

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., 87Sr/86Sr = 0.707413-0.709090) compared with data from ODP767 and 768,

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

## 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

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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 (Ir = 16.7 x 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

enstatite chondrites have relatively high Pd concentrations, compared to the other highly siderophile elements. Our new data show that enstatite chondrites have Pd/Ru and Pd/Ir ratios of  $0.987 \pm 0.102$  and  $1.48 \pm 0.18$ . Carbonaceous chondrites and ordinary chondrites have distinctly lower Pd/Ru and Pd/Ir ratios. Pd/Ru and Pd/Ir in carbonaceous chondrites average  $0.754 \pm 0.104$  and  $1.08 \pm 0.17$ , respectively. Similarly, ordinary chondrites have average Pd/Ru and Pd/Ir ratios of  $0.759 \pm 0.088$  and  $1.153 \pm 0.153$ . The cause of high relative Pd concentrations in enstatite chondrites is not well understood. Its ubiquitous presence, regardless of the presence of brecciation, degree of metamorphism and terrestrial weathering, suggests that it also occurred early in the history of the solar system. The distinguishing HSE characteristics of chondrites may permit better characterization of the source of the terrestrial and lunar late influx materials. The Os isotopic composition of the terrestrial primitive upper mantle indicates late accretion dominated by materials with Re/Os most similar to enstatite and ordinary chondrites than to carbonaceous chondrites. Published data for samples from fertile, terrestrial mantle yield broadly chondritic ratios of Pd/Ir and Pd/Ru, but are suggestive of some variation in those ratios among upper mantle reservoirs. Better constraints on the composition of terrestrial late influx may come from new analyses of upper mantle material and in lunar impact breccias.

## V21D-04 0915h

### Targeting the (3.8-4.0 Ga) Impactors: Siderophile Element Signatures of Lunar Impact Melts

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Significant gaps remain in our understanding of the early impact history of the Earth and Moon, and their influence on geologic and biologic development. Outstanding controversies include whether or not the Moon, and by inference the early Earth, was hit by an unusually heavy "terminal cataclysm" of collisions during the period 3.8 to 4.0 Ga, and the number of large impact events represented by lunar samples. Coincidentally or not, the large nearside lunar basins are almost identical in age with the oldest terrestrial rocks, and are therefore relevant for consideration of the possible role of impacts in shaping the terrestrial continents and early life environments. To improve our understanding of the impact history of the Moon and to provide new information about the types of planetesimals that were involved in the early impact history of the inner Solar System, we measured the concentrations of highly siderophile elements (HSE: Re, Ir, Pt, Pd, Ru) in a suite of Apollo 17 impact melt breccias using high precision ID-ICPMS methods. These breccias all have poikilitic textures, relatively mafic bulk compositions, and high levels of incompatible trace elements and all likely represent ejecta from the Serenitatis basin. Ar-Ar ages are consistent with the formation of these breccias in a single impact event at  $3893 \pm 9$  Ma.

HSE from 11 representative samples have W-shaped patterns on CI-normalized diagrams, with enrichments in Re, Ru and Pd relative to Ir and Pt, and absolute abundances ranging from ~0.5 to 4% of CI reference values. Stronger depletions of Ir and Pt relative to Re, Ru, and Pd are correlated with decreasing HSE concentrations. The samples with the highest HSE concentrations have patterns that are identical to those of EH chondrites, but the patterns become increasingly less diagnostic of meteorite group with decreasing concentrations. The systematic variation of HSE patterns with decreasing concentration suggests that simple chemical fingerprints of impactor type using individual samples can potentially give misleading results and consideration of impact-related fractionation using high precision data for suites of impact breccias is required. An additional sample (77035) has a distinctly different HSE pattern and is more consistent with an impactor of ordinary or EL-type chondrite composition. It likely represents a discrete impact event that was sampled at the Apollo 17 site. The clear recognition of specific and different types of meteoritic impactors indicates a diverse population of planetesimals bombarded the Moon, and that the lunar crust was not heavily contaminated with HSE prior to 3.8-4.0 Ga, a feature more consistent with a late cataclysm than a smoothly declining accretionary flux.

