Osmium isotopic compositions of Os-rich platinum group element alloys from the Klamath and Siskiyou Mountains, USA

Running Title: Os isotopes

Anders Meibom[1*], Robert Frei[2], Norman H. Sleep[3]

[1] Geological and Environmental Sciences,
320 Lomita Mall, Stanford University,
CA 94305-2115, USA

[2] Geological Institute, University of Copenhagen,
Øster Voldgade 10, DK-1350 Copenhagen,
Denmark

[3] Department of Geophysics, Mitchell Building,
Stanford University, CA 94305-2115, USA

[*] To whom correspondence should be addressed:
meibom@pangea.stanford.edu

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ABSTRACT

We present new measurements of $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ in ten Os-rich platinum group element alloys from placer deposits formed by the mechanical erosion of peridotite-bearing ophiolites in the Klamath and Siskiyou Mountains in northern California and southwestern Oregon. These data nearly double our database of high-precision $^{186}Os/^{188}Os$ measurements on such samples. Together with previously published data, our new results reinforce the conclusion that the radiogenic $^{186}Os/^{188}Os$ compositions of these PGE alloys are very difficult to reconcile with a derivation of their Os from the outer core. Such a model requires extremely early growth of the inner core to its present size, within several hundred million years after accretion of the Earth, which is geophysically implausible.

Collectively, our data suggest instead that partial melting, or metasomatic processes in the upper mantle play a primary role in controlling the Os isotopic systematics of these Os-rich PGE alloys and suggest the existence of upper mantle components characterized by radiogenic $^{186}Os/^{188}Os$ ratios. Pyroxene-rich lithologies are possible candidates.

1. INTRODUCTION

The idea that outer core material, i.e. highly siderophile elements (HSE), can be transported back into the mantle as trace elements in plumes rooted at the core-mantle boundary has recently received a great deal of attention [e.g., *Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Brandon et al.*, 2003; *Righter et al.*, 2000; *Snow and Schmidt*, 1998; *Walker*, 2000; *Walker et al.*, 1997; *Walker et al.*, 1995; *Walker et al.*, 1994; *Widom and Shirey*, 1996]. Concentrations of HSE are expected to be significantly higher in the core than in the mantle and it has been suggested that even modest amounts of back-mixing of outer core material might affect the HSE budget of the entire mantle [e.g., *Righter et al.*, 2000; *Snow and Schmidt*, 1998; *Walker*, 2000]. It has also been argued that abyssal peridotites show fractionated (i.e. non-chondritic) HSE abundance patterns qualitatively similar to those predicted for the present day outer core [*Snow and Schmidt*, 1998]. However, others have argued that qualitatively similar abundance patterns can be produced by metasomatic upper mantle processes involving mobilization and precipitation of sulfide phases [e.g., *Alard et al.*, 2000; *Alard et al.*, 2002; *Luguet et al.*, 2001; *Rehkämper et al.*, 1997; *Schmidt et al.*, 2000].

The Os isotopic system provided the geochemical basis for the suggestion that certain mantle plumes originate at the core-mantle boundary and transport dissolved trace amounts of HSE to the surface of the Earth [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Walker et al.*, 1997; *Walker et al.*, 1995; *Walker et al.*, 1994; *Widom and Shirey*, 1996]. ^{190}Pt, which is a relatively rare isotope of Pt (0.013 at.%), decays to ^{186}Os with a half-life of ~449.4 Ga [*Brandon et al.*, 2000]. Furthermore, ^{187}Re, which is the more abundant isotope of Re (62.2 at.%), decays to ^{187}Os with a half-life of ~41.6 Ga [*Shen et al.*, 1996; *Smoliar et al.*, 1996]. Over time, a reservoir with non-chondritic Pt/Os and Re/Os elemental ratios will develop non-chondritic ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios [e.g., *Shirey and Walker*, 1998; *Walker et al.*, 1997]. Therefore, the discovery of simultaneously enhanced ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios (over present day chondritic values) in Hawaiian picrites implies that the source region is characterized by time-integrated supra-chondritic Pt/Os and Re/Os ratios [*Brandon et al.*, 1999; *Brandon et al.*, 1998b].

Presumably because of the common implicit association of the Hawaiian Islands with a deep-rooted mantle plume, it was envisaged that the radiogenic Os isotopic composition in the Hawaiian picrites could be a signature of the outer core [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Walker et al.*, 1997; *Walker et al.*, 1995; *Walker et al.*, 1994]. It was suggested that, as a result of inner core crystallization, the present day outer core could have developed supra-chondritic Pt/Os and Re/Os ratios and coupled enrichments in ^{186}Os and ^{187}Os, similar to those measured in Hawaiian picrites and Gorgona Island komatiites [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Brandon et al.*, 2003].

In this paper we present new, high-precision Os isotopic data (^{186}Os/^{188}Os and ^{187}Os/^{188}Os) from ten Os-rich platinum group element (PGE) alloys derived from placer deposits associated with peridotite-bearing ultramafic rocks in the Klamath and Siskiyou mountains in northern California and south-west Oregon, USA. Integrated with previously reported Os isotopic measurements from similar samples [*Bird et al.*, 1999; *Meibom and Frei*, 2002; *Meibom et al.*, 2002] we evaluate our data within the framework of the core-mantle interaction model [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Brandon et al.*, 2003]. We then proceed to discuss alternative, upper mantle mechanisms for the production of radiogenic ^{186}Os/^{188}Os in these Os-rich PGE alloys.

2. PREVIOUS OS ISOTOPE WORK ON OS-RICH PGE ALLOYS

It is generally agreed that peridotite-derived Os-rich PGE alloys are very robust representatives of the mantle Os isotopic reservoirs from which they form [*Allegre and Luck*, 1980; *Brandon et al.*, 1998b; *Hattori and Hart*, 1991; *Hirata et al.*, 1998; *Walker et al.*, 1997]. Because of a very high Os concentration, typically higher than 10 wt%, and low Pt and Re concentrations, typically less than 1 wt% and 0.1 wt%, respectively, the Os isotopic compositions of these samples do not evolve over time but represents the composition of the reservoir from which they form, at the time of formation of the alloy. Furthermore, the highly refractory and inert nature of these alloys makes subsequent exchange of Os in different environments (e.g. in the upper mantle, crust, and during alluvial transport) virtually impossible.

A number of studies have reported Os isotopic analyses of Os-rich alloys and sulfides (e.g. iridosmine, osmiridium and laurite) associated with ultramafic rocks. Here we list some examples, in chronological order.

i) Allegre and Luck [1980] reported $^{187}Os/^{186}Os$ ratios of ten osmiridium and laurite samples derived from a variety of ultramafic sources of different ages and constructed the first Os isotopic "mantle evolution line".

ii) Hart and Kinloch [1989] reported $^{187}Os/^{186}Os$ ratios of osmiridium and laurite grains from several gold-mines in Witwatersrand and several locations in the Bushveld complex. The Bushveld samples were found to have remarkably homogenous, but highly radiogenic Os isotopic compositions. Assimilation of crustal materials by the Bushveld magmas was the favored interpretation. The Witwatersrand samples, on the other hand, displayed a remarkable diversity in Os isotopic compositions, with several grains seemingly predating the deposition of the Witwatersrand supergroup, based on their Re depletion minimum ages. The old grains, it was argued, could be detrital.

iii) Hattori and Hart [1991] measured $^{187}Os/^{186}Os$ ratios in more than 50 iridosmine and laurite grains from ultramafic sources world wide. These authors found a remarkable variation in $^{187}Os/^{186}Os$ ratios in Os-rich alloys from individual localities. This variation was attributed to long-term heterogeneity of Re/Os in the oceanic upper mantle as a result of preferential removal of Re by partial melting events that took place ~2 Ga ago.

iv) Hirata *et al*. [1998] analyzed $^{187}Os/^{188}Os$ in three iridosmine grains; one from the Urals (Nevdansk) Russia, one from Hokkaido (Horonobe) Japan, and one from California (Lower River) USA. They found the $^{187}Os/^{188}Os$ ratios of the Urals and Hokkaido samples to be consistent with a HSE reservoir evolving with long-term chondritic Re/Os ratio. The sample from California, on the other hand, was characterized by a low $^{187}Os/^{188}Os$ ratio and a corresponding Re-depletion age of 700 Ma, much lower than any potential host rock

v) Walker *et al*. [1997] and Brandon *et al*. [1998b] reported both $^{187}Os/^{188}Os$ and $^{186}Os/^{188}Os$ for several Os-rich alloys derived from ultramafic rocks in California and the Urals. A relatively large variation in $^{187}Os/^{188}Os$ was observed among these grains, but the $^{186}Os/^{188}Os$ ratios were found to be chondritic (0.119834) within error [*Brandon*, 2003; *Brandon et al.*, 2000].

`vi)` Bird *et al.* [1999] reported $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ in two osmiridium grains collected from the black (i.e. chromite-rich) beach sands at the pacific coast near Port Orford, Oregon, USA; most likely derived from ultramafic outcrops in the Klamath Mountains. Both samples showed enrichment in ^{186}Os similar to that observed in the most radiogenic Hawaiian picrites. Their results were interpreted within the frame work of the Brandon *et al.* [1998b] core-mantle interaction model (see below), in corroboration of an earlier proposal by Bird and Bassett [1980] that clusters of PGE alloys formed directly in the outer core or in the core-mantle boundary region and was transported to the surface of the Earth as xenoliths in deep rooted mantle plumes.

`vii)` Meibom and Frei [2002] analyzed thirteen Os-rich PGE samples from the same general region. These grains showed large variations in $^{187}Os/^{188}Os$ and the majority of the samples had higher than chondritic $^{186}Os/^{188}Os$ ratios. It was concluded that if the outer core was the source of the Os in these samples, then this would require that the inner core formed to its present size no later than ~250 My after accretion of the Earth, which is in conflict with geophysical modeling that indicates a much later onset of inner core formation [e.g., *Buffett et al.*, 1992; *Buffett et al.*, 1996; *Labrosse et al.*, 2001; *Stevenson et al.*, 1983].

