurs at an earlier stage in the melt aggregation process. The less radiogenic isotopic compositions of one inclusion may be explained by entrapment of melt that was affected by incipient crustal contamination, possibly at the margins of the magma chamber, or may be evidence of small-scale mantle source variability. Further study, including analyses of additional basalts, is being conducted to distinguish between these two possibilities.

V42D-0388 1330h POSTER

Global Pb Isotopic Signatures: Implications for Precambrian Mantle Reservoirs

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Precambrian age-provinces have coherent Pb isotopic signatures that commonly differ from one craton to another. These distinctions have been exploited in paleogeographic reconstruction to test the affinities of potentially exotic terranes with host cratons or potential parent cratons. However, the global variability and distribution of these signatures was not well defined.

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Based on a compilation of whole-rock Pb isotopic compositions of Precambrian juvenile intrusions we conclude that; 1) Rocks in ca. 2.8-2.6 Ga, ca. 2.0-1.8 Ga, and ca. 1.3-1.0 Ga age-provinces in eastern Laurentia have coherent Pb isotopic signatures that vary systematically as if they were derived from the same homogeneous mantle reservoir that evolved with a constant μ-value. 2) Signatures of ca. 1.3-1.0 Ga age provinces from Amazonia, Antarctica, Australia, Baltica, Kalahari, Oaxaca, and Laurentia overlap each other and define two global Pb isotopic signatures suggesting the presence of at least two large, isotopically-distinct mantle reservoirs during the Mesoproterozoic. Pb isotopic compositions of modern oceanic crust indicate the existence of two Mesozoic/Cenozoic, isotopically-distinct mantle reservoirs, referred to as "normal" mantle in the northern hemisphere and DUPAL mantle in the southern hemisphere. Compositions of Precambrian juvenile intrusions indicate that similar, long-lived reservoirs may have existed earlier in Earth's history.

V42D-0389 1330h POSTER

Ion Microprobe U-Pb Dating and REE Analysis of Apatite from Kerogen-rich Silica Dike from North Pole Area, Pilbara Craton, Western Australia

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In order to provide a time constraint on the 13C-depleted kerogen in silica dikes that intruded 3.5 Ga greenstone from Pilbara Craton in Western Australia, we have carried out an ion microprobe U-Pb dating and rare earth element (REE) analysis of apatite from the dike. Two types of apatite were identified in the dikes based on their occurrences. One is stick-shape apatites (Type 1) in secondary silica micro-veins that cut the silica dike. The other is granular apatites (Type 2) that occurs in matrix of the dike. Occurrence in the secondary micro-veins (Type 1), non-igenous chondrite normalized REE patterns (Type 1 and 2), chemical zoning (some of Type 1 and 2), and presence of mineral inclusion that is composed of Fe and S (some of Type 2) suggest that both Type 1 and 2 apatites were crystallized in the silica dike. Ion microprobe U-Pb dating of Type 1 apatite did not give a meaningful age, while Type 2 apatite yields a Tera-Wasserburg concordia intercept age of 3214 +/- 140 Ma (95 per cent confidence level, MSWD = 0.6) in a three-dimensional 238U/206Pb-207Pb/206Pb-204Pb/206Pb diagram, and a 204Pb/206Pb-207Pb/206Pb isochron age of 3191 +/- 150 Ma (95 per cent confidence level, MSWD = 0.5). It is difficult to judge whether the U-Pb and Pb-Pb age of Type 2 apatite is crystallization age or metamorphic age, since the estimated range of closure temperature of U-Pb system in the apatite and that of metamorphic temperature is partly overlapped. In either case, it can be safely concluded that the minimum age of the dike and kerogen is 3.0 Ga. These ages might allow the interpretation that the kerogen was produced by biological carbon fixation and/or abiological reaction (such as Fischer-Tropsch Type reaction) at least before 3.0 Ga.

