V52A-1055 1330h POSTER

A structural model guide for geothermal exploration in Ancestral Mount Bao, Leyte, Philippines

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The Tongonan Geothermal Field, located on the eroded flank of Ancestral Mount Bao (AMB) volcano, is the largest producing geothermal field in the Philippines. It produces about 640 MW of energy supplying power to the grid of Luzon, Visayas, and Mindano, the three major islands of the Philippines. The Tongonan geothermal field is host to several major power plants that tap geothermal power from the northern flank of the AMB volcano. I present a structural model guide for delineating exploration targets in other flanks of the ~1,200 km2 area of the AMB volcano. The model limits the exploration area, where more detailed investigations involving geophysical, and geochemical methods can be applied. This structural model guide is based on analogue sand cone experiments, their comparison with the natural prototype (i.e. AMB volcano), and the observation of the geographic positions of producing geothermal power plants within the Tongonan Geothermal Field. Based on this structural model, I suggest an ideal exploration target on the south-southeastern flank of the AMB, directly overlying the left-lateral Philippine fault.

V52A-1056 1330h POSTER

Holocene Volcanic Records in the Siple Dome Ice Cores

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Using both the SO_4^{2-} and Cl^- time series and tephrochronological analyses, a highly detailed record of Holocene volcanism is being reconstructed from the Siple Dome A ice core. The volcanic glaciochemical record is being developed at a 2-4 year resolution for the last 10,000 years. Volcanic peaks were identified as those having a concentration of 2σ above the mean positive residual of the spline fit, as was done for the GISP2 volcanic record. We identified about 70 volcanic events for the mid-late Holocene. The largest sulfate signal (350 ppb) over the time period evaluated occurs at 2242 years ago. Large signals of volcanically enhanced sulfate in the ice core record also occur around 720 years ago (1280 C.E.;194-249 ppb)and 4710 years ago (378ppb). Ages for large equatorial or southern hemisphere volcanic eruptions are synchronous with identified sulfate peaks in the reconstructed volcanic record. However, the continuous scan for volcanic glass in these same samples yielded glass compositions more in-line with Antarctica volcanic zones (i.e., local eruptions). Nevertheless, our record provides important information on the atmospheric impact of volcanism in Antarctica geochemical cycles.

The glass (i.e., tephra) found in various samples indicate that volcanoes within the McMurdo Volcanic Center (Victoria Land and the islands off its coast) including Mt. Melbourne, The Pleaides and Buckle Island appear to be the most active in Antarctica during the late Holocene. Rhyolitic shards of a composition not found in Antarctica also are present in some layers, although they are not overly abundant. The presence of dust with a Patagonian origin in East Antarctica ice cores as well as the nature of the Antarctica vortex indicate that material from this part of the southern hemisphere can reach various parts of Antarctica. Common circulation patterns around the Ross and Amundson Seas as well as the satellite trace of aerosols from the 1991 Cerro Hudson eruption, Argentina, provide a possible transport route for glass to reach the Siple Dome site. Our tephra work is providing a new chronology of Antarctica volcanism.

V52B MC: 304 Friday 1330h

Geochemical and Isotopic Tracers of Earth Processes: Earth Reservoirs and Continental Mantle/Crust System (a session in honor of Gil Hanson) *(joint with H, T, GC, MR)*

Presiding: **S B Shirey,** DTM**; P I Nabelek,** University of Missouri

V52B-01 1330h

Trace Element and Os-Hf-Nd-Sr Isotope Systematics of Pervasively Metasomatised Ancient Lithospheric Mantle at the Southeastern rim of the Siberian Craton

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Spinel peridotite xenoliths in Late Cenozoic basalts from the Aldan-Stanovoi shield show effects of Meso-Cenozoic tectonic re-activation and magmatism on the ancient lithospheric mantle. Most of the xenoliths are harzburgites and cpx-poor lherzolites; less common are fertile lherzolites and olivine-rich cumulates. Petrographic and chemical data indicate profound metasomatic alteration of the refractory peridotites, possibly due to interaction with evolved magmatic liquids: precipitation of secondary clinopyroxene and gabbroic interstitial material, low Mg-numbers of olivine and whole-rocks in combination with high Cr in spinel; high whole-rock Ca/Al, enrichments in highly incompatible elements and/or inversely U-shaped REE patterns.