`viii)` Meibom *et al.* [2002] reported $^{187}Os/^{188}Os$ ratios of more than 700 Os-rich PGE grains derived from the same region in southwest Oregon and northern California. This large data set forms an essentially gaussian distribution, which was interpreted as a signature of a random mixing process between depleted (unradiogenic) and enriched (radiogenic) domains in the highly heterogeneous upper mantle. This would imply that the Os isotopic systematics of these mantle derived Os-rich PGE alloys is controlled by upper mantle processes.

3. SAMPLES AND THEIR POTENTIAL SOURCE ROCKS

The samples studied here are millimeter-sized, homogenous iridosmine and osmiridium grains [*Harris and Cabri*, 1973; *Harris and Cabri*, 1991] from placer deposits formed by the mechanical erosion of peridotite-bearing ophiolites in the Klamath and Siskiyou Mountains in northern California and southwestern Oregon [*Bird et al.*, 1999; *Meibom and Frei*, 2002; *Meibom et al.*, 2002]. Iridosmine is an Os-rich OsIrRu alloy, which typically has a chemical composition in the range Os: 55-90 wt%, Ir: 20-40 wt%, and Ru: 0-10 wt% [*Harris and Cabri*, 1973]; with minor amounts of Pt (<1 wt%) and Re (<0.1 wt%). In the new nomenclature of PGE alloys osmiridium and iridosmine are referred to simply as 'iridium' or 'osmium', respectively [*Harris and Cabri*, 1991]. Here we do not distinguish between osmiridium and iridosmine, but refer to these samples simply as "Os-rich PGE alloys".

All occurrences of Os-rich PGE alloys in northern California and southwestern Oregon are, without exception, associated with chromite-rich (black sand) placer deposits formed as a result of mechanical erosion of chromite bearing peridotite bodies [*Clark*, 1970; *Meibom et al.*, 2002]. Perhaps the best example of such a peridotitic source rock in this region is the Josephine peridotite. The Josephine peridotite body is one of the largest in the US (> 800 km^2) and consists mainly of harzburgite overlain by scarce cumulate ultramafics, gabbro, diorite, sheeted dikes, and pillow lavas; together these rocks constitute the Josephine Ophiolite [*Harper*, 1984]. The lavas and dikes are chemically distinct from mid-ocean-ridge-basalt (MORB) but have affinities to island-arc, supra-subduction magmatism [*Harper*, 1984; *Harper*, 2003; *Harper et al.*, 1990]. Preponderance of opinion is that the Josephine Ophiolite formed at the back-arc spreading center that developed behind the coeval Chetco magmatic arc complex ~160 Ma [*Harper*, 1984; *Harper et al.*, 1990]. Subsequently, this newly formed piece of oceanic crust, including its peridotite base, was thrust over the still active Chetco magmatic arc complex to the west [*Harper et al.*, 1990]. PGE minerals, including Os-rich PGE alloys, have been found *in situ* in the Josephine peridotite, in association with podiform chromite deposits [*Stockman and Hlava*, 1984].

It is important to consider two possible primary origins of Os-rich PGE alloys derived from ophiolites. These alloys can originate from the ultramafic peridotite tectonites or from the overlying cumulate ultramafics at the base of gabbro section. The peridotite tectonites represent the depleted mantle residue. The Os-rich alloys in this study could in principle be derived from both types of settings. Our petrographic inspection of the mounted and polished PGE grains show that a relatively large fraction has chromite inclusions or have chromite attached to their surfaces. This provides an indication that the Os-rich PGE alloys included in this study were primarily associated with the peridotite tectonites (in which chromite is more abundant) before being eroded out of this setting, consistent with the findings of Stockman and Hlava [1984].

Through an investigation of syn- and pre-genetic inclusions (including silicate and chromite) in similar Os-rich PGE alloys from the same source region as the samples studied here, Brenker *et al*. [2003] found evidence for a hydrous magmatic origin of the Os-rich PGE alloys in the shallow upper mantle, most likely in an arc-environment [*Matveev and Ballhaus*, 2002]. Indeed, the common occurrence of Os-rich PGE alloys as primary inclusions in massive (often podiform) chromite deposits and, conversely, the occurrence of chromite, olivine, pyroxene, laurite, and siliceous (boninitic) melt inclusions in Os-rich PGE alloys suggest a common origin for all these minerals [*Amossé et al.*, 2000; *Auge and Johan*, 1988; *Barnes et al.*, 1985; *Brenan and Andrews*, 2001; *Capri et al.*, 1996; *Fleet and Stone*, 1991; *Hagen et al.*, 1990; *Johan et al.*, 1990; *Leblanc*, 1991; *Malitch and Thalhammer*, 2002; *Matveev and Ballhaus*, 2002; *McElduff and Stumpfl*, 1990; *Nakagawa and Franco*, 1997; *Nilsson*, 1990; *Peck and Keays*, 1990; *Slansky et al.*, 1991; *Stockman and Hlava*, 1984; *Talkington et al.*, 1984; *Tornroos and Vuorelainen*, 1987].

Brenker *et al*. [2003] supported a model in which massive chromite deposits, dunite, laurite and Os-rich PGE alloys form in a single magmatic process [*Ballhaus*, 1998; *Brenan and Andrews*, 2001; *Matveev and Ballhaus*, 2002]. In an arc-environment, both H_2O-rich fluids and siliceous melts (e.g. boninites) are produced in the mantle wedge above the descending and dehydrating plate. Large differences in interfacial energy between the precipitated chromite plus PGE alloys and the hydrous fluid(s) and siliceous melt(s) cause a strong concentration of chromite and PGE alloys in the hydrous fluid(s) [*Matveev and Ballhaus*, 2002]. Such a unified formation scenario is consistent with the geological setting and the supra-subduction geochemical signatures of the ophiolites in northern California and southwest Oregon [*Harper*, 2003], and is capable of simultaneously explaining a number of key observations, including *a*) the formation of massive chromite deposits [*Matveev and Ballhaus*, 2002], *b*) nodular chromite textures

[*Matveev and Ballhaus*, 2002], *c*) Os-rich PGE alloys, laurite, olivine and pyroxene as common inclusions in massive chromite, and *d*) inclusions of chromite, olivine, pyroxene and hydrated siliceous inclusions [*Brenker et al.*, 2003] in the Os-rich PGE alloys.

An implication of this co-genesis model for massive chromite deposits and Os-rich PGE alloys is that their Os-isotopic signatures should be qualitatively similar. In Fig. 1 we show that this is the case for $^{187}Os/^{188}Os$, for which data for both chromite and Os-rich alloys exist. Fig. 1a shows the variation in $^{187}Os/^{188}Os$ (expressed as $\Delta(^{187}Os/^{188}Os)_i(\%)$; the percent variation in initial $^{187}Os/^{188}Os$ from that of the chondritic reference at the presumed time of formation of the host peridotite) in samples from seven occurrences of massive chromite in peridotitic host rocks around the world [*Walker et al.*, 2002]. The chromite data are shown in direct comparison with the nearly gaussian distribution of $^{187}Os/^{188}Os$ ratios from Os-rich PGE alloys from northern California and southwest Oregon (Fig. 1b) [*Meibom et al.*, 2002]. As discussed by Meibom *et al*. [2002], the wide gaussian distribution in $^{187}Os/^{188}Os$ among the Os-rich PGE alloys can be a signature of mixing, or averaging, of an underlying distribution of radiogenic and unradiogenic domains in the upper mantle during partial melting events, or mantle metasomatism. A similar range in $^{187}Os/^{188}Os$ ratios within each massive chromite deposit is observed with a much smaller number of samples (2-4 *vs*. >700; Fig. 1) indicating that the Os isotopic composition of the massive chromite deposits reflect an equally heterogeneous Os isotopic distribution in the upper mantle, which is generally consistent with a common origin for the massive chromites and the Os-rich PGE alloys [*Hattori and Hart*, 1991; *Meibom et al.*, 2002; *Walker et al.*, 2002].

In this study, five of the analyzed Os-rich PGE alloys were from placer deposits along the Rogue River, which is a main drainage of the Josephine peridotite. Five other alloys were from placer deposits around Port Orford, Oregon; near the ocean entry of the Rogue River. The Rogue River grains are from the Naturhistorisches Museum in Vienna (Sample ID: A. a. 5432). The Port Orford grains are from the Yale Peabody Museum (Sample ID: YPM MIN.1.182).

4. ANALYTICAL METHODS

Grains of Os-rich PGE alloys were mounted in epoxy and polished to a 1 micrometer finish using diamond suspensions. Pt/Os and Re/Os ratios and preliminary $^{187}Os/^{188}Os$ ratios were obtained with the Stanford/USGS SHRIMP RG ion microprobe; elemental ratios were obtained by comparison to pure PGE metal standards and $^{187}Os/^{188}Os$ ratios by comparison to a pure Os metal of known isotopic composition [*Meibom et al.*, 2002]. Based on the obtained $^{187}Os/^{188}Os$ ratios, a subset of the Os-rich alloys were selected for simultaneous high precision $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ analysis using the Negative Thermal Ionization Mass Spectrometer (N-TIMS) at the Geological Institute, University of Copenhagen. Material was recovered for N-TIMS analyses by attacking the Os-rich PGE alloys with concentrated, inversed (14N HNO_3 : 10N HCl = 3:1) *aqua regia* in Carius tubes at 230ºC for one week. The PGE alloys were usually, but not always, completely dissolved during the Carius tube attack period. From our experience, Os dominated OsIrRu alloys ("iridosmine") dissolve more easily than Ir dominated ("osmiridium") alloys. Ion microprobe analyses on single Os-rich PGE alloys did not detect any compositional heterogeneities that could raise concerns regarding incomplete dissolution, and we therefore regard the partial Os-solutes as grain-representative. Os was distilled from *aqua regia* directly into 8N HBr [*Naegler and Frei*, 1997] and purified according to the method of *Birck et al.* [1997]. Os isotopic analyses were performed on the VG Sector 54 solid-source negative thermal ionization mass spectrometer at the University of Copenhagen, using a multi-collector dynamic routine. $^{189}Os/^{188}Os = 1.21978$ was used for in-run fractionation corrections.

