

strategy should be applicable to a range of other molecules and materials. In our system, the driving force for the stacking is the aromatic/fullerene interaction in the concave cavity, and the incompatibility of the fullerene/aromatic system and the aliphatic side chain/solvent system^{2,20}. The R₅C₆₀H core structure used here exhibits electron absorption spectra and electrochemical properties similar to those of its C₆₀ parent²², and we therefore expect that the liquid crystalline material described here might exhibit interesting optical and electrochemical properties. Moreover, the species R₅C₆₀H can be transformed into a variety of stable η⁵-metal complexes R₅C₆₀M (where M is metal)²³, such as a redox-active ferrocene/fullerene hybrids²⁴; this property might allow metal-doping of the fullerene-based crystals and liquid crystals and thus expand the scope of this type of material²⁵. □

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Correspondence and requests for materials should be addressed to E.N. (e-mail: nakamura@chem.s.u-tokyo.ac.jp).

Re–Os isotopic evidence for long-lived heterogeneity and equilibration processes in the Earth's upper mantle

Anders Meibom*, Norman H. Sleep†, C. Page Chamberlain*, Robert G. Coleman*, Robert Frei‡, Michael T. Hren* & Joseph L. Wooden§

* Geological and Environmental Sciences, 320 Lomita Mall; and † Department of Geophysics, Mitchell Building, Stanford University, California 94305, USA

‡ Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark

§ United States Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, USA

The geochemical composition of the Earth's upper mantle^{1–3} is thought to reflect 4.5 billion years of melt extraction, as well as the recycling of crustal materials. The fractionation of rhenium and osmium during partial melting in the upper mantle makes the Re–Os isotopic system well suited for tracing the extraction of melt and recycling of the resulting mid-ocean-ridge basalt³. Here we report osmium isotope compositions of more than 700 osmium-rich platinum-group element alloys derived from the upper mantle. The osmium isotopic data form a wide, essentially gaussian distribution, demonstrating that, with respect to Re–Os isotope systematics, the upper mantle is extremely heterogeneous. As depleted and enriched domains can apparently remain unequilibrated on a timescale of billions of years, effective equilibration seems to require high degrees of partial melting, such as occur under mid-ocean ridges or in back-arc settings, where percolating melts enhance the mobility of both osmium and rhenium. We infer that the gaussian shape of the osmium isotope distribution is the signature of a random mixing process between depleted and enriched domains, resulting from a 'plum pudding' distribution in the upper mantle, rather than from individual melt depletion events.

During partial melting in the upper mantle, Re is mildly incompatible, whereas Os is strongly compatible, resulting in high Re/Os elemental ratios in mid-ocean-ridge basalts (MORB) and correspondingly low Re/Os ratios in the depleted solid residue left behind³. As ¹⁸⁷Re decays to ¹⁸⁷Os with a half-life of about 42 billion years (Gyr) (ref. 4) the ¹⁸⁷Os/¹⁸⁸Os ratios of MORB and depleted mantle residue will diverge. The MORBs develop high, radiogenic ¹⁸⁷Os/¹⁸⁸Os ratios while the depleted mantle residues develop relatively low, unradiogenic ¹⁸⁷Os/¹⁸⁸Os ratios. When MORB is subducted back into the upper mantle re-equilibration with the depleted mantle residue is expected to take place, but the timescales and length scales on which this re-equilibration occurs are poorly constrained. One expectation has been that the present-day upper mantle would be characterized by a lower-than-chondritic ¹⁸⁷Os/¹⁸⁸Os ratio reflecting the time-averaged depletion in Re as a result of continuous extraction of MORB and preferential long-term storage of slabs of oceanic crust in the lower mantle. Estimates of the degree of slab isolation in the lower mantle vary widely, but are made with the assumption that the upper mantle is homogeneous with respect to its ¹⁸⁷Os/¹⁸⁸Os evolution^{5–7}. However, mounting evidence indicates that ¹⁸⁷Os/¹⁸⁸Os heterogeneities can survive on long timescales in the upper mantle^{8–12}. Examples include the discovery of ancient (0.8–1.2 Gyr) melt depletion events recorded in peridotite samples drilled from the young (~45 million years, Myr) Izu–Bonin–Mariana fore-arc subduction zone⁹ and large variations among the subchondritic ¹⁸⁷Os/¹⁸⁸Os ratios measured in peridotite samples drilled from a single section of the

Kane transform in the Atlantic Ocean¹⁰. These findings indicate that the present-day upper mantle perhaps is not homogeneous enough to be described by a single, representative ¹⁸⁷Os/¹⁸⁸Os ratio.