## V21D-05 0930h INVITED

### Siderophile Element Fractionation in the Earth's Core: Direct Estimate of Partition Coefficients from Primitive Siberian Flood Basalts

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Evidence from Os isotopes suggests that the siderophile element signature in some deep-mantle plumes may be derived from the outer core. The siderophile element pattern in the least fractionated plume basalts therefore may reflect solid-liquid metal fractionation, rather than that from partial melting of the upper mantle.

Partition coefficients (D) derived from IIAB irons are governed by three major factors; element melting point, atomic radius and electron configuration. Values for Au, Ni, Re and the heavy platinum group elements (HPGE) plotted against melting point lie on a hyperbola with Os at the maximum. The light PGE (LPGE) also show a trend of increasing D with melting point but lie below the HPGE trend, perhaps due to differences in free atom electronic configuration.

Siberian Flood Basalts (SFB) are of plume origin, and the Mokulaevsky and Morongovsky flows are the least crustally contaminated. Abundances of Ni, Rh, Pd, Ir, Pt and Au in these flows plot on a smooth curve against melting point when chondrite-normalized, but not when mantle-normalized. Thus, we explore the possibility that the SFB distributions reflect fractionation in the core rather than in the upper mantle. For 5.5 per cent crystallization, iron meteorite data yield much less fractionation of Ir than is seen in SFB, suggesting that D for Ir in the Earth's core is larger. Inversion of the SFB data yields a smooth curve when D values of PGE, Au and Ni are plotted against melting point. The D value for Ir is estimated to be about 5 times larger than in iron meteorites. If values for Re and Os are similarly enhanced, as suggested by high pressure experiments, Os isotopes in plumes may be more compatible with gradual formation of the inner core rather than early growth to the present size.

## V21D-06 0950h

### <sup>187</sup>Os-<sup>186</sup>Os and He Isotope Systematics of Iceland Picrites

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Iceland is one of the longest-lived modern plumes, and seismic imaging supports a model where the roots of this plume are at the base of the lower mantle. Hence, Os isotopic data for lavas from this plume are ideal for further testing the role of core-mantle chemical exchange at the site of plume generation in the lower mantle, and for addressing the origin of Os-He isotopic variation in plumes. Recent work has shown that lavas from some plume systems (Hawaii, Noril'sk-Siberia, Gorgona) show coupled enrichments in <sup>186</sup>Os/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os, not observed in upper mantle materials including abyssal peridotites. Picrites from Hawaii display a positive correlation between <sup>186</sup>Os/<sup>188</sup>Os and He isotopes (R/Ra), where range in <sup>186</sup>Os/<sup>188</sup>Os of  $0.119834 \pm 28$  to  $0.1198475 \pm 29$  and corresponding R/Ra from +7 to +25. These systematics are consistent with a lower mantle source for the radiogenic <sup>186</sup>Os signal in the Hawaiian plume. The coupled Os enrichments in these plumes has been attributed to core-mantle chemical exchange, consistent with generation of the Hawaiian plume at the base of the lower mantle in D". Other potentially viable models await additional scrutiny. New He isotope and high precision <sup>186</sup>Os/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os measurements for Iceland picrites show unique systematics compared to Hawaii. These picrites have <sup>187</sup>Os/<sup>188</sup>Os ranging from 0.1297 to 0.1381 and R/Ra of +9 to +18, with generally higher R/Ra correlating with higher <sup>187</sup>Os/<sup>188</sup>Os. Unlike the Hawaiian picrites from Hualalai and Loihi, which have coupled enrichments in <sup>186</sup>Os/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os, the Iceland picrites show no enrichment

<sup>186</sup>Os/<sup>188</sup>Os -  $0.1198363 \pm 28$  (2s, n=14). Such Os-He isotopic variations require one end-member source that has high R/Ra, coupled with a long term elevated Re/Os and Pt/Os similar to that of the upper mantle. These systematics are inconsistent with either known upper mantle materials or those purported for ancient recycled slabs and may be a previously unidentified component in the lower mantle.