In Table 1 we report the number of filament loads for each sample. Each filament load was run five times; i.e. five averages were obtained from each filament load. Each average consists of 120 ratios divided into 6 blocks. The precision of each average $^{186}Os/^{188}Os$ ratio was usually better than +/- 30 ppm (one standard error) and averages overlap within their standard error. The errors reported in Table 1 are two standard deviations of the population of averages obtained from the filament loads of each sample solution.

We achieved a long-term external reproducibility of the Maryland [*Shirey and Walker*, 1998] Johnson Matthey Os solution of ±48 ppm (two standard deviations of the mean) on a ratio $^{186}Os/^{188}Os = 0.119845$ (n = 28). This long-term reproducibility of +/- 48 ppm on the $^{186}Os/^{188}Os$ ratio of the Os reference solution was achieved with only 50 ng loads of Os on each filament, which yielded beam intensities of 50-70 mV on mass 234 ($^{186}Os^{16}O_3^-$). In contrast, most of our samples ran with beam intensities at mass 234 of 120-150 mV. The variability on the $^{186}Os/^{188}Os$ ratio of the Os reference solution is mainly due to background fluctuations; possible W isotopic interferences are discussed below. In each measurement, the baselines were measured for 5 seconds at one half mass unit above and below the respective Os trioxide masses. The average 2σ stability of the baselines on each collector (baselines varying from ca. 1.6 to 2.8 mV dependent on the collector) is better than +/- 0.6 % during sample analysis. This variation corresponds to a signal variation of between 9 and 16 μV (dependent of the collector), which can account for the ~50 ppm external reproducibility of the reference solution. By running the standard solution at higher beam intensities, the impact of the background fluctuations would be reduced and the reproducibility of the standard Os solution be improved; the +/- 48 ppm (2σ) external reproducibility of the standard solution is therefore considered a conservative, or maximum, estimate.

With the exception of two samples, the standard deviation of the population of averages is smaller than the long-term external reproducibility of our Os reference solution. We note that the two samples (AM-10-95; AM 9-85.1) that yielded greater population standard deviation ran with beam intensities significantly lower than 100 mV on mass 234 ($^{186}Os^{16}O_3^-$). All other samples ran with beams intensities between 120 to 150 mV. This confirms the conclusion of Brandon *et al.* [1999] that beam intensities of >80 mV on mass 234 must be achieved in order to ensure high precision replication of Os isotopic ratios.

The possible isobaric interference of $^{186}W^{16}O_3^-$ on $^{186}Os^{16}O_3^-$ was monitored at mass 232 ($^{184}Os^{16}O_3^-$; $^{184}W^{16}O_3^-$) through the 232/236 ($^{184}Os/^{188}Os$) ratio (which does not vary in nature) [*Brandon et al.*, 1999] and no deviating detections were made. However, tungsten interferences on ^{186}Os are a major concern. An interference of $^{186}W^{16}O_3^-$ on the order of 4 μV (4×10^{-17}A) on a $^{186}Os^{16}O_3^-$ beam with an intensity of 100 mV would account for about 40 ppm of the $^{186}Os/^{188}Os$ ratio. Thus, for example, a hypothetical W interference of this size could account for almost the entire long-term 2σ reproducibility of our Os standard solution. Simultaneous collection of the ^{184}Os/^{188}Os ratio during a run with a ^{186}Os beam intensity of 100 mV would not detect a W interference of this size in a Faraday cup collection. Such a small interference contribution would be smaller than the long-term external precision of about +/- 0.7% of the ^{184}Os/^{188}Os ratio of our Os reference solution, which is mainly due the very low beam intensities for mass 232 relative to the other Os trioxide masses. A variation of 0.7% in the ^{184}Os/^{188}Os ratio, if it was only due to ^{184}Os fluctuations, is equivalent to an instability of about +/- 10 μV on a 1.5 mV beam of ^{184}Os. A comparison between the ^{184}Os/^{188}Os ratio of the reference solution and the ^{184}Os/^{188}Os ratios during sample runs does therefore not exclude potential W interferences on the order 10 μV $^{186}W^{16}O^{3-}$, which could cause variations of +/- 50 ppm on the ^{186}Os/^{188}Os ratio of a sample. We therefore evaluated potential W interference in each analysis by checking the $^{182}W^{16}O_3^-$ (mass 230, an Os-free mass) on the electron multiplier before and after every dynamic run. In neither the reference solution loads nor the sample loads have we ever detected mass 230 beam intensities above 100 counts per second (usually 0-20 cps is observed), corresponding to a maximal 2.5 μV of $^{186}W^{16}O^{3-}$. This is at least four times smaller than the $^{186}W^{16}O^{3-}$ beam required to explain a +/- 50 ppm uncertainty on the measured ^{186}Os/^{188}Os ratios.

We therefore conclude that neither baseline instabilities nor W interferences can explain the observed variations of ^{186}Os/^{188}Os in our samples beyond the maximum external reproducibility of +/- 48 ppm achieved on our Os reference solution.

5. RESULTS

The Os-rich PGE grains, for which Re and Pt concentrations were measured, are characterized by distinctly sub-chondritic Pt/Os and Re/Os ratios (Table 1) that rule out significant *in-situ* production of ^{186}Os and ^{187}Os after their formation. Thus their Os isotopic composition represents that of the mantle reservoir from which they formed. This is most likely true for all samples listed in Table 1. Of the many hundred similar Os-rich PGE alloys measured by Meibom *et al*. [2002] none have Re/Os ratios higher than chondritic; the vast majority of these samples have Re/Os ratios $<10^{-3}$. Table 1 lists the measured $^{187}Os/^{188}Os$ ratios, which span a wide range from 0.1166 to 0.1595. Combined with the data from Meibom and Frei [2002] and Meibom *et al*. [2002] the total variation in $^{187}Os/^{188}Os$ ratios recorded by the Os-rich PGE alloys from northern California and southwest Oregon ranges from 0.1095 to 0.1870, with a majority of the analyses defining an essentially gaussian distribution in the interval from about 0.1200 to 0.1300 (Fig. 1b) [*Meibom et al.*, 2002].

In Figure 2a, the data from Table 1 are shown as a histogram of $\varepsilon_{186}(T_{RD})$ values together with data on similar samples reported by Meibom and Frei [2002] and by Bird *et al*. [1999]. $\varepsilon_{186}(T_{RD})$ is the deviation in parts per 10^4 from the chondritic $^{186}Os/^{188}Os$ at a time, T_{RD}, calculated as the minimum Re-depletion age [*Shirey and Walker*, 1998] from the $^{187}Os/^{188}Os$ ratio of each sample. For samples with radiogenic $^{187}Os/^{188}Os$ ratios, relative to the present day chondritic $^{187}Os/^{188}Os$ ratio of 0.1276 [*Walker et al.*, 2001], $\varepsilon_{186}(T_{RD})$ is calculated relative to the present day chondritic $^{186}Os/^{188}Os$ ratio of 0.119834 [*Brandon*, 2003; *Brandon et al.*, 2000; *Walker et al.*, 1997]. Positive values of $\varepsilon_{186}(T_{RD})$ indicate long term evolution of a reservoir with a higher than chondritic Pt/Os elemental ratio. Negative $\varepsilon_{186}(T_{RD})$ values indicate long term evolution with a lower than chondritic Pt/Os elemental ratio. With one exception, the Os-rich PGE alloys plot at positive $\varepsilon_{186}(T_{RD})$ values and span a slightly wider range than the $^{186}Os/^{188}Os$ data from the Hawaiian picrites and the Gorgona Island komatiites (Fig. 2b) [*Brandon et al.*, 1999; *Brandon et al.*, 2003]. In general, the Os-rich PGE alloys are more radiogenic in $^{186}Os/^{188}Os$ than the Hawaiian and Gorgona Island samples. Furthermore, even though the number of analyses is still too low to expect smooth statistical distributions to arise from this data set, the twenty-six analyses of Os-rich PGE alloys from northern California and southwest Oregon begin to define a distribution that arguably is approaching a gaussian shape with a mean around $\varepsilon_{186}(T_{RD}) = 1$ to 1.25. We discuss the potential significance of this observation in context of the findings of Meibom *et al*. [2002] (Fig. 1b).

In Fig. 3 we plot our data in a diagram of $^{186}Os/^{188}Os$ *vs*. $^{187}Os/^{188}Os$ together with analyses on a variety of mantle derived materials reported in the literature, including the Hawaiian picrites [*Brandon et al.*, 1999], the Gorgona Island komatiites [*Brandon et al.*, 2003], abyssal peridotites, chromitites and other Os-rich PGE alloys [*Brandon et al.*, 1998a; *Brandon et al.*, 1998b]. Brandon *et al*. [2003] argued, based on the smaller data set in [*Meibom and Frei*, 2002], that the Os isotopic analyses of the Os-rich PGE alloys fall on a linear array (parallel to the line labeled *b* in Fig. 3) pointing towards their inferred Os isotopic composition for the present day outer core. The larger data set presented here (Fig. 3) clearly shows that no such linear array exists among the Os isotopic data from the Os-rich PGE alloys.