Using the Stanford/USGS Sensitive High Resolution Ion Microprobe Reverse Geometry (SHRIMP RG), we have analysed the ¹⁸⁷Os/¹⁸⁸Os composition of more than 700 submillimetre to millimetre-sized grains of Os-rich platinum group element alloys derived from back-arc, tectonite peridotite bodies in northwestern California and southwest Oregon¹³, USA (Fig. 1). The minerals studied are iridosmine and osmiridium that primarily consist of Os (10–95 at.%), Ir (5–90 at.%) and Ru (0–15 at.%). Rhenium concentrations are at the p.p.m. level and therefore no age correction of the measured ¹⁸⁷Os/¹⁸⁸Os ratios is necessary. Iridosmine and osmiridium are cumulate minerals formed by partial crystallization of basalts. They occur worldwide in association with podiform chromitites in tectonite harzburgite peridotite bodies and as detrital grains in chromite-rich placers produced by the mechanical erosion of their peridotite host rocks^{8,14,15}. The grains included in this study are solid crystals that frequently contain inclusions of chromite or have chromite attached to their surface and/or show well-developed exsolution patterns consistent with a high-temperature, that is, magmatic origin¹⁴. Iridosmine and osmiridium have previously been used to trace the Os isotopic evolution of the mantle through geological time (see, for example, refs 8 and 16). We have studied a roughly equal number of grains collected from placers at the mouth of the Rogue river (Naturhistorisches Museum in Vienna, sample A.a. 5432), from placers on the Pacific coast near Port Orford (Yale Peabody Museum, sample MIN.1.182) (Fig. 1), and from unspecified localities in northern California (Chicago Field Museum, sample M 8122); all known occurrences of iridosmine and osmiridium in northern California are found in close association with tectonite harzburgite peridotite outcrops¹⁷ (Fig. 1). Thus, the grains included in this study are derived from a large number of peridotite bodies and are expected to represent a less biased sample of the upper mantle than grains derived only from one specific peridotite source. Indeed, the three different grain samples yield similar ¹⁸⁷Os/¹⁸⁸Os distributions, supporting this conjecture.

The measured ¹⁸⁷Os/¹⁸⁸Os isotope ratios span a wide range from

extremely unradiogenic values, as low as 0.1095, to radiogenic values as high as 0.1870 (Fig. 2a). Individual grains are homogeneous with respect to their Os isotope composition⁸. This was checked by traversing (3–7 analyses) across about 50 individual grains; in each traverse all analyses yielded identical ¹⁸⁷Os/¹⁸⁸Os ratios within the precision of the analysis (2–4‰, ±1σ). The measured ¹⁸⁷Os/¹⁸⁸Os ratios do not correlate with Os concentration.

Figure 2b shows an expanded view of the central peak in the obtained ¹⁸⁷Os/¹⁸⁸Os distribution. Our data form a wide, gaussian distribution centred around 0.1245. Also shown in Fig. 2b is the compiled data set for abyssal peridotites that have been obtained over the last two decades. The abyssal peridotite data include samples from three geologically independent regions, the mid-Atlantic ridge, the southwest Indian ridge and the American–Antarctic ridge and plot under the footprint of the gaussian distribution. This is an indication that our data set is fairly representative of the upper mantle. The average ¹⁸⁷Os/¹⁸⁸Os value of our data set (0.1245) is lower than the currently accepted value for the primitive mantle (0.1296), which is based on Re–Os isotope systematics of spinel- and garnet-bearing xenoliths¹⁸. With the assumption of a homogeneous upper mantle this would argue in favour of long-term storage of Re in the lower mantle⁵. However, although the ¹⁸⁷Os/¹⁸⁸Os ratio of the present-day primitive mantle is expected to be broadly chondritic, that is, in the range 0.127–0.129, a recent re-evaluation of the xenolith data⁷ demonstrates that error propagation prevents the present-day ¹⁸⁷Os/¹⁸⁸Os ratio of the primitive mantle from being determined with high precision. Furthermore, as we argue below, the upper mantle is not homogeneous with respect to its Os isotope composition. These considerations make estimates of the degree to which Re might be isolated in the lower mantle ambiguous. However, our data set will offer an interesting constraint on this controversial issue when a more precise estimate for the primitive mantle becomes available.

