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# Osmium isotope compositions of detrital Os-rich alloys from the Rhine River provide evidence for a global late Mesoproterozoic mantle depletion event

Arjan H. Dijkstra[1,*], Christopher W. Dale[2], Thomas Oberthür[3], Geoffrey M. Nowell[2], D. Graham Pearson[2,4]

[1]*Centre for Research in Earth Sciences, University of Plymouth, Plymouth, United Kingdom;*
** Corresponding author arjan.dijkstra@plymouth.ac.uk*
[2]*Department of Earth Sciences, Durham University, Durham, United Kingdom*
[3]*Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany*
[4]*Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, Canada*



## Abstract

We report osmium isotopic compositions for 297 mantle-derived detrital Ru-Os-Ir alloy grains found in gold and platinum-group mineral bearing placers of the Rhine River. These alloys were likely formed as a result of high degree melting in the convective mantle and derived from residual Paleozoic mantle peridotites in the Alps of Central Europe that were accreted as part of a collage of Gondwana-derived 'Armorican' terranes before the Variscan Orogeny. The $^{187}Os/^{188}Os$ isotope ratios of the Os-rich alloys show a wide distribution, with two modes at 0.1244 and 0.1205. These two modes correspond to rhenium depletion ages, interpreted to correspond with episodes of high-degree mantle melting, at ~0.5 and ~1.1 Ga. The data confirm the ability of the oceanic mantle to preserve evidence of ancient melting events. Our new data, in combination with published data on Os-rich alloys from the Urals and Tasmania and with data for abyssal peridotites, indicate a geographically widespread record of a major global Late Mesoproterozoic (1.0-1.2 Ga) high-degree melting event in Paleozoic oceanic mantle rocks. This model age peak is essentially absent from the crustal record of Central-Western Europe, but does coincide with the apparent peak in global continental crust zircon ages at this time. Thus, high-degree mantle melting peaking in the 1.0-1.2 Ga interval may have affected a large part of Earth's mantle. This interval occurred during a period of relative super-continental stability, which may have been accompanied in the oceanic realm by rapid seafloor spreading and extensive subduction, and by unusually high activity of mantle plumes forming two active mantle superswells.

### *1. Introduction*

This paper aims to contribute to the on-going debate in geodynamics as to whether the rate of melt extraction from the Earth's mantle has varied over time, in particular whether there have been episodes of increased mantle melting in the last 2-3 Ga that can be attributed to large-scale mantle geodynamic events (Condie, 1998).
It has long been thought that rocks from the Earth's convecting mantle are not suitable recorders of distinct past events in Earth history due to the homogenizing effects of convective stirring. However, it has become clear over the last decade that the convecting mantle is less effectively homogenized than previously thought. There is considerable osmium isotopic heterogeneity in the modern convective mantle, with unradiogenic Os isotopic compositions (i.e., low $^{187}Os/^{188}Os$) being common (e.g., Pearson & Wittig, 2004); such isotopic compositions must have resulted from geologically old melting events which stripped mantle rocks of rhenium, the parent of the radiogenic $^{187}Os$ nuclide. For instance, many abyssal peridotites, which are samples of the convecting mantle exposed near present-day mid-ocean ridges, record depletion events in the ancient geological past (e.g., Brandon et al., 2000; Alard et al., 2005; Harvey et al., 2006; Liu et al., 2008; Dijkstra et al., 2010); the same is observed in mantle rocks from the Izu-Bonin-Mariana fore-arc (Parkinson et al., 1998). The mean age of partial melting is recorded by Os isotope model ages, which, for refractory abyssal, fore-arc and ophiolitic peridotites, are typically very Early Paleozoic, Proterozoic or Archean (Parkinson et al., 1998; Meibom et al., 2002; Walker et al., 2002b; Harvey et al., 2006; Pearson et al., 2007; Liu et al., 2008; Dijkstra et al., 2010). The record of Os isotopic heterogeneity of convective mantle rocks is relatively well constrained for the modern mantle and for the Cenozoic and Mesozoic using ophiolites (e.g., Walker et al., 2002b; Alard et al., 2005), however, the record becomes poorly constrained for the Paleozoic and Proterozoic due to the general scarcity of suitable old ophiolites.

Pearson et al (2007) studied a large number of Os-rich alloy grains from ophiolites and found a common ~ 1.2 Ga age peak in Phanerozoic ophiolite massifs from three widely disparate areas and proposed that this resulted from extensive global mantle melting coupled to crust generation. Here we set out to test that initial hypothesis applying statistical analysis to a large new dataset of alluvial Ru-Os-Ir alloys (n=297; Oberthür et al., 2016) from Rhine River placers, derived from mantle peridotite massifs exposed in the European Alps. These mantle rocks provide a window into the composition of the convective mantle in the Paleozoic, as they are derived from fragments of Early Paleozoic oceanic mantle accreted to stable Europe during the Silurian to Devonian. This location is significant as it is the first Central-Western European locality investigated, and because of the general scarcity of late Mesoproterozoic ('Grenvillian') crustal rocks in Europe, providing a good test of the global prevalence of late Mesoproterozoic-aged Ru-Os-Ir alloys produced by a high-degree mantle melting episode.