## V21D-07 1025h

### Osmium-Isotope Variations in Cameroon Line Basalts: HIMU Mantle Versus Crustal Contamination

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The Cameroon volcanic Line (CVL) is a chain of Tertiary to Recent, transitional to strongly alkaline intraplate volcanoes extending from the S. Atlantic island of Pagalu to the continental interior of West Africa (Biu Plateau). This geographic distribution provides a ideal opportunity to compare the subcontinental and suboceanic mantle sources of intraplate magmatism. Basalts erupted in the continental and oceanic sectors of the CVL are chemically and petrologically indistinguishable. Therefore, the magmas must have originated at sublithospheric depths [1]. CVL lavas also display a lead isotope anomaly (HIMU type) at the continent/ocean boundary (COB) which has been attributed to a fossil mantle plume [2,3].

Osmium isotopes and Re/Os have been measured in more than twenty well-documented [4] young alkaline basalts (<10 Ma) from oceanic (Pagalu, S. Tom, Principe) continental (Manengouba) and COB (Mt Cameroon) sectors of the CVL. Os and Re concentrations range between 1.72 and 108 ppt and between 0.143 and 1.28 ppb respectively. No relationship is observed between common Os concentrations and isotopic compositions. The basalts from the oceanic sector display a range of initial <sup>187</sup>Os/<sup>188</sup>Os ratios between 0.1280 and 0.1876 and those from the continental sector range between 0.1449 and 0.5565. The samples from the COB characterised by the high <sup>206</sup>Pb/<sup>204</sup>Pb (>20.2) yield an initial <sup>187</sup>Os/<sup>188</sup>Os ratio of 0.153 consistent with the value attributed to the HIMU end-member (Tubuai-Mangaia) [5]. However, most of the lavas from the continental sector show highly radiogenic initial <sup>187</sup>Os/<sup>188</sup>Os ratios (0.294 to 0.557) that increase with decreasing <sup>206</sup>Pb/<sup>204</sup>Pb. This variation can be attributed to the assimilation of continental material by the ascending magma, which appears to have significantly modified neither the Sr and Nd isotopic compositions [6], nor the U/Pb or La/Th ratios. The systematic change in lead isotope composition from the COB oceanwards is positively correlated with decreases in <sup>187</sup>Os/<sup>188</sup>Os (0.140 to 0.128). This covariation can be attributed to the mixing of plume material (HIMU) with the ambient upper mantle (DMM) characterised by radiogenic Pb and Os.

[1] Fitton, J.G. and Dunlop, H.M., EPSL, 72, 23-38, 1985. [2] Halliday, A.N. et al., J. Petrology, 29, 181-211, 1988. [3] Halliday, A.N. et al., Nature, 347, 523-528, 1990. [4] Barford, D.N. et al., (Submitted to EPSL). [5] Schiano, P. et al., EPSL, 186, 527-537, 2001. [6] Rankenburg, K. et al., AGU abstracts, 81, 48, 2000.

## V21D-08 1040h

### Extreme Unradiogenic Os Isotopes in Hawaiian Mantle Xenoliths: Evidence for Preservation of Ancient Melt-Depleted Domains in the Convecting Upper Mantle

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Constraints on the Os-isotopic composition of the upper mantle derive mainly from studies of abyssal peridotites and ophiolite massifs. Os-isotopes in abyssal and ophiolite peridotites are heterogeneous and

generally sub-chondritic ( $0.120 <^{187}\text{Os}/^{188}\text{Os} < 0.130$ ), reflecting Re removal from the upper mantle through crust formation (and subduction). It is unclear whether these samples accurately reflect the range and average composition of the upper mantle. The majority of ophiolites derive from arc or back-arc tectonic settings and the Os-isotopes may therefore reflect interaction with subduction-derived melts or fluids. Os-isotopes in abyssal peridotites are on average less radiogenic than ophiolites. However, some researchers have suggested that abyssal peridotites do not representatively sample the convecting upper mantle, but instead reflect ancient melt-depleted residues "floating" on top of the convecting mantle. In addition, most abyssal peridotites have experienced significant seawater alteration, which may also bias Os-isotopes to high values. Mantle xenoliths from ocean island basalts may provide a less altered and more representative sampling of the shallow oceanic mantle. To better constrain the extent and origin of Os-isotope heterogeneity in the oceanic lithosphere, we have examined Os-isotope and mineral major and trace element compositions in a suite of lherzolite xenoliths from Salt Lake Crater (SLC), Oahu, Hawaiian Islands. Previous studies indicate that these xenoliths derive from a residual melting column presumably formed at the mid-ocean ridge at 90 Ma.