6. DISCUSSION

In the following we discuss our data set (Fig. 3) within the framework of the core-mantle interaction model. The conclusions of this analysis are pertinent to the inferences by Bird *et al*. [1999] who asserted that the Os-rich PGE alloys formed in the outer core or in the core-mantle boundary region and were brought to the surface of the Earth as xenoliths in deep-rooted mantle plumes. Alternatives to the core-mantle interaction model are discussed subsequently.

The Core-Mantle Interaction Model

Walker *et al*. [1997; 1995; 1994] and Brandon *et al*. [1999; 1998b; 2003] proposed that, as a result of inner core crystallization, the present day outer core have developed supra-chondritic Pt/Os and Re/Os ratios and coupled enrichments in ^{186}Os and ^{187}Os, more radiogenic than the most radiogenic Hawaiian picrites. This model was based on a number of assumptions:

1) That Os, Re, and Pt partitioned into the inner core with solid-metal/liquid-metal partition coefficients similar to those inferred for IIA iron meteorites; in this way Os would have been preferentially incorporated into the inner core leaving the outer core with supra-chondritic Pt/Os and Re/Os ratios [*Brandon et al.*, 1998b; *Walker et al.*, 1995]. Subsequently, in a effort to also explain Gorgona Island komatiite data within the framework of the core-mantle interaction model, Brandon *et al*. [2003] adjusted upward the partition coefficients for Os and Re and arrived at a substantially more radiogenic present day outer core than that required to explain the Hawaiian data.

2) That, because of the very long half-lives of the parent isotopes, in particular ^{190}Pt, this inner core/outer core HSE fractionation must have commenced relatively early in the Earth's history, in order to allow time for the observed radiogenic ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios to develop [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Brandon et al.*, 2003].

3) That radiogenic Os can be transferred across the core mantle boundary by physically mixing small amounts of outer core material into the lower most mantle in the D" layer.

The "Hawaiian mixing line" (Fig. 3), defined by Brandon *et al*. [1998b], primarily based on data from Hawaiian picrites, is created by mixing enough outer core material into the lower mantle at the core-mantle boundary to the point where the radiogenic Os from the outer core dominates the Os budget of the ascending Hawaiian mantle plume, which is assumed to *a*) exist, *b*) to originate at the core-mantle boundary, and *c*) to bring the radiogenic Os to the surface as a trace element (the same assumptions apply to assumed Gorgona Island plume). Here the radiogenic outer core Os can mix with the broadly chondritic upper mantle Os and define a mixing array. Brandon *et al*. [1999; 1998b] argued that, as a result of the relatively high Os concentration in the outer core, less than one weight percent of outer core material needs to be physically mixed into the lower mantle in order for the radiogenic Os from the outer core to dominate the Os budget of the lower mantle assemblage. In contrast, based on measured PGE abundances and radiogenic ^{187}Os/^{188}Os compositions of the Kostomuksha komatiites and basalts, Puchtel and Humayun [2000] argued that the nature of such core-mantle interaction is isotopic equilibrium between the liquid outer core and the solid lower mantle at the core-mantle boundary, as opposed to physical admixture of outer core material into the lower mantle. At the same time, Walker [2000] argued that simple diffusive transfer of an Os isotopic signal from the outer core into the lower mantle is an inadequate mechanism and proposed instead that Fe-oxides, which was proposed to exsolve as inner core crystallization drives the (unknown) oxygen content of the liquid outer core past oxygen saturation, can transfer PGE into the lower mantle. This disagreement about the preferred transfer mechanism of PGE across the core-mantle boundary (and the potential elemental fractionations associated with it) illustrates that, for the time being, such a mechanism can be subject only to loosely constrained speculation.

Evaluating an Outer Core Origin of the Radiogenic ^{186}Os Signatures in the Os-rich PGE Alloys

In an attempt to fit our Os-isotopic data from the Os-rich PGE alloys in northern California and southwest Oregon into the core-mantle interaction model, we have plotted our data together with the Brandon *et al*. data in Fig. 3., which we accompany with the following general remarks.

If, as proposed by Bird et al. [1999], the Os-rich PGE alloys formed in the outer core or in the core-mantle boundary layer, their ^{187}Os/^{188}Os ratios reflect their formation age(s) and their Os isotopic compositions represent that of the outer core at the different times when individual Os-rich alloys formed. In this scenario, each Os-rich PGE alloy with a distinct Os isotopic composition requires a distinct formation event. Transport of individual alloys to the upper mantle at different times requires a multitude of deep-rooted mantle plumes, originating the core-mantle boundary.

If the Os-rich PGE alloys did not form in the outer core or in the core-mantle boundary, but formed in the upper mantle, as evidence from field relationships worldwide, ^{187}Os/^{188}Os isotopic systematics (Fig. 1), and experimental work strongly suggest [e.g. *Brenan and Andrews*, 2001; *Brenker et al.*, 2003; *Capri et al.*, 1996; *Hattori and Hart*, 1991; *Matveev and Ballhaus*, 2002; *Meibom et al.*, 2002], a fraction of their Os could, in principle, be derived from the outer core, transported to the upper mantle as a trace element in mantle plumes originating at the core-mantle boundary. However, the measured ^{186}Os/^{188}Os ratio of a given Os-rich PGE alloy then provides a minimum estimate of the ^{186}Os/^{188}Os isotopic composition of the outer core during mixing with the broadly chondritic [*Brandon*, 2003; *Brandon et al.*, 2000; *Walker et al.*, 1997; *Walker et al.*, 2002] upper mantle. Hence, the Os isotopic composition of individual Os-rich PGE alloys would still constrain the Os isotopic evolution of the outer core.

Thus, no matter which of these formation models for the Os-rich PGE alloys is preferred, if one assumes that a fraction of the Os that went into the formation of each Os-rich PGE alloy is derived from the outer core, their Os isotopic composition can be used to constrain the required Os isotopic evolution of the outer core, within the framework of the core-mantle interaction model.

Partition Coefficients

The solid line labeled *a* in Fig. 3 is the original outer core evolution line based on the assumptions 1-3 listed above [*Brandon et al.*, 1998b]. Specifically, Model *a* uses IIA iron meteorite solid metal/liquid metal partitioning coefficients: D_{Os} = 19, D_{Re} = 14, and D_{Pt} = 2.9, chondritic Os isotope starting composition (i.e. $(^{187}Os/^{188}Os)_i$ = 0.0962; $(^{186}Os/^{188}Os)_i$ = 0.119823), and initially chondritic elemental ratios (i.e. $(^{187}Re/^{188}Os)_i$ = 0.4224 ; $(^{190}Pt/^{188}Os)_i$ = 0.001692) [*Brandon et al.*, 1998b]. If the inner core is assumed to have grown to its present size (5.5 vol % of the total core volume) within the first couple of hundred million years after Earth's formation [*Brandon et al.*, 1998b], this outer core evolution model develops coupled enrichments in ^{186}Os and ^{187}Os similar to the values measured in the most radiogenic samples from Hawaii.

It is clear that outer core evolution Model *a* does not explain the radiogenic $^{186}Os/^{188}Os$ ratios of the majority of the Os-rich PGE alloys that plot to the left of the "Hawaiian mixing line". In Model *a*, the outer core does not become radiogenic enough in ^{186}Os, early enough in its evolution, to allow the radiogenic Os in the PGE alloys to be derived from it. This was also discussed by Meibom and Frei [2002] who presented the outer core evolution Model *b* in Fig. 3 in an attempt to reconcile the radiogenic Os in the PGE alloys with an outer core derivation of the Os.

Outer core evolution Model *b* is based on the assumptions of initially chondritic Os isotopic ratios and Re/Os and Pt/Os elemental ratios and the assumption of inner core formation within the first 250 My after Earth's formation [*Meibom and Frei*, 2002]. What sets Model *a* and Model *b* apart is the solid metal/liquid metal partitioning coefficients used. Model *b* uses D_{Os} = 36, D_{Re} = 23.3, and D_{Pt} = 2.9. These values were essentially chosen to "custom-fit" an outer core evolution that would be able to develop sufficiently radiogenic Os, early enough in its evolution, in order to allow the PGE alloys to have been be formed from outer core-derived Os, and, at the same time, meet the requirement that the Os isotopic composition of the present day outer core must fall on the Hawaiian mixing line [e.g. *Brandon et al.*, 2003] (Fig. 3).

There are several important observations to be made with respect to Model *a* and *b* in Fig. 3. The increased partitioning coefficients used in Model *b* are very different from those derived from the IIA iron meteorite fractional crystallization trends (D_{Os}: 36 *vs* 19 ; D_{Re}: 23.3 *vs*. 14). By increasing the partitioning coefficient of Os and Re to obtain the required hypothetical outer core evolution, we have abandoned the original idea that fractional crystallization trends in asteroidal cores can be representative of the partitioning behavior of the PGEs under the high P-T conditions and the (still unknown) minor element composition of Earths core [*Brandon et al.*, 1998b; *Walker et al.*, 1997; *Walker et al.*, 1995; *Walker et al.*, 1994]. On the other hand, if iron meteorite fractional crystallization trends do not provide a suitable analog to the partitioning behavior at the inner core/outer core interface, the core-mantle interaction model is based on an essentially unconstrained set of partition coefficients, which are key parameters in the model.