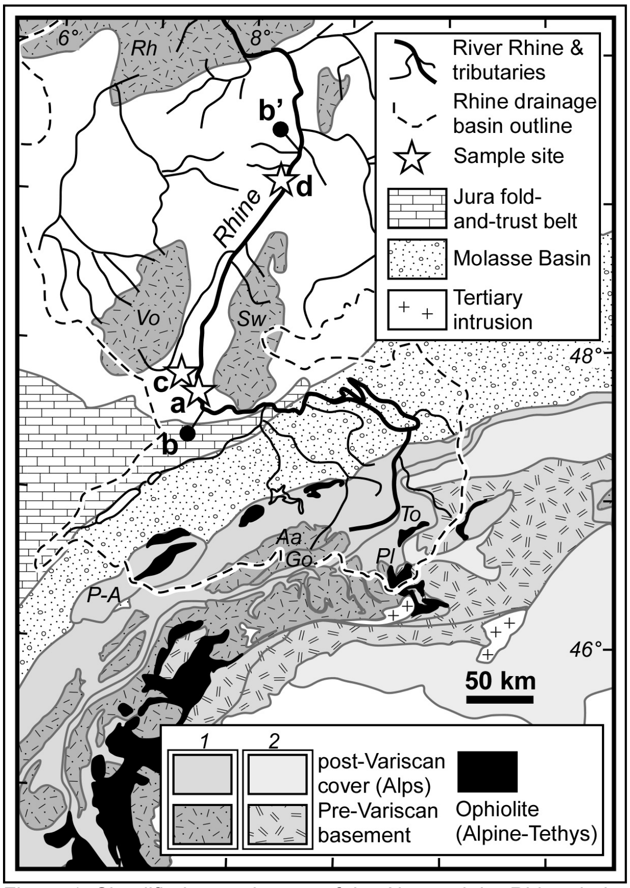


Figure 1. Simplified tectonic map of the Alps and the Rhine drainage basin, modified from Stampfli et al. (2002). Sample localities along the Rhine are indicated with a-d, with b-b' showing the stretch of the Rhine from which sample B discussed in text was derived. Within the Alpine chain, basement of Variscan and pre-Variscan age is distinguished from the post-Variscan cover. Numbers 1 and 2 in key indicate Helvetic-Penninic (1) and South Alpine-Austroalpine (2) zones; the former zone was already part of the European stable continent by Variscan times, whereas the latter zone represents Apulian lithosphere that was only accreted to stable Europe during the Alpine orogeny. Ophiolitic rocks from the Mesozoic Alpine Tethys shown in black. Areas discussed in text: To = Totalp Massif; P-A = Pre-Alps; Pl = Platta Massif; Aa = Aar Massif; Go = Gotthard Massif; Vo = Vosges Massif; Sw = Schwarzwald Massif; Rh = Rhenish Massif.

## *2. The formation of Os-rich alloys*

The element osmium is a platinum-group element (PGE) which is generally assumed to be hosted in Os-rich alloys of the nearly complete Ru-Os-Ir solid solution system, in PGE-sulfides, or at trace element concentrations in base metal sulfides in mantle rocks (e.g. Ballhaus et al., 2006). During partial melting of fertile mantle rocks, base metal sulfides melt to form a Cu-rich-sulfide melt and a more refractory sulfide solid-solution residue which concentrates the compatible PGE, namely Os, Ir, and Ru (Bockrath et al., 2004; Ballhaus et al., 2006; Luguet et al., 2007; Fonseca et al., 2012). Experimental work has shown that during high-degree mantle melting, at levels of complete or nearly complete sulfur removal from the rock, the residual sulfides can become saturated in the Os, Ir and Ru and exsolve these elements as alloys or as PGE-sulfides (Brenan & Andrews, 2001; Brenker et al., 2003; Ballhaus et al., 2006; Fonseca et al., 2012). The degree of melting at which sulfides are removed from a peridotite residue depends on the sulfur concentration of the fertile starting material, but is typically 15%-25%; such high degrees of mantle melting are uncommon (Luguet et al., 2007; Fonseca et al., 2012) and should only occur under unusual circumstances such as hydrous re-melting of fore-arc mantle, or high-degree mantle melting in plume heads. Therefore, such high-degree melting events should be associated with the production of discrete Os-rich Platinum-Group Minerals (PGM). Oxidation of mantle rocks, for instance by hydrous fluids, can desulfurize PGE-enriched refractory sulfides and also lead to exsolution of Os-rich PGM such as Ru-Os-Ir alloys (Fonseca et al., 2012). It has been further proposed that these Os-rich PGM grains can be physically transported by flotation in water-rich bubbles and be concentrated in podiform chromitite bodies near the crust-mantle boundary (Matveev and Ballhaus, 2002). This mechanism can explain why chromitites are generally strongly enriched in Os, Ir and Ru compared to mantle peridotites.

In bulk mantle peridotites, Os behaves as a compatible element, whereas rhenium is typically almost completely removed by melting, stopping the in-growth of radiogenic $^{187}$Os in the residue (Ballhaus et al., 2006; Pearson et al., 2004). As a result, high-degree melting of a volume of mantle effectively freezes in its $^{187}$Os/$^{188}$Os isotope ratio at the time of melting. This signature is then robustly recorded in newly-formed Os-rich, Re-poor PGM, which are isotopically difficult to reset due to their Os rich nature (typically 10-70 wt% Os), low solubility in mantle melts and resistance to alteration. Therefore, the $^{187}$Os/$^{188}$Os model ages of Os-rich PGM, either from residual mantle rocks or from chromitites, should represent the age of Re depletion - and therefore the age of melting – of their mantle source (Fonseca et al., 2012).

Studies designed to find Os-rich PGM *in-situ* in mantle rocks have experienced difficulties: Luguet et al. (2007) extracted µm-scale Os-bearing PGE-sulfides and two alloys in refractory mantle rocks from the Lherz massif after complete acid digestion of the silicate rock portion. It has become apparent that such phases are rare, and generally very small - of the order of a few to tens of micrometers - consistent with the typical low Os concentrations in bulk mantle rocks of only around 3-4 ppb Os (Pearson et al., 2004; Becker et al., 2006). In contrast, Os-rich PGM such as Ru-Os-Ir alloys or Ru-Os-Ir sulfides and arsenides occur in much greater abundance in podiform chromitites (e.g., Malitch, 2004). However, in localities around the world, variably Os-rich alloys of the Ru-Os-Ir system as large as 200 µm occur as a relatively abundant component of a PGM assemblage in alluvial or beach placer deposits. Because of their chemical and physical resistance to weathering, alloys are expected to have a much better preservation potential during transport than most other PGM, such as for instance Ru-Os-Ir sulfides and arsenides. Using placer-derived Ru-Os-Ir alloys, Pearson et al. (2007) demonstrated that ophiolitic mantle massifs exposed in California, the Urals, Tibet, and Tasmania contain Os-rich alloys that record long-term depletion in Re as a result of mantle melting significantly older than the Phanerozoic emplacement ages of the ophiolites, showing conclusively that convective mantle rocks preserve a record of ancient mantle melting events. The mantle rocks from three of their locations contained a small but significant contribution of ~1.0-1.2 Ga Os-rich alloys, providing the first support from the mantle perspective for a late Mesoproterozoic mantle event of a global nature (Pearson