Re abundances in all xenoliths are <0.06 ppb; Os abundances range from 0.1 to 4 ppb. Re and Os (0.9-3 ppb) in a subset of samples (including all cpx-rich lherzolites) that show no or limited metasomatism are positively correlated with modal clinopyroxene or whole-rock Al. 187/188Os in those xenoliths show linear correlations with Al or modal cpx consistent with a depletion age about 2 Ga and the formation of the lithosphere in the Precambrian. By contrast, the metasomatised refractory (2-7% cpx) xenoliths show a broad range in Os abundances and 187/188Os values (0.116-0.127), possibly due to disturbance of the Re-Os system during metasomatism. 176/177Hf is above the N-MORB average in one clinopyroxene separate and range between BSE and MORB values in the few other samples analysed. The 176/177Hf variations could be explained by mixing of ancient depleted mantle with an OIB-type metasomatic agent.

We conclude that the xenoliths represent cratonic mantle strongly modified by metasomatism in hot-spot or subduction-related environments, possibly following removal of the cratonic keel and involving underplating of basaltic melts and their cumulates.

V52B-02 1345h

Tracing Archaean Intracrustal Processes With Hf, Nd and Pb Isotopes: TTGs and Granites From the Barberton Mountain Land, South Africa

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The petrogenesis of the oldest silicic rocks preserved on earth, the Tonalites-Trondhjemites-Granodiorites (TTGs), and the first appearance of 'classical' K-granites (GRs) have been intensely discussed over the last few decades. In this study TTGs and GRs from the Barberton Mountain Land (Kaapvaal Craton, South Africa) were compared using a multi isotope approach (Sm-Nd, Lu-Hf, Pb-Pb) to constrain and date early lithospheric evolution and intracrustal differentiation.

For the petrogenesis of the GRs a one-stage process combined with extraction from a source with near-chondritic composition is proposed. The GRs display similar mean Hf and Nd mantle extraction ages of 3.26+/-0.08 Ga (calc. after Kramers et al. (2001), EUG XI Abstr. Vol.: 421) and 3.26+/-0.09 Ga (calc. after Naegler and Kramers (1998), Precam. Res., 91: 233-252), respectively. Additionally, the Pb/Pb-errorchron gives an age of 3.15+/-0.08 Ga, which agrees well with their mean intrusion age of 3.1 Ga as calculated from U/Pb-zircon ages (Kamo and Davis (1994) Tectonics, 13: 167-192). No intracrustal recycling is seen in their geochemical fingerprint as no decoupling behaviour is visible for the pairs Th/U and Nd/Hf. Supportingly, initial isotope compositions of Nd and Hf scatter around chondritic values and their mean mu-value of 8.84 agrees well with the range for the Archaean mantle of 7 to 9 giving evidence for a juvenile dominated source.

A two-stage petrogenetic process combined with anatectic melt origin from hydrated and metamorphosed basaltic crust is proposed for the TTGs. Their mean Nd mantle extraction age of 3.46+/-0.13 Ga agrees well with existing U/Pb-zircon ages of 3.4 Ga to 3.5 Ga. However, their mean Hf model age is 3.35+/-0.11 Ga, which is similar to the Pb/Pb-errorchron age of 3.35+/-0.16 Ga. These ages are interpreted to date the two main events of the TTG-petrogenesis. Firstly, crystallisation of the mafic precursor and secondly, anatectic melt extraction, which has resetted the common Pb and Hf chronometer. Supportingly, intracrustal recycling is evident by a decoupling of the pairs U/Th and Hf/Nd and a higher mean mu-value of 11.2. Therefore, the recalculation of Hf isotope composition of the TTGs to the zircon age is too far back in time and results in positive epsilon values. This is not the case for Nd isotope composition as this is still connected to the zircon age. In conclusion no highly differentiated Archaean mantle is needed to explain isotope characteristics of TTGs.