The width and gaussian shape of the distribution in Fig. 2b has several important ramifications. First, this data set supports the emerging view that the upper mantle might be characterized by substantial, long-lived Os isotope heterogeneity^{9–12}. The least

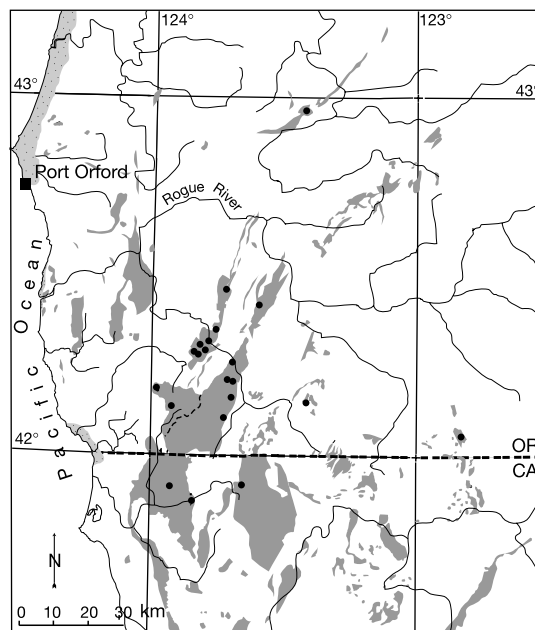


Figure 1 Map showing the distribution of ultramafic rock in southwest Oregon and northwest California and major rivers transporting chromite and platinumoids to the Pacific beaches. Peridotite–serpentinite is shown as dark grey areas. Known occurrences of

platinumoids in chromite deposits within ultramafic rock are shown as black circles²⁶. Ancient terrace deposits of black sands containing chromite and platinumoids are shown as dotted, light grey areas along the Pacific coast²⁹.

radiogenic sample has a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1095, corresponding to a Re-depletion age³ of about 2.6 Gyr. This age provides a minimum timescale on which Os isotope heterogeneity can survive in the upper mantle, in agreement with previous observations^{9–12}. Second, because each iridosmine or osmiridium grain is homogeneous with respect to its Os isotope composition, our data provide some constraints on the minimum length scale involved in Os isotopic homogenization in the upper mantle. Assuming an Os concentration¹⁸ of 5 p.p.b. and a density of 3.3 g cm^{-3} for the upper mantle, a typical iridosmine or osmiridium grain contains Os equivalent to a mantle volume of the order of 1 m^3 . Hence, as a minimum estimate, homogenization of pre-existing Os isotopic heterogeneities has occurred on a length scale of metres. The main carrier phases for Os in the mantle are sulphide minerals^{11,12,19}. Burton *et al.*^{11,12} have demonstrated that exchange of Os by solid-state diffusion between individual sulphide inclusions hosted by mantle silicate or chromite is strongly impaired by the high (10^4 – 10^6) sulphide/silicate or sulphide/chromite partition coefficients for Os. Sulphide minerals hosted by mantle silicates can therefore remain out of Os isotopic equilibrium under mantle conditions for billions of years. Partial equilibration of Os isotopes on a length scale greater than about one metre might require partial melting to the point where sulphide inclusions are released from their host

silicate or chromite phases and dissolved into the melt. Indeed, the harzburgitic peridotite host rocks and in particular their dunite/podiform chromite regions in which the iridosmine and osmiridium grains occur *in situ*^{15,20,21} have probably experienced high degrees of partial melting and metasomatic melt-rock reactions^{22,23} that would facilitate homogenization of Os from radiogenic (MORB-rich) and unradiogenic (MORB-depleted) domains on a minimum length scale of metres. On the other hand, the Os isotope data set described here offers no constraints on the maximum length scales on which the upper mantle is heterogeneous. The width of the gaussian distribution in Fig. 2 and the low $^{187}\text{Os}/^{188}\text{Os}$ ratios of the most depleted samples (down to 0.1095) provide an indication that, in the absence of partial melting, equilibration between the radiogenic (MORB-rich) and unradiogenic (MORB-depleted) domains is inefficient. Observations of substantial Os isotope heterogeneity in abyssal peridotites on length scales of 10–100 m (refs 9, 10) might be interpreted as the characteristic length scale for upper-mantle Os isotope heterogeneity consistent with the minimum estimates made above.

We propose that the gaussian $^{187}\text{Os}/^{188}\text{Os}$ distribution in Fig. 2b is the manifestation of a process involving metasomatic melt-rock reactions that most probably took place under upper mantle conditions characterized by high degrees of partial melting, such as under a mid-ocean-ridge segment or in a back-arc setting. Generally, MORB-rich domains melt first²⁴ and the melts so produced will percolate upwards through an increasingly dense network of grain-scale pores and fractures and react with solid mantle material at shallower depths and even higher degrees of partial melting^{22–24}. Here ancient, unradiogenic Os-rich mantle sulphides encapsulated in host silicate and chromite phases^{11,12,19} are capable of equilibrating with more radiogenic Os in the melt. Thus, the gaussian distribution in Fig. 2b carries no specific age information about one or more distinct Re depletion events.