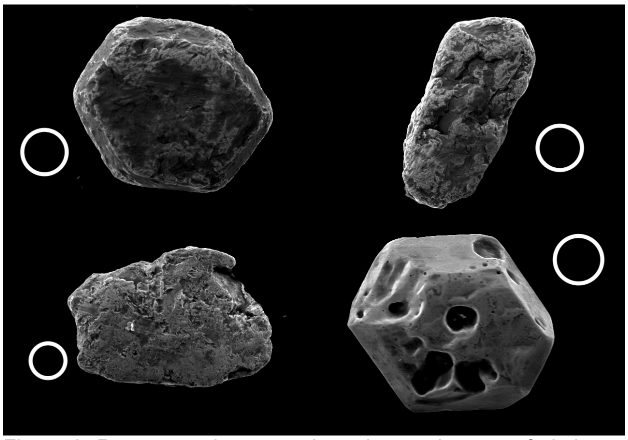

Figure 2. Representative secondary electron images of platinum-group minerals from the Rhine placers. Top left: Os-rich (Ru-Os-Ir) alloy; Top right: Ir-rich (Ru-Os-Ir) alloy; Bottom left: (Fe,Pt) alloy; Bottom right: Sperrylite crystal. Circle next to each grain has 20 μm diameter.

et al., 2007). Similar variable and old Re-depletion model ages have been reported for comparably limited datasets of Os-rich PGM found *in-situ* in chromitites (e.g., Malitch, 2004), strongly suggesting that placer-found PGM can be derived from chromitites in ophiolitic mantle rocks (also see figure SI-2 in the supplementary text).

*3. Samples and Methods*

Detrital platinum-group minerals (PGM) including Os-bearing alloys were extracted from several placer localities along the river Rhine in southern Germany (Figure 1). Details of the sample locations and sampling methods are found in the supplementary text. Some representative secondary electron images are shown in Figure 2. Around 70% of PGM consisted of alloys of the Ru-Os-Ir system. A total of 307 Os-bearing grains were analysed for Os isotopes at Durham University using a New Wave UP 213 nm laser and Thermo Fisher Neptune MC-ICPMS. Details of the method are given in the supplementary text. Of the 307 isotope analyses of Os-bearing alloys, 10 were discarded for further analysis because they had $^{187}Re/^{188}Os>0.01$; such relatively Re-rich grains are less likely to provide meaningful Re-depletion ages due to ingrowth of $^{187}Os$ and potentially the difficulty in correcting for an isobaric interference with $^{187}Re$ (Nowell et al., 2008). $^{187}Os/^{188}Os$ isotope ratios of the remaining 297 Ru-Os-Ir alloys were analysed using statistical methods involving Probability Density Distribution analysis using two statistically sound bandwidth choices and Gaussian mixture modeling. Details of the statistical treatment can be found in the supplementary text.

Rhenium-depletion model ages were derived from $^{187}Os/^{188}Os$ ratios by assuming Re/Os ratios of zero in the samples (an assumption justified by the measured very low Re concentrations, $^{187}Re/^{188}Os<<0.01$) and by projecting the measured isotope ratio back to the $^{187}Os/^{188}Os$ growth curve for the mantle. All model ages plotted and discussed in this paper – including those based on results from previous studies - are calculated assuming a present-day chondritic $^{187}Os/^{188}Os$ ratio of 0.1276 and $^{187}Re/^{188}Os$ of 0.397 (Walker et al., 2002a). The choice of the model reservoir values generates age uncertainties that are greater for younger samples, but generally less than 100Ma. For instance, Re-depletion ages calculated using the ordinary chondrite values employed by Pearson et al. (2007) are up to 80 Ma older for the Phanerozoic, and up to 50 Ma younger for the Early Proterozoic, compared to ages used in the present study.

*4. RESULTS*

The Probability Density Distribution of $^{187}Os/^{188}Os$ for the 297 measured Ru-Os-Ir alloy grains with low Re ($^{187}Re/^{188}Os<0.01$) from the Rhine River is shown in Figure 3. There is a clear and significant deviation from a unimodal distribution. The Os-bearing alloys are characterized by a $^{187}Os/^{188}Os$ distribution with a main mode of around 0.125, independent of the choice of bandwidth. Depending on the choice of bandwidth, there is a shoulder or second peak with a $^{187}Os/^{188}Os$ ratio of ~0.12. The distribution with the smaller bandwidth (see supplementary text for methods of sound bandwidth choice) reveals a very minor peak around 0.113, but this peak does not withstand rigorous significance testing. There are 17 grains with low $^{187}Re/^{188}Os$ (<0.01) but nonetheless suprachondritic $^{187}Os/^{188}Os$ isotope ratios (0.1277-0.1463), which give negative Re-depletion ages. These were probably derived from melting residues of non-peridotitic mantle lithologies such as mantle pyroxenites, which generally yield radiogenic Os isotope ratios.