V52B-03 1400h INVITED

Geochemical and Geophysical Constraints on Diamond Formation and Lithospheric Mantle Evolution Beneath Southern Africa.

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Seismic study of the lithospheric mantle of the Kaapvaal-Zimbabwe-Limpopo cratons has produced a detailed picture of the lithospheric mantle at depths within the diamond stability field. Tomographic inversion of P-wave velocity shows that at 150-225 km depths, the craton has relatively faster lithospheric mantle that occurs in two prominent, irregularly shaped lobes separated by a broad west-northwest trending band of relatively slower mantle. Thus, Jwaneng, Letlhakane, Orapa, Premier, and Venetia diamonds were hosted in slower lithospheric (P-wave velocity anomalies of -0.4 to 0.0 %) whereas De-Beers Pool, Finsch, Roberts Victor, Jagersfontein, and Koffiefontein diamonds were hosted in faster mantle (P-wave velocity anomalies of +0.1 to +0.5 %). Diamonds from the seismically slower areas show a 1.0-2.9 Ga age range in sulfide inclusions, a greater percentage of younger sulfide inclusion ages, and consistently younger silicate inclusion ages. The only locality with no appreciable Proterozoic inclusion component (sulfide or silicate) is the DeBeers Pool which sits directly within one of the seismically faster lobes of Archean lithosphere. Nonetheless, 2.9 Ga sulfide inclusion Re-Os ages are common at every locality studied so far and confirm the importance of an Archean eclogitic diamond paragenesis. The range in carbon isotopic composition between diamonds hosted in seismically fast vs slow lithosphere is similar ($\delta^{13}C$ of 1 to 24) with a higher percentage diamonds from seismically slow lithosphere in an isotopically light histogram tail with $\delta^{13}C$ ranging from 8 to 20. This seismically light tail is dominated by eclogitic paragenesis diamonds which, with the exception of Venetia and Jagersfontein, are found to greater abundance in the seismically slower areas of

the lithosphere. Thus paragenesis governs any subtle C isotopic differences between diamonds from fast versus slow lithosphere. Nitrogen aggregation data show the clearest correlation with lithospheric seismic structure with diamonds from seismically slower mantle, having lower % of Type II diamonds, higher % of Type IaB diamonds and a ratio of II(%) to IaB (%) that ranges from 0.1 to 0.3 (as compared to 0.3 to >6 for diamonds from faster mantle).

The prevalence of eclogitic sulfide inclusion ages and cratonic peridotite mantle model ages near 2.9 Ga confirm that cratonwide diamond formation and stabilization of the cratonic root took place near this time. Diamonds from regions of seismically slower lithosphere have a higher proportion of Proterozoic Re-Os and Sm-Nd ages, greater component of eclogitic parageneses in the diamond population and greater percentage of diamonds with IaB N aggregation. Together these features show that the current lithospheric siesmic structure of the craton is a mid-Proterozoic modification of an Archean keel by tectonothermal events that heated the lithosphere, altered its composition chiefly by metasomatism, and added new eclogitic diamonds to an extant lithospheric Archean diamond population.

V52B-04 1415h

Looking up at Mountain Building: Tracing Orogeny Using Isotopes from Alpine Peridotites