On the other hand, a gaussian distribution is the expected result of the random mixing between ancient radiogenic and unradiogenic mantle domains under conditions of relatively high degrees of partial melting²⁵. This is a consequence of the ‘central limit theorem’ according to which independent averaging of samples from any given distribution will approach a gaussian distribution with a variance that becomes smaller as the sampled volume increases^{25,26}. In terms of its Re–Os isotopic systematics, the upper mantle can therefore be envisioned as a highly heterogeneous ‘plum pudding’ mixture of these two endmembers that is sampled by the complicated processes of partial melting and infiltrative reaction. The mass balance between radiogenic and unradiogenic components determines the average $^{187}\text{Os}/^{188}\text{Os}$ of this process (that is, the peak of our gaussian distribution), which might therefore not reflect the true average $^{187}\text{Os}/^{188}\text{Os}$ ratio of the entire upper mantle.

Overall, our data lend strong support to the view that secondary metasomatic melt-rock processes define not only the major- and trace-element chemistry of mantle-derived rocks^{22,23}, but also their Re–Os isotope systematics. These processes can mask primary melt depletion features related to previous times that the material passed through an upper-mantle region with high degrees of partial melting. □

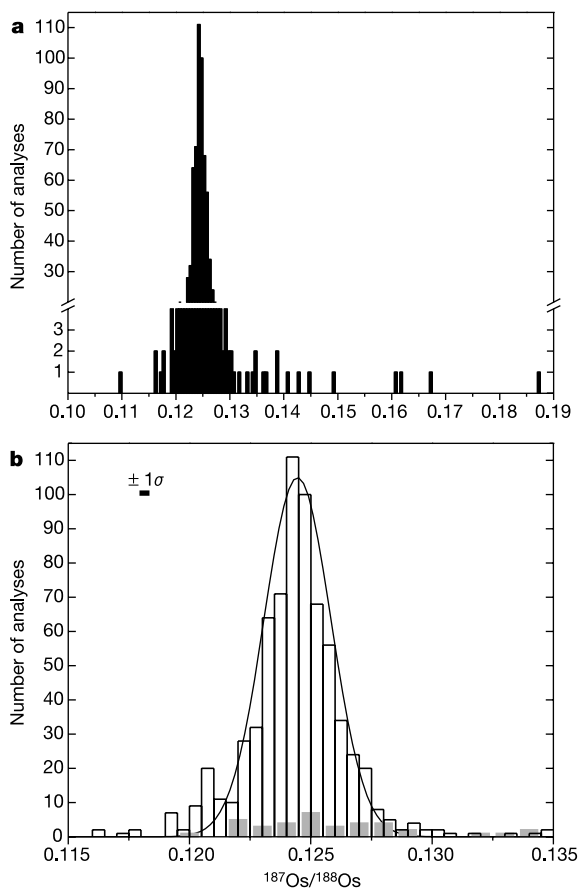


Figure 2 Histograms of Os isotope compositions of more than 700 mantle-derived iridosmine and osmiridium grains from ultramafic rock in northwest California and southwest Oregon. (See Supplementary Information.) **a**, The break in the y axis serves to increase the visibility of unradiogenic and radiogenic outliers. **b**, The histogram of the measured data points forms a gaussian distribution with a mean of around 0.1245. Solid line, fitted gaussian curve. Existing data for abyssal peridotite samples from three different oceans (compiled in refs 6 and 19) plot under the footprint of the gaussian distribution (grey columns). The $\pm 1\sigma$ error bar interval indicates the typical precision of an individual ion microprobe analysis.

Methods

The Stanford/USGS SHRIMP RG was used to measure $^{187}\text{Os}/^{188}\text{Os}$ ratios of iridosmine and osmiridium samples (see Supplementary Information) mounted in epoxy and polished to a $1\text{-}\mu\text{m}$ finish using diamond suspensions. A primary beam of O_2^- was focused to a diameter of about $30\text{ }\mu\text{m}$ on the sample with currents ranging from 20–30 nA. The magnitude of instrument mass-dependent fractionation of the SHRIMP RG was assessed by sampling an 99.99%–pure Os pellet of known Os isotope composition ($^{187}\text{Os}/^{188}\text{Os} = 0.1090081 \pm 0.0000029$) as determined by negative-ion thermal ionization mass spectroscopy (N-TIMS) at the University of Copenhagen²⁷. By measuring $^{186}\text{Os}^+$, $^{187}\text{Os}^+$, $^{188}\text{Os}^+$, $^{189}\text{Os}^+$, and $^{190}\text{Os}^+$ in an electron multiplier in peak-jumping mode the mass-dependent instrumental fractionation was found to be less than 2‰ per a.m.u. Mass 191 was monitored in order to assess the hydride contribution. Measured count rates at this mass were less than 1 c.p.s., which is insignificant in comparison with the count rates