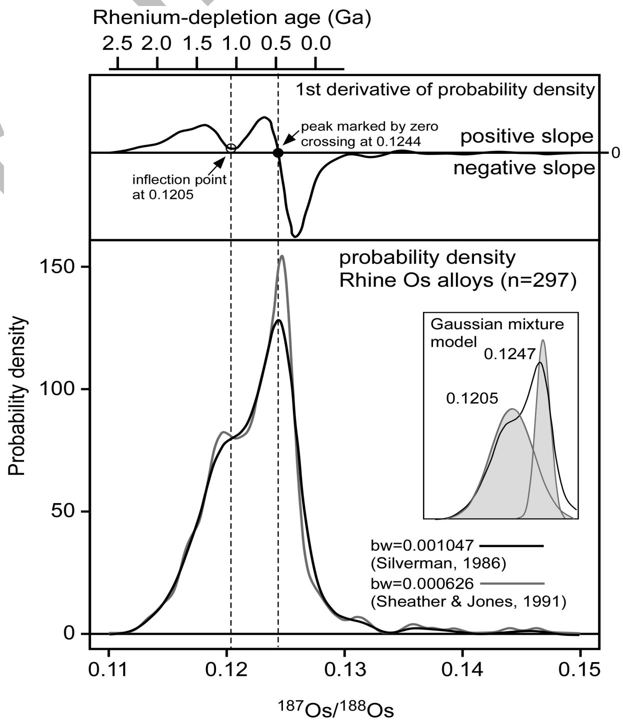


Figure 3. Probability density functions of measured Ru-Os-Ir alloys from the Rhine placers. Lower panel shows the same data processed using two different statistically sound bandwidths ('bw'). Upper panel shows the 1st derivative of the probability density function using the bandwidth of Silverman's Rule of Thumb; zero crossing indicates primary peak at $^{187}Os/^{188}Os=0.1244$ and trough point approaching zero slope in the derivative function indicates secondary shoulder at $^{187}Os/^{188}Os=0.1205$. Corresponding Re-depletion ages (0.48 Ga and 1.06 Ga respectively) are shown in scare-bar at the top of the diagram (assuming mantle evolution model with present-day values $^{187}Os/^{188}Os=0.1276$ and $^{187}Re/^{188}Os=0.397$ – Walker et al., 2002). Inset shows results of Gaussian mixture modeling. See supplementary text for more details about the statistical methods employed.

The most robust estimate of the peak positions in the isotope distribution of the sub-chondritic alloys is derived from the 1st derivative of the probability density distribution (shown in the top part of Fig. 3), using the Silverman's-Rule-of-Thumb bandwidth: this method yields the position of a $^{187}Os/^{188}Os$ peak at 0.1244 and an inflection point at 0.1205. These values correspond to Re-depletion model ages of 0.48 and 1.06 Ga (or 0.55 and 1.10 Ga using the alternative set of values for the mantle Os growth curve applied in Pearson et al., 2007). The Gaussian mixing model gave very similar results, resolving two peaks at $^{187}Os/^{188}Os$ ratios of 0.1205 and 0.1247 when two peaks were specified in the a-priori model assumptions (Fig. 3 inset). The probability density distribution calculated with the smaller bandwidth is shifted to a somewhat less radiogenic Os isotope ratio corresponding to an older model age around 1.2 Ga. Given the total uncertainties associated with the exact determination of the peaks and with the model age calculations, it is concluded that the Rhine detrital Ru-Os-Ir alloy populations show evidence for two major depletion events around 0.5 and 1.0-1.2 Ga.

## *5. DISCUSSION*

### *5.1. Source Areas of the Rhine Detrital Platinum-Group Minerals*

Mineralogical analysis of the platinum-group minerals, supported by the complementary study of Oberthür et al. (2016), shows that the PGM from all four samples are dominated by alloys of the Ru-Os-Ir system. The elements Os, Ir and Ru (the Iridium-group PGE) are generally considered compatible in mantle rocks, as opposed to the incompatible platinum-group PGE (PPGE; Rh, Pd and Pt; Barnes et al. 1985). The dominance of IPGE-rich alloys (70% of the total PGM) and the relatively low abundance of PPGE-rich PGM suggest that most of the PGM, and specifically the Os-bearing alloys analyzed in this study, were derived from residual mantle rocks such as harzburgite, or from chromitite-bearing dunite within harzburgite.

Possible source rocks for the Os-bearing alloys are residual mantle rocks in the Alps, or sedimentary rocks derived from their erosion, with the Alpine molasse as an obvious candidate. The involvement of southwards-transported glacial sediments derived from residual mantle rocks or sedimentary rocks from further north (e.g., Scandinavia) is much less likely, considering the transport distances involved, and since PGM are extremely rare in Central and Northern Germany. Very few PGM have been reported from tributaries to the Rhine or other smaller rivers in Southern Germany (Oberthür et al., 2015), despite extensive gold panning in the region. Rare PGM derived from local sources outside of the Rhine drainage area have been reported from the Danube in SE Germany (Dill et al., 2009) and the river Saale in Central Germany (Wolf et al., 2011). Residual mantle rocks in the Black Forest (Schwarzwald) massif, extensively affected by Variscan metamorphism, are relatively rare and it seems unlikely that they can be the major source of the recovered PGM. Gold prospecting in the Black Forest area has yielded sperrylite, but no other PGM (minifossi.pcom.de, c. 2005). Therefore, a source of PGM in the Alps is by far the most plausible provenance.

Several key areas exposing residual mantle peridotites exist in the Alps, within the present-day drainage basin of the Alps. Fig. 1 shows the areas where ophiolitic rocks are exposed, which typically include an important proportion of residual mantle rocks. Mid-Jurassic ophiolitic rocks are found in the Gets Nappe in The Pre-Alps, and further east, in the Totalp and Platta massifs of the Arosa zone (P-A, To and Pl respectively in figure 1). Extensive whole rock Os isotope data exist for the Totalp Massif (Van Acken et al., 2008): the Totalp peridotites least affected by late-stage melt-rock reactions have unradiogenic $^{187}Os/^{188}Os$ ratios (~0.1213) with corresponding late Proterozoic depletion ages. The ultramafic rocks from the Gets nappe and from the Arosa zone are interpreted as mantle rocks exhumed during post-Variscan rifting without evidence of extensive melting during exhumation or seafloor spreading (Müntener et al., 2004). They are mostly lherzolites with abundant pyroxenites and they are an unlikely host-rock for chromitites; they do not seem sufficiently refractory to be a major source of the abundant Ru-Os-Ir alloys of the Rhine.