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Lenses of mantle-derived rock (variously called alpine-type peridotites, orogenic massifs and orogenic lherzolites) are embedded within many mountain systems and contain geochemical information on the evolution of those mountain systems. This information constrains subduction polarity, the nature of the mantle wedge above subduction zones, and the type and timing of collision. Their presence within a mountain system calls for tectonic events where slices of crust are subducted deeply into the mantle so that fragments of the overlying mantle-wedge can become entrained in the crust. They subsequently are exhumed as the inherently buoyant crustal slab returns towards the surface (eduction) and erosion exposes deeper levels of the orogen. Where not severely altered, the peridotite, pyroxenite and eclogite that comprise these lenses contain minerals and mineral assemblages that can be studied through a variety of stable and radiogenic isotopes. Garnet-bearing assemblages are particularly useful because they can be dated by Sm-Nd, U-Pb and Lu-Hf techniques and have proven useful at constraining tectonic events and processes in the Alps, Variscides and portions of the Caledonides. Garnet-free systems are less tractable to radiometric dating although recent advances in Re-Os dating of sulfides using LAM-ICPMS techniques show promise. Isotopes, in conjunction with major and trace element studies, from minerals can reveal mantle depletion and enrichment events that may or may not be correlated with the Wilson. Clinopyroxenes (cpxs) are particularly useful because of their measurable concentrations of Sr, Nd, Pb and Hf. In the Bohemian Massif of the Variscides, for example, cpxs from depleted lherzolites define linear arrays on Sr-Nd and Sm-Nd diagrams that are interpreted as marking melt-extraction at MOR systems during the early oceanic stages of the Variscan Wilson Cycle. Cpxs from associated pyroxenites define younger arrays that probably mark enrichment by fluids and melts from subduction zones related to the closure stages of the Variscan Cycle. These patterns indicate the involvement of sub-oceanic lithosphere in the evolution of the Variscan belt. Completely different cpxs arrays from two peridotite-bearing terranes in the Caledonides fail to relate either depletion or enrichment events to the Caledonian Cycle, showing instead the involvement of pre-Caledonian sub-continental mantle lithosphere. These patterns suggest Caledonian collisions involved micro-continents and ancient cratons and sutures that, during the culminating Scandian phase, reached deeply into the mantle to tap ancient sub-continental lithosphere.

V52B-05 1430h

Hf-Nd Isotopic Correlation in the Deccan Flood Basalt Province

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Hafnium isotopes along with other isotopic and geochemical characteristics, including incompatible trace elements, of several of the lower formations of the Deccan Flood Basalt Province were analyzed to characterize petrogenesis of different tholeiitic lava suites, especially with respect to potential mantle and crustal sources.

The rare earth elements of the different formations (from top to bottom- Mahabaleshwar, Ambenali, Bushe, Khandala and Neral) all show an LREE-enriched signature, concentrations varying between 30 to 60 times chondrite for La. $(La/Lu)_n$ values range from 4.1 to above 8 with the exception of Ambenali, which has a less LREE-enriched signature with $(La/Lu)_n$ values ranging between 3.6 to 5.3.

Hafnium isotopic data of the lower formations of the Deccan show initial ϵ_{Hf}(T) values covering a range from -3 to -28. $^{176}Lu/^{177}Hf$ varies between 0.20 to 0.70. f(Lu/Hf) varies within a narrow range, between -0.90 to -0.97 while f(Sm/Nd) ranges from -0.84 to -0.86. Bushe gives the lowest range of ϵ_{Hf}(T) from -21 to -28 with the corresponding ϵ_{Nd}(T) varying between -4.0 and -16.9, while Khandala for almost the same range of neodymium isotopic values has ϵ_{Hf}(T) between -11 and -15. The ϵ_{Hf}(T) values of Neral is in between those of Khandala and Bushe, around -19. Ambenali, has the narrowest range with ϵ_{Hf}(T) of -3 and ϵ_{Nd}(T) between 3 and 5. The Ambenali suite reflects the least contaminated of the Deccan suite of lavas as analyzed here and previously confirmed by other isotopic studies. In Hf-Nd isotope correlation plot, the lower Deccan formations of Neral, Khandala and Bushe define individual subparallel arrays that are shallower than the oceanic basalt array and the overall terrestrial array, including the crustal array, although the bulk of the lower formation data fall within the crustal array of Vervoort et al (1999). From these subparallel Hf-Nd arrays, it is evident that the other end-members contributing to the Ambenali-type source magmas are distinctly different for each of these lava suites, and can be characterized by their ϵ_{Hf}(T) values as mentioned above. Although these end-members are discernible in ϵ_{Nd} vs ϵ_{Sr} plot (e.g., Peng et al, 1994) of previous studies, our new Hf-isotopic data provide clear evidence of major contributions from the ancient Indian continental crustal reservoirs in the petrogenesis of the lower lava formations of the Deccan Flood Basalt Province.