Brandon *et al*. [2003] noted that the increased partitioning coefficients for Os and Re used in Model *b* (i.e. $D_{Os} = 36$ and $D_{Re} = \sim 23$) are not inconsistent with values obtained from recent experimental work [*Walker*, 2000]. Walker [2000] reported qualitatively similar values for D_{Os} and D_{Re} based on partitioning experiments conducted at 100 kbar; more than two orders of magnitude lower than the pressure at the inner core/outer core interface. In these experiments it was assumed that sulfur is the most abundant minor element in the liquid outer core (about 8 wt% S) and the synthetic Fe-Ni alloys used in the experiments were heavily loaded with PGEs (a total of more than 10 wt% Os, Re and Pt) to the point where the normal partitioning behavior of Ni was reversed (i.e. $D_{\mathrm{Ni}} < 1$) [*Walker*, 2000]. While we can not rule out the possibility that this set of experiments provides a good approximation to the partitioning behavior of the Os, Re, and Pt at the inner core/outer core interface, we find it reasonable to approach such an extrapolation with caution. In light of the fact that, for example, the minor element composition of the bulk core [e.g. *Hillgren et al.*, 2000] and the crystal structure of the inner core [e.g. *Belonoshko et al.*, 2003] are still not known, we consider the partitioning behavior of Os, Re and Pt at the inner core/outer core interface to be largely unconstrained at this point.

Timing of Inner Core Crystallization

With regard to an outer core origin of the radiogenic ^{186}Os/^{188}Os ratios in the Os-rich PGE alloys, an even more problematic issue is the timing of inner core crystallization. Brandon *et al*. [1999; 2003] discussed several inner core crystallization scenarios that satisfy the constraints imposed by the Hawaiian and Gorgona data. Models *a* and *b*, treated above, assumes that the inner core grew to its present size within the first ca. 200-250 My after formation of the Earth. In an alternative scenario, Brandon *et al*. [1999] envisaged that the inner core grew continuously at a constant rate, up to the present day. With solid metal/liquid metal partition coefficients adjusted further upwards (D_{Os} = 44.2, D_{Re} = 26.2, and D_{Pt} = 2.9) this scenario allows the present day outer core to develop Os isotopic compositions radiogenic enough to account for the Hawaiian and Gorgona data [*Brandon et al.*, 2003]. However, even though a scenario with slow, continuous inner core crystallization is geophysically more realistic than those involving very early, complete inner core formation (Models *a* and *b*), it is not possible to reconcile the former type of model with the Os isotopic compositions of the Os-rich PGE alloys, as is obvious from Fig. 3; dotted line.

The Os isotopic compositions of the Os-rich PGE grains, interpreted within the framework of the core-mantle interaction model [*Brandon et al.*, 1999; *Brandon et al.*, 1998b], clearly requires that the inner core grew to its present size no later than about 250 My after formation of the Earth, preferably earlier [*Meibom and Frei*, 2002]. This is a radical assumption, which is not consistent with geophysical modeling of inner core crystallization, according to which the inner core started forming relatively late in Earth's evolution (2-3 Ga) [*Buffett et al.*, 1992; *Labrosse et al.*, 2001; *Stevenson et al.*, 1983]. Even if inner core crystallization commenced right after core formation had taken place, it does not seem intuitively correct to imagine that the inner core would grow to its present size within a very limited time interval during the earliest and presumably hottest period in the evolution of the Earth, and then cease to grow any further despite substantial cooling of our planet in the ~4.3 Gy that followed.

For the reasons given above, it seems extremely difficult to reconcile the radiogenic ^{186}Os/^{188}Os ratios of the Os-rich PGE alloys with an outer core origin of the Os. We emphasize that our samples, data and the above analysis has no direct impact on the interpretation of the Hawaiian Island and Gorgona Island data [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Brandon et al.*, 2003], except by providing an evaluation of the assumptions upon which this model is based. In the following we discuss other, upper mantle mechanisms that, independent of processes in the core, might be able to generate the radiogenic Os isotopic signatures of these Os-rich PGE alloys.

Potential Mechanisms for Generating Radiogenic ^{186}Os/^{188}Os in the Upper Mantle

Several authors have discussed alternatives to the core-mantle interaction model in search of a mechanism that might explain the radiogenic ^{186}Os signals measured in a variety of mantle derived materials. Most of these models have focused on the recycling of crustal materials; e.g. basaltic crust and sediments [*Brandon et al.*, 1999; *Brandon et al.*, 1998b; *Peuker-Ehrenbrink and Ravizza*, 2000; *Puchtel and Humayun*, 2000; *Ravizza et al.*, 2001; *Smith*, 2003].

Brandon *et al.* [1999; 1998b] concluded that although recycling of old oceanic crustal materials (typically; Re/Os >150) is well known to lead to enrichments in ^{187}Os (^{187}Os/^{188}Os > 0.5 in just 500 My), this is not likely to be the primary process for generating the compositions of the Hawaiian picrites; i.e. coupled enrichment in ^{186}Os/^{188}Os and in ^{187}Os/^{188}Os (Fig. 3). For example, Brandon *et al.* [1999; 1998b] estimated that the most radiogenic samples among the Hawaiian picrites would require substantially more than 50% of a 2 Gy old oceanic basalt/sediment mixture to be recycled into their source. However, a mantle source with such large proportions of recycled basalt and sediment would produce much more siliceous melts than observed in Hawaii. Similar conclusions were reached by Smith [2003] and also by Puchtel and Humayun [2000] who modeled PGE abundances and radiogenic ^{187}Os/^{188}Os signatures in the Kostomuksha komatiites and basalts.

In contrast, Ravizza *et al.* [2001] and Peuker-Ehrenbrink and Ravizza [2000] have argued that metalliferous sediments (e.g. umbers rich in Fe-Mn-oxides) can develop the required radiogenic ^{186}Os/^{188}Os ratios combined with moderately radiogenic ^{187}Os/^{188}Os to become a suitable radiogenic endmember in recycling models that might explain the Os isotopic compositions of the Hawaiian picrites. Although this type of process was rejected by Brandon *et al.* [2003], based on mass-balance calculations, as a viable explanation for the Hawaiian and Gorgona data, it can not be ruled out as a possible source of the radiogenic Os in the Os-rich PGE alloys. Metalliferous sediments might indeed provide one of several upper mantle processes that can produce radiogenic ^{186}Os-isotopic signatures in the upper mantle.

At the same time, a large ^{187}Os/^{188}Os data set on Os-rich PGE alloys (Fig. 1b) [*Meibom et al.*, 2002] provides an interesting hint to another possible mechanism that could play an important role in generating their Os isotopic signatures by common upper mantle processes: partial melting and/or metasomatism, as discussed in the following.

Statistical Mixing During Partial Melting

The following discussion is based on the observed similarities between the $\varepsilon_{186}(T_{RD})$ distribution in Fig. 2a, to which our new data contribute substantially, and the γ_{Os} distribution shown in Fig. 1b, both of which are based on Os isotopic analyses of Os-rich PGE alloys from northern California and southwest Oregon.

Fig. 1b shows the results of ion microprobe analysis of ^{187}Os/^{188}Os ratios in more than 700 Os-rich PGE alloys from northern California and southwest Oregon [*Meibom et al.*, 2002]. The width and gaussian shape of this distribution support the mounting evidence that the upper mantle is characterized by substantial, long-lived Os isotopic heterogeneity [e.g. *Brandon et al.*, 2000; *Burton et al.*, 1999; *Burton et al.*, 2000; *Haessler and Shimizu*, 1998; *Parkinson et al.*, 1998; *Schaefer et al.*, 2002]. The least radiogenic Os-rich PGE alloy has a ^{187}Os/^{188}Os ratio of 0.1095 corresponding to a Re-depletion age [*Shirey and Walker*, 1998] of ~2.6 Ga, which provides a minimum time scale on which Os isotopic heterogeneity can survive in the upper mantle, in agreement with previous observations. Qualitatively similar ^{187}Os/^{188}Os heterogeneities were observed among iridosmine grains from other ultramafic sources [*Hattori and Hart*, 1991] and among peridotites drilled from the Izu-Bonin-Mariana forearc [*Parkinson et al.*, 1998] and the Kane transform [*Brandon et al.*, 2000].

Meibom *et al*. [2002] interpreted the gaussian $^{187}Os/^{188}Os$ distribution in Fig. 1b to be the manifestation of a process involving metasomatic melt-rock reactions that most likely took place during partial melting events in the upper mantle. In a partial melting event in the upper mantle, domains with relatively low solidus temperature and presumably radiogenic Os isotopic compositions (see below) will melt first at depth. The melts so produced will percolate upwards through an increasingly dense network of grain-scale pores and fractures, mix with other melts and react with solid mantle material at shallower depths and higher degrees of partial melting [e.g. *Asimow and Langmuir*, 2003; *Braun and Kelemen*, 2002; *Hirschmann and Stolper*, 1996; *Kelemen et al.*, 2000; *Kelemen et al.*, 1992; *Sleep*, 1984]. Here ancient, unradiogenic Os, can be released from host sulfides encapsulated in host silicate and chromite phases and mix with the more radiogenic Os in the melt [*Alard et al.*, 2000; *Alard et al.*, 2002; *Burton et al.*, 1999; *Burton et al.*, 2000; *Standish et al.*, 2002]. Thus, in this scenario the gaussian distribution represents a strong signal from the upper mantle of a random mixing between suites of unradiogenic and radiogenic Os isotopic domains, presumably of variable age and in different proportions. Similar conclusions about the chemical and isotopic heterogeneity of the upper mantle have been reached by a number of other researchers based on studies of different types of oceanic basalts [e.g. *Allegre and Turcotte*, 1986; *Fornari et al.*, 1988; *Keken et al.*, 2002; *Kellogg et al.*, 2002; *Meibom et al.*, 2003; *Meibom et al.*, 2002; *Prinzhofer et al.*, 1989; *Salters and Dick*, 2002; *Wood*, 1979; *Zindler et al.*, 1984]. The data in Fig. 1b support to the view that partial melting and metasomatic melt-rock processes define not only the major and trace element chemistry of mantle-derived rocks [e.g. *Hirschmann and Stolper*, 1996; *Kelemen et al.*, 1992; *Niu et al.*, 1997], but also to a large degree their Re-Os isotope systematics [e.g. *Alard et al.*, 2000; *Alard et al.*, 2002; *Brandon et al.*, 2000; *Burton et al.*, 1999; *Burton et al.*, 2000]. Indeed, the Os isotopic systematics of the Os-rich PGE alloys seem to be controlled largely by such metasomatic processes.