V42D-0390 1330h POSTER

Flux and size fractionation of IDP-borne ^{3}He from Antarctic ice core samples

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Previous measurements of helium isotopes in particles from polar ice yielded extraterrestrial ^{3}He fluxes similar to results from marine sediments (Brook et al., 2000, GRL, 27, 3145-3148). The agreement is surprising since the area-time product (sample mass divided by mass accumulation rate) for these samples is relatively small. We now report new helium measurements from larger samples of the Vostok Ice Core (Antarctica) and results of a series of size fraction experiments designed to determine the dominant particle size transporting ^{3}He in Interplanetary Dust Particles (IDP's) to earth. The mean ^{3}He flux from 8 longitudinally cut replicate ice samples (821-1201 g each) from the 112-115 m interval (3.8-4 ka) at Vostok is 1.1$\pm$0.3 x 10^{-12} cm^3 STP cm^{-2} ka^{-1}. These samples have a mean area-time product of 0.05 m^{2}a, which is 5 times that of the previous ice measurements. The inferred ^{3}He fluxes are similar to values previously reported from late Quaternary ice samples and marine sediments, further demonstrating the potential of ice cores as archives of ^{3}He accretion. We also separated dust from one 1.5 kg sample of Vostok ice into 5 size fractions, >63, 20-63, 10-20, 5-10, and 0.45-5 microns, using sieves and filters. Models predict that most ^{3}He in IDP's is carried in relatively large particles, in the 5-35 micron range. However, the new data shows that over 76% of the ^{3}He is found in the 5-10 micron size interval, and only 18% of the ^{3}He in size classes larger than this. Implications for reconstructing the IDP ^{3}He flux will be discussed.

V42E MCC: 3008 Thursday 1340h

Melting of the Mantle and Formation of Basalt Magmas: Experiments, Field Studies, and Models II *(joint with OS)*

Presiding: **G Gudfinnsson,** Carnegie Institution of Washington**; S Keshav,** Florida International University

V42E-01 1345h

Eclogitic Minerals in Diamond: MORB Reincarnated

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Following participation in creation of oceanic lithosphere, MORB and related rocks can be altered, contaminated and eventually subducted. Evidence for these processes survives in Alpine eclogites, subcratonic eclogite xenoliths and especially in some diamonds. One of the key pieces of evidence exists as anomalous oxygen isotope values of silicates in these high-pressure assemblages. Sea floor alteration changes the d18-O VSMOW values of MORB from +5.7 +/- 0.2 per mil in fresh samples, to values as high as +27 per mil in examples that have undergone low-T ocean floor weathering. High d18-O values are also found in ophiolite basalts (to +20 per mil) and Alpine eclogites (to +16 per mil), but d18-O values of mantle eclogite xenoliths are only somewhat anomalous (to +9.3 per mil). Using SIMS, we have studied the stable isotope composition of diamonds and their eclogitic mineral inclusions from Guaniamo, Venezuela, in situ in polished section. The d18-O values of six coesite inclusions in four diamonds are in the range +10.2 to +16.9 per mil, and eight garnets in five diamonds are in the range +8.8 to +12.9 per mil, with a ninth example at +5.5 per mil. As oxygen isotope fractionations are known to be small under mantle conditions, these data provide compelling evidence for an altered ocean floor basalt protolith for this eclogitic diamond suite. Carbon isotope values (d13-C PDB) of host diamonds are very low (approximately in the range -12 to -22 per mil), values considered by many workers to indicate a significant component of biogenic carbon in the diamonds. Two stones have higher values of d13-C (-7 to -8 per mil), more typical of mantle carbon, but also consistent with a crustal source. Although isotopically light carbon can be created by mantle fractionation processes, the correlation we have shown here between anomalous oxygen and carbon isotope signatures within single diamonds strongly supports a crustal biogenic source for the carbon in these diamonds.