V52B-06 1445h

Laser Ablation Analyses of Pb Isotopes in Ancient Feldspars: Application to a Polymetamorphic Terrane, West Greenland

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Laser ablation was used to sample the Pb isotopic compositions of various feldspars, as well as isotopic standards. The ablated material was analyzed by MC-ICP-MS. The resulting accuracy and external precision are comparable to conventional (i.e., not double or triple-spiked) feldspar Pb isotope analyses done by TIMS. However, the data can be acquired with no chemical separation and require only a few minutes per sample. A pilot study was made of the feldspars from a polymetamorphic terrane in West Greenland, in which Late Archean gneisses were deformed and metamorphosed during the Early Proterozoic. In this terrane, isotopic contrasts have long been sought to delineate any suture between discrete Archean continental blocks that might mark the site of ocean closure. Previous whole rock Nd and Pb isotopic studies had yielded equivocal results on the presence of such an isotopic discontinuity. The laser ablation feldspar data presented here, combined with existing whole rock Pb data, point to real differences in the sources of gneisses from various parts of the orogen. This indicates that the laser ablation method of sampling feldspar Pb holds real potential for future reconnaissance studies of old continental crust in a manner similar to that of zircon U-Pb geochronology studies.

V52B-07 1520h

Integrated Structural and Geochemical Studies of Granite Magmatism, Maine Appalachians

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Crustally derived granites are important probes of the unexposed cores of extinct orogens. In southern Maine a variety of magmatic and deformational textures characterize the diverse granites that crop out within and adjacent to the Norumbega shear zone system (NSZS). Existing regional maps reflect the general lack of understanding of the relation between granites of various scales and their hosts. Field evidence for synkinematic transport and emplacement is abundant, hence we seek to define the extent to which regional metamorphism and deformation accompanied granite magmatism, and whether these processes were phased, as is the traditional concept, or diachronous, as permitted by field relations. The only appropriate means of considering such problems integrate thorough field and structural analysis with precise geochronology and isotopic/elemental geochemistry.

We focus on a ~70 km cross-strike transect from the core of the Sebago pluton (c. 293 Ma) southeast into the highest strain portion the NSZS along the coast of Maine. The pluton was previously considered the largest exposed batholith in New England, but new mapping shows a clearly separate central body of homogeneous granite (<400km^{2}2) derived from Avalon-like sources is flanked by an area permeated by smaller bodies of more geochemically heterogeneous granite and migmatites (the Sebago migmatite domain). Extant geochemical data are consistent with derivation of these subconcordant granites from materials similar to their host metasedimentary rocks. In the migmatite domain adjacent to the pluton deformational fabrics in amphibolite facies country rocks are relatively variable in orientation. In contrast, penetratively parallel planar structures with consistent NE-SW-striking- and steeply SE-dipping orientations dominate the area ~50 km from the zone exhibiting the highest recorded strain fabrics. Protracted pre- and syn-Acadian magmatism has been recognized in similarly structurally complex parts of the N. Appalachians (Sevigny and Hanson, 1993; 1995; GSA Bull.), so it is important to test if Acadian-Alleghanian plutonism in southern Maine was similarly extended.

V52B-08 1535h

Generation of Leucogranites and Testing of the Trace Element Batch-Melting Equation

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The trace element batch melting equation of Schilling (1966), $C_l = C_o/[D(1-F)+F]$, is a simple yet an elegant description of the equilibrium and mass-balance relationships of trace element distribution in a partially molten system. The power of this equation was demonstrated in classic papers by Gil Hanson (1978, 1980) on trace element modeling of igneous processes. However, a frequent drawback in its application is that there are usually too many unknowns: the trace element concentration in the source (C_o), the fraction of melting (F), and the residue/melt distribution coefficient (D), which depends on knowledge of mineral proportions in the residue.