obtained from the Os standard and the iridosmine grains, of the order of 10^5 to 8×10^5 for $^{188}\text{Os}^+$. Analysis of the iridosmine grains were performed by measuring $^{185}\text{Re}^+$, $^{187}\text{Os}^+$, $^{188}\text{Os}^+$ in an electron multiplier at a mass resolution of 6,000–7,000 in peak-jumping mode. The 99.99%-pure Os metal pellet was used as an internal standard. Typical $\pm 1\sigma$ error bar interval of individual $^{187}\text{Os}/^{188}\text{Os}$ measurement is around 3‰, similar to the external reproducibility of the standard (see Supplementary Information). $^{185}\text{Re}^+$ was measured in order to correct for the contribution of $^{187}\text{Re}^+$ to the $^{187}\text{Os}^+$ peak and, by comparison with a pure Re metal standard, estimate the Re concentration of each unknown sample.

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Correspondence and requests for materials should be addressed to A.M. (e-mail: meibom@pangea.stanford.edu).

Linearly concatenated cyclobutane lipids form a dense bacterial membrane

Jaap S. Sinninghe Damsté*, Marc Strous†, W. Irene C. Rijpstra*, Ellen C. Hopmans*, Jan A. J. Geenevasen‡, Adri C. T. van Duin§, Laura A. van Niftrik† & Mike S. M. Jetten||¶

* Royal Netherlands Institute for Sea Research (NIOZ), Department of Marine Biogeochemistry and Toxicology, PO Box 59, 1790 AB Den Burg, The Netherlands

† Department of Microbiology, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

‡ University of Amsterdam, Institute of Molecular Chemistry (IMC), Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

§ Newcastle University, Department of Fossil Fuels and Environmental Geochemistry, Drummond Building, Newcastle upon Tyne NE1 7RU, UK
|| Department of Biotechnology, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands

Lipid membranes are essential to the functioning of cells, enabling the existence of concentration gradients of ions and metabolites. Microbial membrane lipids can contain three-, five-, six- and even seven-membered aliphatic rings^{1–3}, but four-membered aliphatic cyclobutane rings have never been observed. Here we report the discovery of cyclobutane rings in the dominant membrane lipids of two anaerobic ammonium-oxidizing (anammox) bacteria. These lipids contain up to five linearly fused cyclobutane moieties with *cis* ring junctions. Such 'ladderane' molecules are unprecedented in nature but are known as promising building blocks in optoelectronics⁴. The ladderane lipids occur in the membrane of the anammoxosome, the dedicated intracytoplasmic compartment where anammox catabolism takes place. They give rise to an exceptionally dense membrane, a tight barrier against diffusion. We propose that such a membrane is required to maintain concentration gradients during the exceptionally slow anammox metabolism and to protect the remainder of the cell from the toxic anammox intermediates. Our results further illustrate that microbial membrane lipid structures are far more diverse than previously recognized^{5–7}.

Recently, Strous *et al.*⁸ reported the identification of a lithotroph 'missing from nature' that was capable of anaerobic ammonium oxidation. On the basis of 16S rDNA phylogeny, *Candidatus* 'Brocadia anammoxidans' and its relative *Candidatus* 'Kuenenia stuttgartiensis' were shown to be deep-branching members of the order *Planctomycetales*, one of the major, distinct divisions of the domain Bacteria^{8–10}. Anammox bacteria derive their energy from the anaerobic combination of the substrates ammonia and nitrite into dinitrogen gas. The anammox bacteria grow exceptionally slowly, dividing only once every 2–3 weeks. Anammox catabolism takes place in a separate membrane-bounded intracytoplasmic compartment, the anammoxosome¹¹. Hydrazine (N₂H₄) and hydroxylamine (NH₂OH) are the toxic intermediates, which were observed to diffuse in and out of anammox cells as free molecules^{8,12}. Indeed, the containment of these chemicals inside the anammoxosome was considered impossible, because both compounds diffuse readily through biomembranes¹³. The present discovery of the unprecedented molecular structure of the anammox membrane lipids challenges that assumption: the anammoxosome membrane is much less permeable than normal biomembranes because of the presence of unique 'ladderane' lipids.

As the starting material for the structural identification of the membrane lipids, we used a mixed bacterial culture in which 81% of

¶ Present address: Department of Microbiology, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.