Instead, suitable ultramafic rocks are present as lenses associated with mafic igneous rocks in the Aar and Gotthard massifs in the Alps (figure 1). These massifs consist of pre-Variscan basement reworked during the Variscan and Alpine orogenies. The mafic-ultramafic rocks are interpreted to represent remnants of supra-subduction zone oceanic lithosphere within accretionary wedge sequences, possibly of Latest Proterozoic to Silurian age, which were accreted together with so-called Armorican terranes to stable Europe in Early Paleozoic times, a process which ended with the collisional Variscan orogeny (Biino & Meisel, 1994; Schaltegger & Gebauer, 1999; Von Raumer et al., 2003). Whole rock Os isotope data of peridotites from the Aar and Gotthard Massifs show evidence for melt impregnation of residual mantle rocks, but the three samples least affected by this refertilization event record a melt depletion event around 2 Ga (Meisel et al., 1996). It is worth noting that the extant residual mantle rocks within the Alps only represent a proportion of all mantle sections that have either wholly or partially been removed by erosion, whose detritus contributed to the Alpine molasse deposits and in turn may have been the source of the PGM recovered from the Rhine River. However, rather than identifying the precise source(s) of the Rhine PGM, the key observation is the existence of suitable refractory mantle rocks with relatively old depletion ages in the Alpine drainage basin of the Rhine.

### *5.2. The ~0.5 Ga depletion age peak in the Rhine PGM population*

The youngest major Re-depletion model age peak recorded by the Rhine Ru-Os-Ir alloys is around 0.5 Ga. This age can easily be explained in terms of the assemblage of pre-Variscan tectonic building blocks of the Alps, which mostly originated at the margin of Gondwana, crossed the Rheic Ocean, and were accreted to stable Europe along an accretionary orogenic margin in the lead-up to the collisional Variscan Orogeny (Von Raumer et al., 2003). These blocks provide a record of Cambrian accretion and arc magmatism at an Andean-type active margin at the edge of Gondwana (the so-called Cadomian orogeny, e.g., Murphy et al., 2013), followed by rifting at the Cambrian-Ordovician boundary and subduction zone magmatism and back-arc seafloor-spreading during the Ordovician to Early Devonian whilst they drifted to be accreted to stable Europe (Murphy et al., 2013 and references therein). The associated oceanic mantle rocks could therefore have recorded *last* ages of melting throughout the Early Paleozoic, but no later than the Variscan orogeny (~300 Ma) when the European terrane assembly was completed. Other mantle rocks in the Alps, such as the peridotites found in the Arosa zone discussed above represent Central European subcontinental mantle of which large fragments later became exposed during post-Variscan rifting and incipient seafloor spreading in the Permian-Mesozoic Piemonte-Ligurian ocean basin; The exhumation of these mantle rocks was accompanied by very limited magmatism (Müntener et al., 2004).

Therefore, the presence of a primary ‘Cadomian’ ~500 Ma age peak with a tail of ages down to 300 Ma in the mantle alloys from the Rhine River is not only unsurprising given the geodynamic context and expected ages of mantle melting of their sources rocks, it also provides confirmation of the robustness of the method of using Os alloys to date mantle melting events.

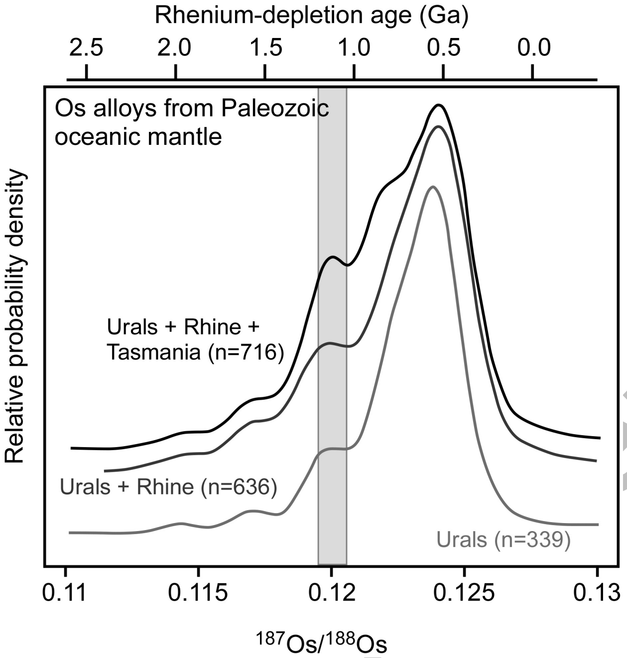


Figure 4. Combined probability density functions of Os-bearing alloys derived from Paleozoic oceanic mantle from the Rhine, Urals and Tasmania, off-set for clarity, all plotted using the same bandwidth of 0.0006 (the optimal bandwidth for the total dataset according to Silverman’s rule of thumb). A clearly defined peak with a ~1.1 Ga Re-depletion age is seen in the combined dataset. Other minor secondary peaks in the combined dataset at 0.117 and 0.114 are probably not statistically significant and require more data to confirm. Data for the Urals and Tasmania from Pearson et al. (2007) and references therein.