Os-isotopes in the SLC xenoliths span a large range ( $0.113 <^{187}\text{Os}/^{188}\text{Os} < 0.125$ ), and extend to significantly less radiogenic values than previously reported in abyssal peridotites. Variable Na, Ti, and LREE enrichment ( $0.5 < \text{La}/\text{Sm}_N < 6$ ) in SLC clinopyroxenes indicate that the xenoliths have experienced variable extents of melt/rock interaction. However, Os-isotopes do not correlate with any indicators of melt/rock interaction. Furthermore, the host lavas have significantly more radiogenic Os-isotopes than the xenoliths. Therefore, melt/rock interaction did not significantly alter the Os-isotopic compositions of the SLC xenoliths. The unradiogenic Os-isotopic values are consistent with Re-depletion model ages ranging from 0.4 to 2 Ga. Such unradiogenic values have not previously been reported from oceanic settings but are common in sub-continental lithospheric mantle (SCLM) xenoliths. However, mineral phases of the SLC xenoliths display major element trends identical to those of abyssal peridotites (e.g., Cr# in spinel ranges from 15 to 45 and covaries with  $\text{opx Al}_2\text{O}_3$  content). Furthermore, olivine mode-composition trends are dissimilar to those observed in SCLM xenoliths. At present there is no evidence to suggest that the Hawaiian xenoliths sample rafted or subducted SCLM. The very old Re-depletion model ages of the SLC xenoliths suggest a melt extraction event significantly predating melt extraction at the mid-ocean ridge at 90 Ma. Os-isotopes do not correlate with major element indices of prior melt extraction (e.g.,  $\text{opx Al}$ -content). However, the recent melt extraction event may have reset mineral compositions and destroyed any preexisting correlation between Os-isotopes and xenolith fertility.

These results indicate that Os-isotopes in the convecting upper mantle are significantly more heterogeneous and extend to more depleted values than reported. If these results are representative, then the upper mantle is significantly more Re (and melt) depleted than previously estimated.

## V21D-09 1055h INVITED

### Platinum-Group Element Abundances in Komatiitic Liquidus Minerals

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Understanding platinum-group element fractionation in mafic-ultramafic magmas is a prerequisite to using magmatic PGE abundances for exploring mantle processes. Currently, PGE carriers in komatiites and basalts and PGE partition coefficients for common liquidus phases are not well known. Previous studies, based mostly on bulk-rock PGE fractionation trends, have proposed that olivine and chromite controlled PGE abundances in these lavas. Here, we report precise PGE (Os, Ir, Ru, Pt, Pd) abundance data, obtained using an ID-ICPMS technique, for pure mineral separates of liquidus olivine and chromite, and for bulk rock samples, collected from a complete section of a 110-m deep well preserved differentiated komatiitic lava lake in the 2.5 Ga Vetryny Belt (Baltic Shield). The olivines have low PGE abundances with a spike at Ru. Comparison of these data with the PGE composition of the erupted liquid indicates that Ru was slightly compatible ( $D = 1.7$ ), Os and Ir were slightly incompatible ( $D = 1.2-0.8$ ), and Pt and Pd were highly incompatible ( $D = 0.08-0.03$ ) in olivine. The PGE abundance patterns in the chromites are similar to those of the olivines, but the concentrations in the chromites are two orders of magnitude higher. The calculated partition coefficients indicate that Ru, Os and Ir were highly compatible with chromite ( $D = 100-150$ ), while Pt and Pd were only slightly compatible ( $D = 1.6-3.3$ ). The preferential incorporation of Ru