Proterozoic leucogranites and metasedimentary rocks in the Black Hills, South Dakota, provide an opportunity to test applicability of the equation to constraining petrogenesis of granites. Previous isotopic evidence indicates that the metasedimentary rocks represent sources for the leucogranites; thus, the leucogranite composition can be assumed to be the product of anatexis of the metasedimentary protoliths. The potential fertility or fraction of melting (F) of the metasedimentary rocks was computed for both muscovite dehydration-melting (MDM) and biotite dehydration-melting (BDM) reactions by least-squares regression of major element whole rock compositions in terms of observed mineral and melt compositions. The metapelites contain quartz, plagioclase, biotite, garnet, muscovite, sillimanite or orthoclase whereas the metagraywackes contain insignificant muscovite and no sillimanite. For MDM, the melt was assumed to contain 4.5% water, appropriate for melting

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at 10 kbar. The calculated F ranges from 7 to 25%. It is controlled by the available water in protolith muscovite. Because the metagraywackes contain insignificant muscovite, they cannot undergo MDM. BDM was modeled assuming nearly complete breakdown of biotite, with melt containing only 2% water. Melt percentages for metapelites range from 0 to 49%, whereas for the metagraywackes from 13 to 40%. The fertility of metapelites during BDM is controlled by the available plagioclase, whereas the fertility of metagraywackes is controlled by the available biotite.

For each metasedimentary rock sample, the calculated melt percentage and Ds for Rb, Sr, and Ba, as determined from calculated residual mineralogy and published distribution coefficient data, were used to calculate concentrations of these trace elements in the partial melts. The ranges of calculated Rb and Sr concentrations for the MDM reaction reproduce well the observed concentration ranges in the leucogranites. In contrast, the predicted range of Ba concentrations is much narrower than the observed range, which spans over a magnitude. The large observed concentration range in Ba is consistent with significant local fractionation of plagioclase from alkali feldspars in the leucogranites. Overall, however, the modeling demonstrates that chemical heterogeneity in the leucogranites is dominantly the function of variable mineralogy and Fs during production of small melt batches in the metapelitic source rocks.

V52B-09 1550h INVITED

Fractionation of Nb/Ta and Zr/Hf in the Mantle-Crust Sytem

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The isovalent element pairs Zr/Hf and Nb/Ta have generally been regarded as behaving identical during most geologic processes. As a consequence, it was expected that the ratios of these elements pairs are more of less constant and chondritic in all reservoirs of the silicate Earth. However, recent measurements of Zr/Hf and Nb/Ta of higher precision have indicated that mantle-derived magmas in certain geochemical environments and tectonic settings are characterized by distinct variations in Zr/Hf and Nb/Ta ratios that deviate significantly from the chondritic values. In comparison to known analytical methods, the resolution of Nb/Ta and Zr/Hf measurements can be improved by nearly a factor of 10 by isotope dilution measurements using a mixed 180Ta-94Zr-180Hf-176Lu tracer. In order to establish the solar system ratios for Nb/Ta and Zr/Hf, chondrites and eucrites were analyzed. The mean Zr/Hf of all chondrites and eucrites investigated in this study is 34.2+/-0.3 (2 RSE) and is indistinguishable from the chondrite-only mean value, which is 34.1+/-0.6. This new mean Zr/Hf value is lower than the previous estimate for the Zr/Hf of 36.3, which was inferred from analyses of OIBs and the chondrite Orgueil (Jochum et al., 1986). The chondritic Nb/Ta of 17.6+/-1.0 determined in this study agrees with previously estimated values (Jochum et al. 2000). A comparison of basalts and peridotites reveals subchondritic Zr/Hf for depleted peridotites and basalts derived from the depleted mantle. Peridotites from the Balmuccia peridotite (Italy) have Zr/Hf as low as 10 and they show an excellent correlation with Zr-contents. Therefore it can be assumed that the lower Zr/Hf in the mantle relative to the chondritic value is a feature caused by melt extraction. Nb/Ta in the Balmuccia peridotites show a similar variation, but no correlation with Ta-contents and Zr/Hf can be observed. This decoupling is caused by the extremely incompatible behavior of Nb and Ta during mantle melting. Small amounts of trapped residual melts can dominate the Nb-Ta budget far more than the Zr-Hf budget. A major problem in mass balancing Earth's Nb-Ta budget is the apparent subchondritic Nb/Ta of the crust at a more or less chondritic Nb/Ta of OIB. This apparent lack of a high Nb/Ta reservoir has invoked models, where the missing Nb-Ta might be stored in subducted refractory eclogites (Rudnick et al. 2000) or in the Earth's core (Wade and Wood 2000). In contrast to the first model, new high precision Nb/Ta and Zr/Hf data from Kamchatka arc rocks (Münker et al., this volume) indicate that Nb/Ta and Zr/Hf appear to be little fractionated in subduction zones.