### *5.3. A regional geological explanation for the Late Mesoproterozoic depletion age peak?*

Unlike the ~0.5 Ga peak, the presence of a strong ~1.0-1.2 Ga age peak for the Ru-Os-Ir alloys from the Rhine River is not obviously supported by current knowledge of the geodynamics of the geological building blocks of Europe. In a global context, major Mesoproterozoic events are associated with the lead-up to the protracted Grenville orogeny that established Rodinia as a super-continent (Hoffman, 1991). However, the crustal record of Central-Western Europe is widely believed to be free of a Grenville age imprint; the nearest crustal rocks of this age are found in southwest Scandinavia, associated with the Sveconorwegian Orogeny (e.g., Bingen et al., 2008). The Paleozoic terranes which are recognized in the Alps are so-called Armorican terranes, derived from the African margin of Gondwana. The general absence of Mesoproterozoic zircons and Nd-Hf bulk rock model ages in Armorican basement rocks is considered the hallmark of the Armorican terranes (Linnemann et al., 2014 and references therein). In contrast, crustal rocks associated with the ‘Avalonian’ terranes which form the basements of northern Germany and the British Isles are thought to be derived from the South American continent and frequently contain reworked detrital zircons and Nd model ages of Mesoproterozoic age (Tait et al., 1997).

Despite the overall lack of signs of Grenville-age tectonic and igneous activity in the upper crustal and basement rocks of the source area of the Rhine sediments, our results clearly show that there is a very strong imprint of 1.0-1.2 Ga high-degree mantle melting in the Alpine mantle source rocks of the Os-bearing alloys. Our study thus provides the first robust evidence for the major importance of mantle melting in this time interval in Central-Western European ophiolitic mantle rocks derived from the convective mantle. Similar Proterozoic Os-based model ages are also recorded in mantle rocks from the mantle lithosphere in Mediterranean Europe (González-Jimenéz et al., 2013).

As this ancient melting event recorded by the Ru-Os-Ir alloys from the Rhine drainage area cannot simply be explained by regional tectonic processes, the most straightforward interpretation is that the alloys yielding Mesoproterozoic ages are ‘inherited’: while they are hosted in mantle rocks which were part of the convective mantle up until Early Paleozoic times, the Ru-Os-Ir alloys phases were formed during a more ancient, Mesoproterozoic mantle depletion event and were preserved. Similar conclusions were reached in previous studies of alloys recording ancient depletion events in ophiolites (Meibom et al., 2002; Pearson et al., 2007). This is probably a common feature of mantle Ru-Os-Ir alloys, and unradiogenic bulk-rock Os isotopic compositions of modern abyssal peridotites (Brandon et al., 2000; Harvey et al., 2006; Liu et al., 2008; Dijkstra et al., 2010) can probably also be attributed to inherited Ru-Os-Ir alloys, or, in some cases to Os-bearing sulphides (Alard et al., 2005).

### *5.4. A late Mesoproterozoic mantle depletion event of global significance?*

The notion of old, inherited mantle depletion ages in oceanic mantle rocks is further illustrated in Figs. 4 and 5. Figure 4 combines the results of studies involving Os isotope ‘dating’ of over 700 Os-rich alloys derived from Paleozoic oceanic mantle, from three localities – the Rhine (this study) and the Urals and Tasmania (Pearson et al. 2007). These Os-rich alloys are probably the most robust recorders of Os isotopic heterogeneity in the convective mantle. It is clear from all three areas that evidence for ancient melting is well preserved in Paleozoic convective mantle, just as it is in modern-day abyssal peridotites. However, none of the available studies allows us to look as far back in time as the earliest Proterozoic or Archean given the rarity of Ru-Os-Ir alloys yielding ages older than ~2 Ga, suggesting Ru-Os-Ir alloys rarely survive for more than 1.5-2 Ga in the convecting mantle; the destruction mechanism is, however, still unclear. Critically, in all three

Paleozoic datasets, there is a clear set of Ru-Os-Ir alloys recording a relatively well-defined 1.0-1.2 Ga late Mesoproterozoic mantle depletion event (Fig. 4). For none of these areas is there a straightforward regional geological context to explain these ages and hence the notion of a widespread 'global' melting event was advanced to explain the presence of this age peak by Pearson et al. (2007). Given the geographic spread of the study areas, and the clear expression of such an age peak in the Rhine River alloys, the case for planet-wide inheritance of 1.0-1.2 Ga mantle depletion ages in Paleozoic oceanic mantle rocks appears strong and convincing. The data further suggest that less high-degree mantle melting occurred around 0.9-1.0 Ga, as evidenced by the relative trough in Re-depletion ages of mantle-derived alloys. Fig. 5 shows that the primary modes in Os isotope ratio distributions plot just below the chondritic evolution reference lines for the mantle, and none of the primary modes in the Paleozoic cases give contradictory younger Mesozoic depletion ages.

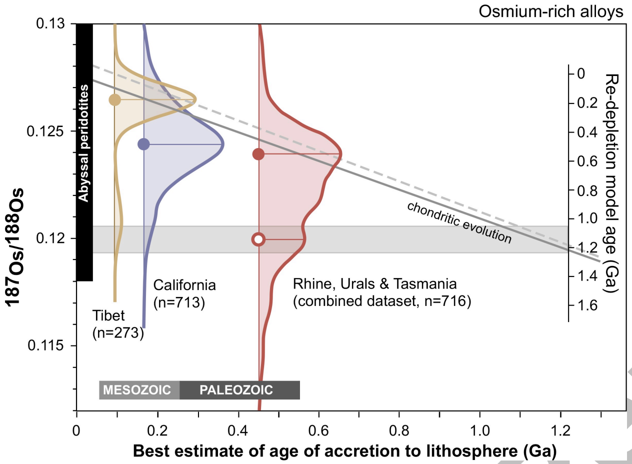


Figure 5. Osmium isotope heterogeneity in the convective mantle in the Mesozoic versus the Paleozoic, as shown by Os-rich alloys. Horizontal axis shows the best estimate of lithospheric accretion of the oceanic mantle rocks (probable age of last melting); Urals and Tasmania alloys are probably derived from ~400 Ma and ~500 Ma ophiolites, whereas Rhine alloys are probably from Early Paleozoic oceanic mantle (see text for discussion). Primary peaks in the alloy isotope distributions are slightly below the model chondritic mantle evolution lines (drawn line: $^{187}Os/^{188}Os$=0.1276 with $^{187}Re/^{188}Os$=0.397; dashed line: $^{187}Os/^{188}Os$=0.1283 with $^{187}Re/^{188}Os$=0.422 – see discussion in methods section). Secondary peak in the Paleozoic samples corresponds to an ancient melting event at ~1.1 Ga, as discussed in the text. Data for California, Tibet, Urals and Tasmania from Pearson et al. (2007) and references therein.