At the same time, the increasing number of high precision $^{186}Os/^{188}Os$ analyses on Os-rich PGE alloys begin to define a qualitatively similar distribution. The data set in

Fig. 2a seems to define a symmetrical distribution that might be approximated by a gaussian. This, we infer, is an indication that the $^{186}Os/^{188}Os$ isotopic systematics of the Os-rich PGE alloys is defined by the same upper mantle process as their gaussian $^{187}Os/^{188}Os$ signature (Fig. 1b).

If this inference is correct, an important question arises about the nature and the distribution of the components that take part in this mixing process. The unradiogenic Os isotopic signatures are likely due to depleted mantle lithologies with Os-rich sulfides, residual after ancient partial melting events in which Re was preferentially lost from the assemblage [e.g. *Alard et al.*, 2002; *Burton et al.*, 1999; *Burton et al.*, 2000]. The nature of the radiogenic domains in this mixing process is, however, less obvious. Recently, Smith [2003] proposed that the most feasible method of generating the coupled enrichments in $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ observed in the Hawaiian picrites is by PGE fractionation into pyroxenites precipitated from Mg-rich melts derived from depleted mantle lithologies. In the following we explore this general idea, as a possible explanation for the Os isotopic signatures in the Os-rich PGE alloys.

Pyroxenites as Possible Radiogenic Os isotopic Domains in the Upper Mantle

Ortho- and clinopyroxene-rich lithologies, or pyroxenites, are present as veins or cumulates in all types of mantle materials, including xenoliths [e.g. *Becker et al.*, 2001], ophiolites [e.g. *Coleman*, 1977] and abyssal peridotites [e.g. *Dick et al.*, 1984] and are normally inferred to have been formed by crystallization from Mg-rich melts. They may constitute as much as 5% of the upper mantle [*Hirschmann and Stolper*, 1996] which, in combination with a significantly lower solidus temperature than their upper mantle (e.g. harzburgitic) host rocks, likely make this mantle component an important contributor to the geochemistry of a wide range of mantle derived melts [e.g. *Allegre and Turcotte*, 1986; *Carlson and Nowell*, 2001; *Hirschmann and Stolper*, 1996; *Lassiter and Hauri*, 1998; *Salters and Dick*, 2002]. As an important role for pyroxenites in the upper mantle it has been suggested that pyroxene-rich lithologies are associated with the “garnet signature” in some MORB. This garnet signature, which manifests itself in MORB as anomalous Lu/Hf isotopic systematics [e.g *Salters and Hart*, 1989], distinct REE systematics [e.g. *Fornari et al.*, 1988], and $^{230}Th/^{238}U$ disequilibrium [e.g. *Bourdon et al.*, 1996] was originally thought be the result of equilibration between partial melts and residual garnet in the garnet-peridotite stability field, i.e. at depths below about 80 km [*Hirschmann and Stolper*, 1996, and references therein]. A potential problem with this interpretation is that if partial melting commences at such great depth, the total melt production at the mid-ocean ridge will greatly exceed that required to form a normal oceanic crust with a thickness of 7±1 km [*Asimow and Langmuir*, 2003]. One possible solution to this problem is that partial melting in fact does takes place in the presence of residual garnet, but commences at much shallower depth in the mantle, in the garnet-pyroxenite/spinel peridotite stability field [*Hirschmann and Stolper*, 1996]. The important role of pyroxenite in this scenario is to stabilize garnet to much lower pressures than garnet in equilibrium with peridotite [*Hirschmann and Stolper*, 1996]. This model allows for a strong geochemical garnet signature to develop while at the same time keeping the total melt production in accordance with the measured thickness of typical oceanic crust. Alternatively, and especially appealing in regard to the hydrous magmatic origin proposed for the Os-rich PGE alloys [*Brenker et al.*, 2003; *Matveev and Ballhaus*, 2002], is the idea that the presence of water substantially extends the low-F (i.e. small degree of partial melting) tail of a partial melting event to greater depths, which can allow for a residual garnet signature in regions otherwise too cold to allow the anhydrous solidus to encounter garnet-peridotite [*Asimow and Langmuir*, 2003].

Pyroxene-rich lithologies in the upper mantle might not only act to stabilize garnet to lower pressures [*Hirschmann and Stolper*, 1996], but might also have the requisite PGE systematics, i.e. relatively high Os concentrations, high Pt/Os and moderate Re/Os elemental ratios, to evolve into important radiogenic Os isotopic reservoirs on relatively short time scales [*Smith*, 2003]. Therefore pyroxene-rich lithologies could potentially provide important endmembers in the upper mantle that can explain the radiogenic Os isotopic signatures of the Os-rich PGE alloys.

In most situations the PGE budget of mantle derived rocks, including pyroxenites, is believed to be dominated by sulfides [e.g. *Alard et al.*, 2000; *Alard et al.*, 2002; *Hart and Ravizza*, 1996; *Leblanc*, 1991; *Lorand*, 1987; *Prichard et al.*, 1996]. The timing of sulfur saturation is therefore an important factor in controlling the PGE distribution of different lithologies crystallizing from a PGE-rich melt. If sulfur saturation is reached late, the earlier formed solids, i.e. dunites and pyroxenites, will have correspondingly low PGE abundances. If, on the other hand, sulfur saturation is achieved early in the crystallization sequence, sulfides rich in PGEs will precipitate together with ultramafics [e.g. *Prichard et al.*, 1996].

Although the data are scarce, the relatively high PGE abundances documented in a number of pyroxene-rich mantle lithologies provide evidence that sulfur saturation in many cases did happen early in the crystallization sequence leading to enriched and fractionated PGE abundances in the crystallizing ultramafics [*Barnes and Giovenazzo*, 1990; *Barnes et al.*, 1985; *Barnes and Pichard*, 1993; *Edwards*, 1990; *Peck and Keays*, 1990; *Prichard et al.*, 1996; *Tanguay and Hebert*, 1990]. PGE analyses from cumulate sequences in the Hazelwood River mafic-ultramafic complex, Tasmania [*Peck and Keays*, 1990], the Bay of Islands ophiolite complex, Newfoundland [*Edwards*, 1990], the Bravo Intrusion of the Cape Smith Fold Belt, northern Quebec [*Barnes and Giovenazzo*, 1990] and the Thetford Mines ophiolite complex, southeastern Quebec [*Tanguay and Hebert*, 1990] all indicate that PGE-enriched pyroxene-rich lithologies crystallized from sulfur saturated melts. As a result, some of these pyroxene-rich rocks are characterized by relatively high Os concentrations, ranging from ~0.1 ppb to ~4 ppb, which is only slightly lower than typical upper mantle values (3-4 ppb Os) [*Meisel et al.*, 2001]. Reported Pt concentrations are substantially higher, from ~2 to 520 ppb, with corresponding Pt/Os elemental ratios ranging from ~3 to ~700 times the chondritic Pt/Os ratio. As shown in Fig. 4, rocks with Pt/Os elemental ratios within this range can develop radiogenic ^{186}Os/^{188}Os signatures on relatively short time scales.

Analyses of Re concentrations in the pyroxene-rich lithologies include a study by Edwards [1990] who reports Re concentrations in ortho- and clinopyroxenites from the Bay of Islands ophiolite corresponding to Re/Os elemental ratios ranging from ~2 to ~100 times the chondritic Re/Os ratio; notably most Re/Os ratios are significantly lower than typical MORB Re/Os ratios (> 150) [*Shirey and Walker*, 1998]. Becker *et al.* [2001] reported high Os concentrations (2.3 ppb) and relatively low Re concentrations (0.08 ppb) in pyroxenes from layered dunite-orthopyroxenite rocks in the southern Bohemian peridotite massif. Similar results were reported by Burton *et al.* [2000] on garnet-peridotite xenoliths from northern Tanzania. Reisberg *et al*. [1991] documented large variations in Os concentration, from 0.01 to 1.2 ppb, and Re/Os elemental ratios from ~200 to ~5 in pyroxenite layers in the Rhonda ultramafic complex in Spain. Carlson and Nowell [2001] reported fairly high Os concentrations (~0.2 ppb), moderate Re concentrations (0.08-0.34 ppb) and correspondingly moderate ^{187}Os/^{188}Os of 0.141-0.146 in volcanic rocks (katungite) from the Navajo Field of the Colorado Plateau. These rocks are believed to be derived primarily by melting of clinopyroxene, possibly present as veins in the mantle source [*Carlson and Nowell*, 2001].

Thus, some pyroxenites seem to be characterized by relatively high Os concentrations that make them important contributors to the Os budget of aggregated melts in the mantle, to which they can contribute substantially [*Asimow and Langmuir*, 2003; *Hirschmann and Stolper*, 1996]. Furthermore, these lithologies might also be characterized by sufficiently high Pt/Os and moderate Re/Os elemental ratios that, on reasonable times scales, can lead to the development of radiogenic Os isotopic compositions appropriate as sources of Os for the Os-rich PGE alloys (Fig. 4). A suite of pyroxenites with different combinations of Pt/Os and Re/Os elemental ratios will, with time, develop a distribution of radiogenic ^{186}Os/^{188}Os and ^{187}Os/^{188}Os ratios.