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V52B-10 1605h

Early Differentiation of the Crust-Mantle System: a Hf Isotope Perspective

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The Lu decay constant recently determined by Scherer et al. 2001 (i.e., 1.865 x 10^{-11} yr^{-1}) agrees with the results of the two latest physical counting experiments (1.86 x 10^{-11} yr^{-1}; Dalmasso et al 1992, Nir-El and Lavi 1998), but is ca. 4 percent lower than the decay constants that have been used throughout the Hf isotope literature (e.g., 1.94 x 10^{-11}, Tatsumoto et al., 1981; 1.93 x 10^{-11} Sguigna et al, 1982). In addition to making Lu-Hf ages older by ca. 4 percent, the revised decay constant also shifts the calculated initial epsilon Hf values of early Archean and Hadean rocks and zircons that are used to constrain crust-mantle differentiation in the early Earth. The initial epsilon Hf values for low-Lu/Hf samples such as zircons and evolved felsic rocks shift downward by 2-4 epsilon units, primarily due to the shift in the position of the CHUR evolution curve rather than that of the samples themselves. Mafic rocks, such as komatiites have higher Lu/Hf ratios that are closer to that of CHUR and therefore their initial epsilon Hf values do not shift as much (up to 1.3 epsilon units lower or 0.4 epsilon units higher). Using the old decay constant, some early Archean rocks (e.g., Amitsoq gneisses; Vervoort et al., 1996, Vervoort and Blichert-Toft, 1999) seemed to have very high initial epsilon Hf values (up to +6), implying that the upper mantle was moderately depleted in the early Archean and that a substantial volume of crust was produced in the Hadean. However, when recalculated with the new decay constant, the data suggest that the mantle was only slightly depleted, requiring less early crust extraction, and allowing a later date for the onset of significant crust production. In contrast, the extremely low recalculated epsilon Hf values of Earth's oldest zircons (Amelin et al., 1999, Amelin et al., 2000) indicate that Earth's first crust formed at or before 4.3 Ga, and that this crust remained intact long enough (>200 million years) to evolve to such low epsilon Hf values. Either the volume of crust that was extracted in the Hadean was too small to cause moderate mantle depletion, or much of that early crust was recycled back into the mantle, thus effectively erasing evidence of early depletion. Importantly, the validity of these conclusions depends on the CHUR parameters (176Lu/177Hf, 176Hf/177Hf) that are used to calculate initial epsilon Hf values.

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Li Isotopes as a Tracer of Earth Processes

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The δ^7Li composition of the bulk Earth is not well established, although it can be estimated from that of mantle-derived magmas and peridotites to be about +4. Presently, there are next to no δ^7Li data for meteorites and this lack of cosmochemical constraint for the Earth needs to be considered in our models. Most upper crustal rocks and sediments have δ^7Li compositions greater than this mantle value and are generally of the order +5 to +15. Continental surface waters typically have δ^7Li values ranging from +15 to +32, while seawater has a nearly constant composition of +32. Collectively, these observations point to a uni-directional evolution in δ^7Li values from an initial mantle composition. Recently, we (Zack et al, this conference) determined that subduction-zone related eclogites and their meta-sediments possess dominantly negative δ^7Li values, ranging down -10. Additionally, the flood basalt sample BCR has a δ^7Li value of +2, which is lower than typical MORB/OIB/arc basalt values and indicates a contribution from an isotopically lighter source component. Collectively, these observations raise 2 interesting questions: (1) What is the physics controlling the fractionation of ^{7}Li from ^{6}Li? In contrast to an anion like O, the heavier isotope of Li is enriched in the fluid not the solid during low P-T processes. (2) Are eclogitic residues from subduction zones stored in the deep mantle as highly negative Li isotope reservoirs? The latter question raises the possibility of finding greater Li isotopic diversity in OIBs than that presently observed.