There are strong indications from the global crustal record that the latter part of the Mesoproterozoic era, from ca. 1.2 to 1.0 Ga, was characterized by unusually active geodynamics, probably on a planetary scale. The highest rates of latitudinal continental drift motions, possibly as high as 35-40 cm/yr, have been measured for this time period (O'Neill et al., 2007), and these very high velocities may be related to a rapid True Polar Wander event around 1.1 Ga (Evans, 2003). Detrital zircons from major rivers around the world show a major peak of U-Pb crystallization ages at 1.0-1.2 Ga, perhaps reflecting widespread magmatic activity at that time (Goldstein et al., 1997; Condie, 1998; Rino et al., 2004; Parman, 2015), although that interpretation has been questioned and it has been suggested that zircon age peaks reflect selective preservation rather than pulsed magma production (Hawkesworth et al., 2009). The lack of an obvious peak in hafnium model ages around ~1.2 Ga (Parman, 2015) seems to be inconsistent with a high rate of juvenile evolved continental crust production around that time.

Some studies suggest that the 1.5-1.1 Ga interval represents one of three prominent Precambrian peaks in the formation of Large Igneous Provinces (LIP) on Earth (Ernst & Buchan, 2003; Prokoph et al., 2004), and saw the emplacement of the well-known 1.27 Ga MacKenzie giant dyke swarm associated with the Coppermine Lavas flood basalts – one of the largest known LIP on Earth – and the 1.24 Ga Sudbury giant dyke swarm (Ernst & Buchan, 2003; Hou et al., 2008). Similar aged giant dyke swarms which may be linked to the MacKenzie swarm occur in Australia and Eastern Antarctica (Hou et al., 2008). In their comprehensive study of proxies for high degree mantle melting events such as flood basalts, high-Mg primary igneous rocks, dyke swarms and Cr-rich layered intrusions, Abbott and Isley (2002) found a high occurrence rate for such events in the 1.3–1.0 Ga interval, which they interpret as a sequence of short-lived super-plume events. Large intra-plate LIP-like mantle melting events may have generated very few evolved crustal rocks at high levels, making such events less visible in the crustal zircon record. The period was also characterized by rearrangements of the continental fragments, ending assembly of the super-continent Rodinia (Hoffman, 1991). This orogenic 'super-event' was associated with unprecedented levels of crustal recycling and sediment subduction (Van Kranendonk & Kirkland, 2013).

This notion of fast continental drift and vigorous plume activity seems to be inconflict with the idea of 'Earth's middle age' (Bradley, 2011; Young, 2013; Cawood & Hawkesworth, 2014): the period between 1.8 and 0.8 Ga that lacks carbon isotopic excursions or glaciations and was characterized by relatively minor plate reorganizations involving the gradual 'morphing' of one supercontinent (Nuna) at ~1.7 Ga into its successor Rodinia, until it broke apart around 0.75 Ga (Cawood & Hawkesworth, 2014). This apparent discrepancy, however, may only be a matter of perspective: relative continental stability in the Mesoproterozoic is expected to have been associated with very active mantle dynamics in the oceanic realm and in the convective mantle underneath the supercontinent. For instance, we speculate that in a tectonic scenario of a long-lived supercontinent with persistent active margins all around its perimeter (figure 6), very old (>200 Ma) and dense oceanic lithosphere from the peripheral 'superocean' may be subducted rapidly, leading to fast spreading rates due to increased slab pull and to increased melting of the mantle wedge. Secondly, continental stability could have led to a large zone of upwelling underneath the supercontinent, accompanied by increased antipodal plume activity in the oceanic domain (Evans, 2003; Maruyama et al., 2007; Li and Zhong, 2009), with concomitant high-degree mantle melting in plume heads. It has been proposed that the 'superswells' recognized at present underneath Africa and the SW Pacific (e.g., Courtillot et al., 2003) are the remnants of these large Mesoproterozoic upwelling structures (Maruyama et al., 2007). Redistribution of the mass heterogeneities would lead to True Polar Wander (TPW), turning the entire mantle with the overlying continent driving the upwelling superswells towards the equator (Evans, 2003), but it is not easy to predict whether TPW would lead to extra vigorous plume activity and mantle melting.

Thus, given the evidence of high rates of oceanic geodynamic processes such as subduction and seafloor spreading – possibly accompanied by multiple plumes or super-plumes – during the late Mesoproterozoic, it seems plausible that the clustering of Re depletion ages of Os-rich alloys from locations around the globe is a reflection of a global mantle super-event (Condie, 1998; Pearson et al., 2007; O'Neill et al., 2007). A model that links the assembly of Rodinia with high-degree melting in the mantle as recorded by Ru-Os-Ir alloys discussed above can explain the observed synchronicity between the supercontinent cycle and mantle super-events. In this view, the Mesoproterozoic mantle super-event is not a single mantle-driven cataclysmic event like a whole-mantle overturn (Condie, 1998), but rather a 'perfect storm' alignment of coupled geodyamic processes which all promote mantle melting, crust production and crust preservation.