into spinel is consistent with experimental data on PGE partitioning between spinel and silicate melts. Comparison of bulk solid-liquid  $D$ s for the lake with those calculated from the olivine and chromite compositions imply that the fractionating mineral assemblage included  $10^{-5} \pm 1$  mass fraction of pyrrhotite. These data provide strong evidence that chromite and sulfide are dominant over olivine in controlling the PGE budget of mafic-ultramafic magmas saturated with ol+chr+/-sulf. The partitioning behavior of PGEs in chromite and olivine is qualitatively consistent with the order of the oxidation potentials of the PGEs, lending credence to the notion that these are incorporated in mineral lattices rather than occurring in the form of alloys.

## V21D-10 1110h

### Why do Some Mantle Peridotites Contain Little Osmium and Iridium?

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In peridotites that undergo moderate degrees of partial melting, Os and Ir behave as compatible elements (Morgan, 1986). Deviations from this rule have been noted recently for dunites and harzburgites that represent former high-permeability pathways of primitive melts in mantle-derived peridotites. Here we briefly discuss occurrences from three different tectonic settings and their implications. (1) Layered dunite-pyroxenite rocks occur in spinel-garnet peridotite massifs in lower Austria, remnants of mantle from a Paleozoic convergent plate margin. The dunite-pyroxenite rocks are characterized by suprachondritic  $\gamma\text{Os}$  (7.2 to 13.9), indicating addition of radiogenic Os from percolating melts. Assuming the dunites originally had a composition similar to harzburgites at the same outcrop ( $\gamma\text{Os}$  of -2.7 to -3.9), the change in  $\gamma\text{Os}$  requires melt/rock ratios between 10 and 400. Os and Cr are depleted in the dunites by at least 50-70 % compared to normal harzburgites at the same outcrop, and enriched in associated orthopyroxenites (up to 3.8 ppb Os, 5700 ppm Cr), indicating substantial transfer of peridotitic Os and Cr into melt. (2) Similar rocks occur in the Lanzo spinel-plagioclase peridotite massif (Italian Alps), a MORB-mantle fragment emplaced during the opening of the Thetys ocean 200 Ma ago. Dunite and harzburgite layers show anomalously low Ir abundances (0.36-1.8 ppb) compared to normal harzburgites (typically near 3-4 ppb Ir). Some Ir may have been deposited in websterite layers (0.8-4 ppb Ir). (3) Alkaline basalts from two off-ridge axis seamounts (<5 Ma) close to the Jan Mayen fracture zone (North Atlantic) contain a large proportion of mantle-derived harzburgitic xenocrysts and xenoliths. Separated xenocryst aggregates (predominantly olivine and orthopyroxene) contain little Os (6-150 ppt), have low Re/Os, and show  $\gamma\text{Os}$  between 0 and 106. The composition of these rocks is inconsistent with simple closed-system melting. Significant quantities of Mg-rich melt must have reacted with these peridotites and dissolved and removed a major proportion of the initial budget of Os, Ir, and to some extent Cr. Unknown fractions of these elements were re-deposited in Mg-Cr-rich pyroxenites. At low pressures, similar processes may play a role during the formation of tabular dunites and associated podiform chromite deposits. The physical and chemical parameters that control these dissolution and precipitation processes are not well understood and require further study.

## V21D-11 1125h INVITED

### The Global Significance of Organic-Rich Sediments for the Crustal TOC, Re, and Os Cycles

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Data on the volume-age relationship of gray and black shales in North and Central America (Cook and Bally, 1975; Berry and Wilkinson, 1994) are used to define their mean age (190 Myr) and, by extrapolation, their total global mass on the continents at  $4.1 \times 10^{20}$  kg. New data on the area-age relationship of

Tertiary-Cambrian sedimentary bedrock in the conterminous U.S. (King and Beikman, 1974) suggest that volume-age relationships of sedimentary rocks are similar to area-age relationships. Thus, volume-age data can be used as proxy for outcrop area, critical for evaluating the role gray and black shales play in the surficial cycle of elements.