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Trace Element and Pb Isotope Constraints on Dynamic Evolution of Earth Reservoirs

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Advances in interpretation of Pb isotope systematics provide constraints for modelling Earth evolution. Such improved understanding of Pb isotope systematics has coincided with advances in techniques for accurate Pb isotope ratio measurement by MC-ICPMS. Continental growth since 3.75 Ga has occurred at convergent margins via dehydration of subducted slabs and supra-subduction zone melting. Nb is preferentially retained in slabs relative to U and Th, which are lost to escaping fluids. Over time, the depleted upper mantle (DM) lost U and Th relative to Nb. Thus Nb/Th and Nb/U of UM mirror amount of continental crust present. Because Nb, Th and U are similarly incompatible during MORB melting, temporal Nb-Th-U systematics of mantle can be reconstructed from uncontaminated, depleted-mantle derived rocks[1]. Excellent agreement exists between crustal growth curve based on Nb/Th and those based on Pb isotope systematics[2] and geophysics [3]. Temporal variation of Nb/U reflects crustal extraction until 2 Ga. It then reflects preferential U recycling into DM, constraining timing of preservation of a pandemic oxygenated atmosphere. Increase in atmospheric O_2 explains the second Pb paradox and refines understanding of DM evolution. Key to understanding mantle Pb isotope evolution is the realization that DM has highly dynamic U/Pb and Th/U ratios relative to undegassed lower mantle (LM). Thus, so-called OIB EM-1 reservoir could reflect LM[4]. Pb data for Phanerozoic and Proterozoic Gp 2 kimberlites from South Africa plot in thorogenic and uranogenic Pb space consistent with a LM source [4]. Mineralogically, chemically and isotopically different Gp 1 kimberlites, which are readily discernable in plots of PM normalized Ta/U and Nb/Th have very radiogenic $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ but relatively unradiogenic $^{207}Pb/^{204}Pb$, compositions identical to HIMU OIB's. We have suggested in [4] that the HIMU isotopic composition can be derived from EM-1 during a transient <100 Ma stage of strong U/Pb fractionation. Recent discovery of LM baddeleyite provides the mineralogical rationale for this scenario. Subducted oceanic crust and continental sediment are unlikely candidates for OIB HIMU source, as trace element fractionation during subduction induced dehydration lowers U/Pb ratio of residual slabs. This has important consequences for genesis of lamproites and minettes. In an speculative model by [5], and supported by seismic tomography, TZ was interpreted as a graveyard for slabs containing high pressure mineralogies such as majorite, NAL phases and hollandite. Partial melts derived from such an environment yield alkaline rocks with Pb isotopic compositions plotting to the left of the Geochron. Significantly, this interpretation is now supported by Pb isotopic data for TZ macrocryst suite xenoliths. An unrelated, now extinct HIMU reservoir, is inferred from Pb isotopes in TTG gneisses in some Archean cratons. Evolution of this source is reflected in Pb isotopic data for galena from Isua that require source separation before 4.3 Ga. The only conceivable long-lived source would have been Hadean crust. Rare examples of pre-plate tectonics TTG gneisses with this isotopic memory occur in the NAC where feldspar Pb isotopes define rotated isochrons that intersect the transient HIMU evolution vector at the time of zircon crystallization of the gneiss protoliths. This transient early Archean HIMU reservoir was subsequently destroyed by subduction.

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