An aggregated basaltic melt with up to 20% contribution from such various pyroxenite sources [*Hirschmann and Stolper*, 1996] could thus inherit radiogenic ^{186}Os/^{188}Os and ^{187}Os/^{188}Os compositions similar to those measured in mantle derived materials, notably the Os-rich PGE alloys (Figs. 2 and 3). Random mixing events between radiogenic Os in pyroxene-rich lithologies of different age and more unradiogenic Os in depleted mantle lithologies might potentially account for the measured radiogenic ^{186}Os/^{188}Os ratios in the Os-rich PGE alloys and could give rise to the essentially gaussian distributions observed in both ^{187}Os/^{188}Os (Fig. 1b) and in ^{186}Os/^{188}Os (Fig. 2a). We note that the relatively unradiogenic Pb isotopic signatures from two Os-rich PGE alloys reported by Bird *et al*. [1999] are not easily reconciled with a pyroxenite source. However, more systematic Pb isotopic measurements are clearly needed in order to establish whether these Pb isotopic signatures are indeed a characteristic of the Os-rich PGE alloys.

7. CONCLUSIONS

In conclusion, we find that the majority of the existing $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ analyses of the Os-rich PGE alloys from northern California and southwest Oregon are very difficult to reconcile with an outer core derivation of the Os. Within the framework of the core-mantle interaction model, these samples require unrealistically early inner core formation and *ad hoc* choices for the solid metal/liquid metal partition coefficients of Os, Re, and Pt during inner core crystallization.

Collectively, our data on the Os-rich PGE alloys suggest instead a strong role for partial melting and/or metasomatic processes in the upper mantle in defining the Os isotopic composition of these samples. In this process(es), Os from depleted (unradiogenic) and enriched (radiogenic) domains of the mantle were mixed. The gaussian distributions observed in $^{187}Os/^{188}Os$ and (tentatively) in $^{186}Os/^{188}Os$ are consistent with such an scenario. Pyroxene-rich lithologies in the upper mantle are potentially good candidates for the radiogenic domains in this mixing process.

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FIGURE CAPTIONS

Figure 1. **a**, The variation in initial $^{187}Os/^{188}Os$ ratios among samples of massive chromite deposits from peridotite bodies around the world in percent of the chondritic reference at the presumed age of formation [*Walker et al.*, 2002]; using the scale in b). **b**, Histograms of more than 700 ion microprobe measurements on mantle derived Os-rich PGE alloys from ultramafic rocks in northern California and southwest Oregon. γ_{Os} is the percent deviation from the average $^{187}Os/^{188}Os$ ratio of the distribution (0.1245) [*Meibom et al.*, 2002]. Solid line: fitted gaussian curve. The variation in initial $^{187}Os/^{188}Os$ of the (small number) of chromite analyses from each different peridotite is similar to the width of the gaussian distribution based on more than 700 analyses of Os-rich PGE alloys from northern California and southwest Oregon. Both types of mantle materials reflect the same degree of Os-isotopic heterogeneity in their sources regions, consistent with a common origin. See text for discussion.

Figure 2. Histograms of $\varepsilon_{186Os}(T_{RD})$ values, i.e. deviations in parts per 10^4, relative to the chondritic $^{186}Os/^{188}Os$ ratio [*Walker et al.*, 2001] at a time T_{RD}, which is the minimum depletion age of Re based on the measured $^{187}Os/^{188}Os$ ratio [*Shirey and Walker*, 1998]. **a**, Data from Os-rich PGE alloys in this study and from Meibom *et al*. [2002] and Bird *et al*. [1999]. With two exceptions the data (Table 1) indicates long term evolution of a reservoir with higher than chondritic Pt/Os elemental ratio; i.e. plots at a positive $\varepsilon_{186Os}(T_{RD})$ values. Although the total number of analyses is still low, the distribution arguably is approaching a gaussian. See text for discussion. **b**, Data on Hawaiian picrites [*Brandon et al.*, 1999] and Gorgona Island komatiites [*Brandon et al.*, 2003].

Figure 3. Os isotope compositions of the Os-rich PGE grains from southwest Oregon and northern California from this study, Meibom and Frei [2002] and Bird *et al*. [1999] plotted together with analyses of Hawaiian picrites [*Brandon et al.*, 1999], the Gorgona Island komatiites [*Brandon et al.*, 2003], abyssal peridotites, chromitites and other Os-rich PGE alloys [*Brandon et al.*, 2000; *Brandon et al.*, 1998b]. Brandon *et al*. [1998b] defined the "Hawaiian mixing line" (dashed) on the basis of the Hawaiian data. The chondritic Os isotopic evolution is shown with numbers denoting the age from present in

million years. The horizontal line indicates the present day chondritic ^{186}Os/^{188}Os ratio of 0.119834 [*Brandon*, 2003; *Brandon et al.*, 1998b]. The pentagon symbol shows the Os isotopic composition of the present day outer core required to explain those data that fall to the left of the “Hawaiian mixing line”. Dotted line represents a hypothetical outer core evolution model with slow, continuous inner core crystallization; after Brandon *et al.* [2003]. See text for discussion.

Figure 4. **a**, Diagram showing the growth in ^{186}Os/^{188}Os, expressed in epsilon units relative to the chondritic ^{186}Os/^{188}Os evolution for different elemental Pt/Os ratios ranging from 20 to 200 times the chondritic Pt/Os elemental ratio of ~2 [*Walker et al.*, 1997]. **b**, Diagram showing the growth in ^{187}Os/^{188}Os, expressed in gamma units relative to the chondritic ^{187}Os/^{188}Os evolution for Re/Os elemental ratios ranging from 5 to 15 times the chondritic Re/Os ratio of ~0.08 [*Shirey and Walker*, 1998]. For comparison, gray areas show the range of radiogenic excesses measured in the Hawaiian picites [*Brandon et al.*, 1999; *Brandon et al.*, 1998b].

Table 1. Osmium isotopic compositions and Pt/Os and Re/Os of ten Os-rich PGE alloys from northern California and southwest Oregon.

Sample	No.*	^{187}Os/^{188}Os	+/- ppm	^{186}Os/^{188}Os	+/- ppm	Re/Os	Pt/Os	Location	Museum	ID
AM 10-28	1	0.1265841	40	0.1198415	37	$<10^{-3}$	0.89	Rogue River	Vienna	A.a. 5432
AM 10-87	1	0.1259158	39	0.1198402	50	$<10^{-3}$	0.61	Rogue River	Vienna	A.a. 5432
AM-10-95	5	0.1595316	94	0.1198236	66	$<10^{-3}$	0.26	Rogue River	Vienna	A.a. 5432
AM 9-85.1	10	0.1408947	78	0.1198350	16			Rogue River	Vienna	A.a. 5432
AM 10-62	5	0.1222953	13	0.1198378	46	$<10^{-3}$	0.43	Rogue River	Vienna	A.a. 5432
AM 21-109	10	0.1202765	29	0.1198397	44	$<10^{-3}$	0.31	Port Orford	Yale Peabody	YPM MIN.1.182
AM 22-125	10	0.1166426	30	0.1198323	25	$<10^{-3}$	0.01	Port Orford	Yale Peabody	YPM MIN.1.182
AM 22-114	7	0.1196370	36	0.1198434	40	$<10^{-3}$	0.09	Port Orford	Yale Peabody	YPM MIN.1.182
AM 9-104.1	3	0.1183486	42	0.1198472	24			Port Orford	Yale Peabody	YPM MIN.1.182
AM 9-71.1	9	0.1184603	35	0.1198421	46			Port Orford	Yale Peabody	YPM MIN.1.182

* Number of filament loads (see text for discussion)