V42E-02 1400h

The Composition of the Depleted Mantle

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We present an estimate for the composition of the depleted mantle (DM), the source for mid-ocean ridge basalts (MORBs). Several avenues are used to derive the estimated composition of the DM. Since trace element ratios can be better determined than absolute concentrations, absolute concentrations are only estimated for a few elements and the majority of the trace element concentrations are based on trace element ratios. The most reliable estimates of trace element ratios are estimates of parent-daughter ratios which are based on the isotopic composition of mid-ocean ridge basalts. These estimates form the "backbone of our trace element estimates. A second way of estimating trace element ratios is through the average composition of primitive normal-type mid ocean ridge basalts. A third group of estimates is derived from the elemental and isotopic composition of peridotites. The major element composition is obtained by subtraction of a low degree melt from a bulk silicate Earth composition. A last group of trace element ratios is derived from continental crust (CC). CC is thought to be approximately complementary to the DM and ratios that are chondritic in the continental crust are expected to also be chondritic in the DM. Volatile element and noble gas concentrations are estimated using constraints from the composition of MORBs and ocean island basalts (OIBs). We have varied the age of the DM and the isotopic composition of the DM to bring La/Nb and Ce/Pb within the range observed in primitive mid-ocean ridge basalts. Only a narrow range of ages, 1.6-2.2Ga, yields appropriate trace element ratios. Mass balance with continental crust indicates that the CC and this estimate of the DM are not complementary reservoirs.

V42E-03 1415h INVITED

Mineralogical and Seismic Heterogeneity of the Mantle; the Fate of Young Slabs

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Can we explain all terrestrial magmatism with a single unifying theory? If the mantle is convectively stirred to the point of homogeneity at all scales, then certainly not. Plate tectonics introduces heterogeneity into the mantle having dimensions of slabs. As a slab sinks it may become deformed or stretched if shear stress gradients are high. The Rayleigh numbers used in simulations of mantle convection lead to chaotic convection and rapid mixing. Plumes are invoked to reintroduce heterogeneity into the upper mantle. These calculations ignore effects of plates, continents, pressure, phase changes, and layered convection. Plate tectonics, lithosphere, continental roots, pressure effects, high Prandtl number, stratification and free-slip boundary conditions organize and impede mantle flow. The mantle, convecting sluggishly and passively, is not well mixed. Convective stirring takes time and heterogeneities are constantly being introduced into the shallow mantle. Processes at ridges, however, homogenize the products of heterogeneous mantle melting. New data confirms that under lower mantle (LM) conditions, material rich in Ca, Al and Na (i.e. eclogite) is less dense than pyrolite or any plausible LM mineralogy. The idea that slabs, particularly young ones, will be stuck in the UM is strengthened. Piclogite, particularly if carbonated, melts deeper and at lower temperature than normal mantle; it can develop low seismic velocities as it equilibrates (Presnall, 2003). About 15% of ocean floor surface area is composed of young (<20 My) lithosphere approaching trenches and in back-arc basins; roughly 0.2 km^3/year of such material is currently entering trenches. This is about the magma budget of 'midplate' magmatism. A similar area (plateaus, aseismic ridges) has thick crust. Young and thick-crust material does not subduct to great depths. It warms up and thermally equilibrates on short times scales, becoming neutrally buoyant, and can be sampled again by partial melting on characteristic time scales of 1-2 Gy at leaky transform faults, incipient plate boundaries, extensional regions of the lithosphere and migrating ridges. Thicker slabs of older oceanic crust are more likely to sink deeper into the mantle, after contributing their sediments and fluids to the shallow mantle. The upper mantle is therefore a highly heterogeneous assemblage of enriched and depleted lithologies representing a wide range in chemical composition, scales, ages, melting point, fertility, and isotopic compositions. The homogeneous nature of MORB usually attributed to long-term stirring and mixing of the mantle source is more likely due to homogenization near the extraction site by the sampling process (partial melting and magma mixing). Ubiquitous crustal and slab-scale heterogeneities comprised of recycled oceanic crust or lithosphere in the shallow mantle explains the statistical properties of oceanic basalts and may also be responsible for melting anomalies themselves. Shallow chemical heterogeneities cause