We use a compilation of TOC, Re, and Os concentrations as well as  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  ( $n=141$ ) to characterize gray and black shales geochemically. Literature compilations of TOC contents of shales together with mass balance calculations restrict the reasonable range of average TOC in gray and black shales to 1-1.5 wt%. The uniform molar Re/TOC and Os/TOC of organic-rich sediments, independent of TOC content, can be used to define average Re (6-9 ng/g) and Os (80-130 pg/g) concentrations,  $^{187}\text{Re}/^{188}\text{Os}$  (260-520) and  $^{187}\text{Os}/^{188}\text{Os}$  (1.4-2.3) of average gray and black shales. Defined this way gray and black shales contain 27-41% of the total sedimentary organic carbon, 72-78% of the upper crustal Re, and 16-22% of the upper crustal Os inventories. Upper crustal Re concentrations need to be revised upward to 500-800 pg/g, while upper crustal Os concentrations (32-36 pg/g) require minimal adjustment compared to upper crustal concentrations derived from loess (Peucker-Ehrenbrink and Jahn, 2001).

Assuming average sedimentary recycling rates, weathering of gray and black shales on the continents releases 44,000 to 88,000 mole Re (assuming 50-100% Re loss during weathering) and about 460 mole Os (assuming 50% Os loss during weathering) annually. These fluxes are equivalent to 50-100% of the riverine Re and 25% of the riverine Os fluxes.

The main advantage of defining organic-rich sediments this way is that we can relate existing geochemical information for such sediments to previously determined volume-age information, critical for evaluating the global significance of any rock type. Most significantly, average gray and black shales a la Cook and Bally (1975) are less radiogenic (1.4-2.3) than usually assumed for this reservoir.

## V21D-12 1140h INVITED

### Applications of Os Isotopes to Subduction Processes

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The Re-Os system has the potential to be a sensitive tracer of crustal recycling at convergent margins due to the very radiogenic nature of sediment and altered oceanic crust relative to mantle. Slab fluid-fluxing during subduction should impart a radiogenic Os isotope signature to the arc mantle, as long as Os is sufficiently mobile in slab-derived fluids.

Recent studies of arc mantle xenoliths show that arc mantle is radiogenic in Os relative to abyssal peridotites and xenoliths of intra-plate continental and oceanic lithospheric mantle, requiring that Os is strongly enriched in slab-fluids or that very high fluid:rock ratios prevail. Regional variations in Os isotope signatures of peridotites from Kamchatka provide evidence for a range of metasomatic styles and intensities that can be correlated with the temperature and depth of the subducting slab, supporting previous suggestions that distinct metasomatic processes have acted, and indicating that slab melts and carbonate-rich fluids are more effective than hydrous slab fluids for transport of radiogenic slab-derived Os. Kamchatka pyroxenites show similar regional variations to the peridotites, but have significantly more radiogenic Os isotope signatures (despite low Re/Os ratios), and are best explained by extensive mantle metasomatism by radiogenic slab-derived fluids or melts.

Re-Os studies of arc lavas are complicated by low Os abundances and the possibility that crustal assimilation may have affected the Os isotope signatures. However, Os isotopes in combination with Sr, Nd or Pb isotopes can serve as a powerful process discriminator, because distinctly different curvature would result on isotope-isotope mixing diagrams for crustal recycling versus crustal assimilation. Os-Sr isotope mixing results for highly potassic lavas from Italy, which exhibit extremely radiogenic Os, are best modeled by recycling of significant quantities of crust (felsic granulites and carbonate-rich marine sediment) rather than crustal assimilation. Radiogenic Os signatures in lavas from several other arcs (Lesser Antilles, Cascades, Papua New Guinea, Indonesia, Kamchatka) also have been interpreted to result from crustal recycling rather than crustal assimilation. In all cases, the arc lavas exhibit Os isotope signatures more radiogenic than arc peridotites, but are within the range of arc pyroxenites, suggesting a link between pyroxenite and arc magma genesis.