Figure. 1

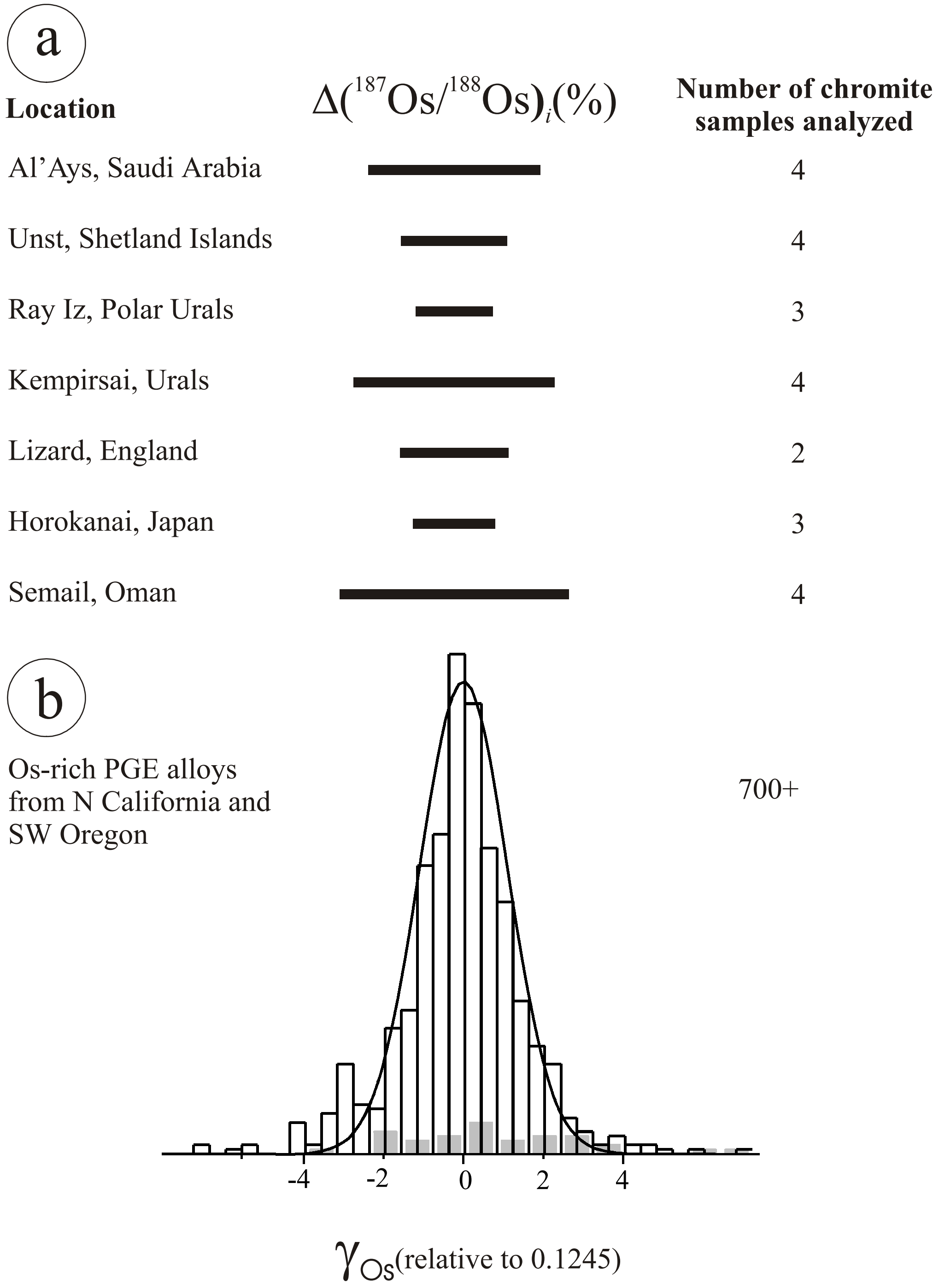

a
Location
Δ(^{187}Os/^{188}Os)$_i$(%)
Number of chromite samples analyzed
Al'Ays, Saudi Arabia
4
Unst, Shetland Islands
4
Ray Iz, Polar Urals
3
Kempirsai, Urals
4
Lizard, England
2
Horokanai, Japan
3
Semail, Oman
4
b
Os-rich PGE alloys from N California and SW Oregon
700+
-4
-2
0
2
4
γ_{Os}(relative to 0.1245)

Figure 2.

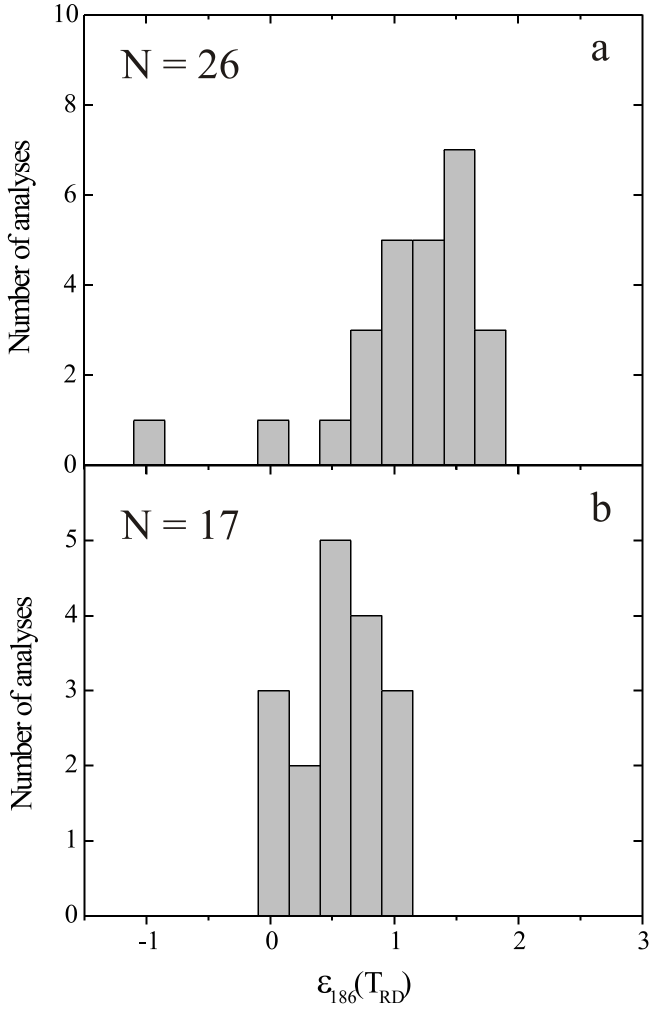
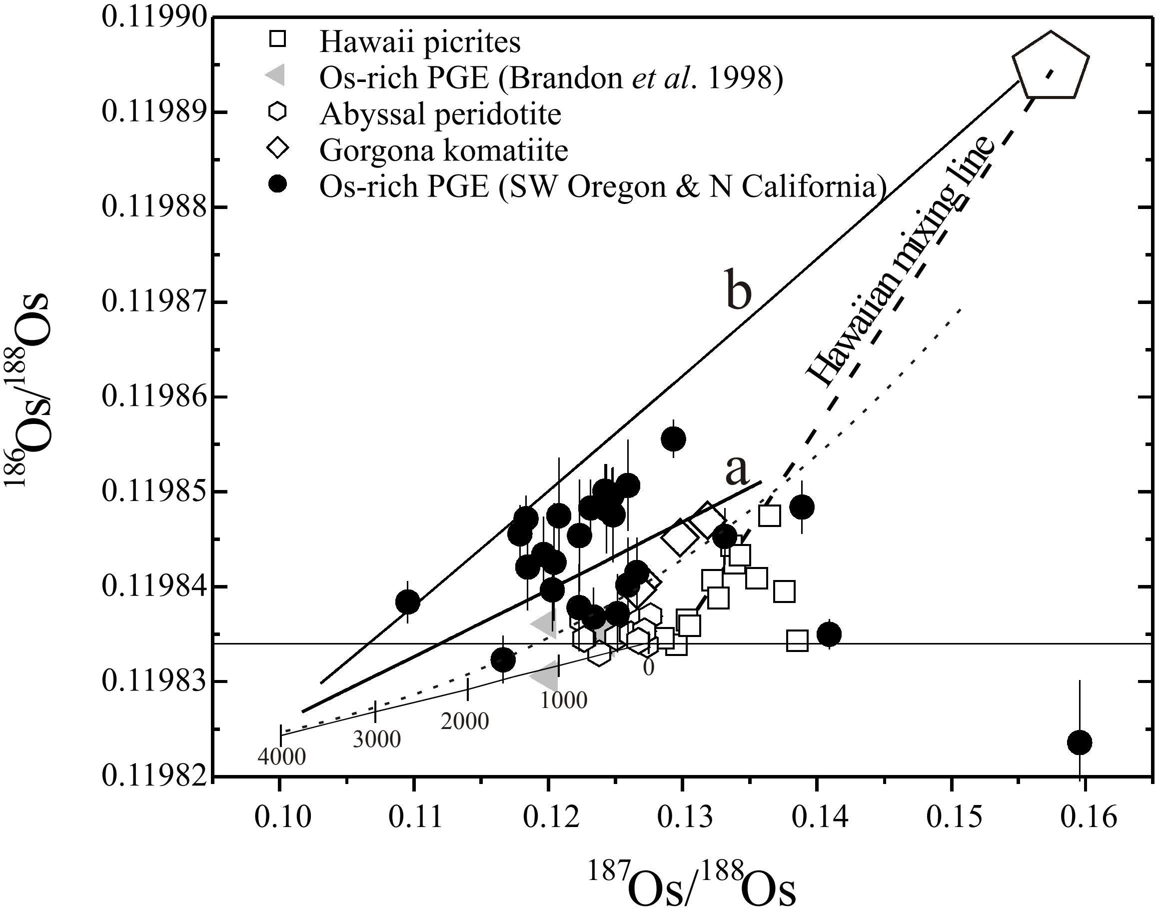
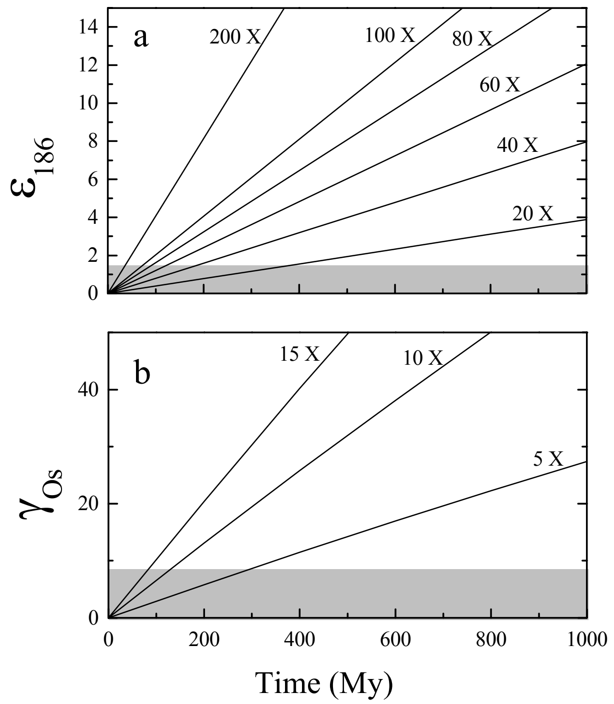

N = 26
a
Number of analyses
10
8
6
4
2
0
N = 17
b
Number of analyses
5
4
3
2
1
0
-1
0
1
2
3
$\varepsilon_{186}(T_{RD})$

Figure 3.



□ Hawaii picrites
◀ Os-rich PGE (Brandon et al. 1998)
⬡ Abyssal peridotite
◇ Gorgona komatiite
● Os-rich PGE (SW Oregon & N California)
b
a
Hawaiian mixing line
0
1000
2000
3000
4000
0.11990
0.11989
0.11988
0.11987
0.11986
0.11985
0.11984
0.11983
0.11982
0.10
0.11
0.12
0.13
0.14
0.15
0.16
$^{186}Os/^{188}Os$
$^{187}Os/^{188}Os$

Figure 4.


a
200 X
100 X
80 X
60 X
40 X
20 X
ε186
0
2
4
6
8
10
12
14
b
15 X
10 X
5 X
γOs
0
20
40
0
200
400
600
800
1000
Time (My)