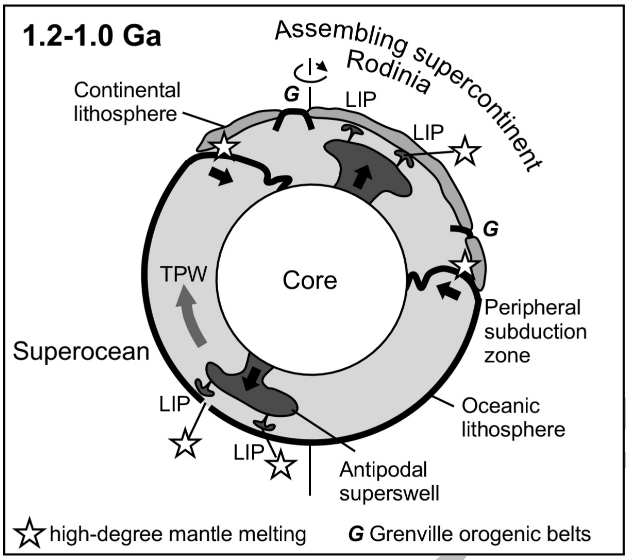


Figure 6. Geodynamic context for high-degrees of mantle melting around 1.0-1.2 Ga as evidenced by the global Ru-Os-Ir alloys data set. Model involving the assembly of supercontinent Rodinia (Grenville Orogeny) and peripheral subduction of a superocean, two antipodal superswells, and anticipated True Polar Wander (TPW) motions driving the superswells towards the equator is discussed in the text. Regions of high-degree upper mantle melting are indicated with stars: in the heads of mantle plumes coming off the superswells producing Large Igneous Provinces (LIP); in the mantle wedge above the peripheral subduction zone 'belt'; at a fast-spreading mid-ocean ridge(s) in the superocean.

## *6. Conclusions*

1. Platinum group minerals in placers from the River Rhine are dominated by Ru-Os-Ir alloys which are likely derived from residual, highly-refractory Early Paleozoic oceanic mantle slivers, as found in the pre-Variscan basement of the Aar and Gotthard massifs in the Alps.
2. The $^{187}Os/^{188}Os$ isotope ratios of 297 Os-rich alloys were measured by LA-MC-ICP-MS and show a wide distribution with two relatively well-defined modes (peaks) at 0.1244 and 0.1205; these modes correspond to Re-depletion ages of ~0.5 and ~1.1 Ga (or 1.2–1.0 Ga taking into account all uncertainties).
3. The ~0.5 Ga ages are fully consistent with an origin in Early Paleozoic mantle rocks, whereas the formation of alloys preserving older, Mesoproterozoic ages cannot easily be explained by local geodynamic processes; indeed, evidence for such ages is essentially absent in the Central-Western European crustal record. Thus, we interpret these alloys to be inherited, recording evidence of ancient depletion.
4. Os isotopic evidence for Mesoproterozoic, 1.2–1.0 Ga high-degree melting is also found in populations of Os-rich alloys from the Urals and Tasmania; together, the evidence suggests that high-degree melting affected mantle rocks from geographically and geologically distinct parts of the planet. This time interval is widely believed to have been characterized by fast spreading rates in a superocean and subduction in a peripheral zone of downwelling, by the assembly of a long-lived supercontinent, and by relatively active mantle plumes, possibly in two superswells. Evidence from mantle-derived Os-rich alloys is now mounting showing that this period was accompanied by globally widespread high-degree mantle melting events and, therefore, by high (mafic) crustal production rates. The name 'mantle super-event' (Condie, 1998) may be appropriate for such an alignment of geodynamic processes promoting mantle melting and crust production in Earth history, and a strong link with the supercontinent cycle is suggested.


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SUPPLEMENTARY TEXT

## Samples and sample collection method

Nine PGM grains, all of them Os-rich alloys, were recovered by the first author from the Altrhein near Kembs, a tract of the natural Upper Rhine channel alongside the new Grand Canal of Alsace (sample A). Heavy mineral ('black sand') separates were obtained in the field by sieving, sluicing and panning of gravels and sands from several gravel bars. Heavy mineral separates were washed in a 'Blue Bowl' hydroseparator in the lab, and PGM grains were picked from the highly concentrated gold-rich separate under a binocular microscope. Our mineral separates contained about one PGM grain for every 500-700 grains of gold. In addition, a sample of fine alluvial 'Rhine gold' weighing two grams and containing PGM was obtained from a professional goldpanner from Karlsruhe (sample B). This sample was the product of conventional gold-washing techniques in the river Rhine at a large number of locations between Basel and Speyer. 167 PGM grains, of which 143 were Os-rich alloys, were hand-picked from amongst the gold grains under a binocular microscope. An additional 40 Os-rich alloy grains were picked from a gold-rich separate (sample C) obtained from washing of a heavy mineral sample from a carpet installed on a conveyor belt in a gravel quarry near Baldersheim, located in the Quaternary floodplain of the Rhine just 2.5 km from the present-day Rhine channel; the gold separate containing these alloys was kindly made available by Alain Devilliers and Zelimir Gabelica. Finally, we included 129 additional Os-rich alloy grains obtained from a professional gold extraction plant based at the Kieswerk Rheinzabern (HOLCIM) close to Karlsruhe; this sample was processed in the laboratories of the AMR Institute at the RWTH Aachen to separate PGM (sample D).

Samples A-C contain three types of platinum-group minerals. PGM grains could be easily recognized in the gold-dominated washings on the basis of their high, metallic reflectance and steely blue or dark grey colour. Ru-Os-Ir alloy grains often show subhedral tabular hexagonal shapes with pitted surfaces. Pt-Fe alloy grains are also common and characterized by their flattened disk-like appearance as a result of their malleability. In addition, four crystals of sperrylite ($PtAs_2$) were detected; the grains have a tin white colour, very high reflectance, multi-faceted isometric forms and locally show conchoidal fracturing. A detailed electron microprobe mineralogical analysis of PGM in sample D, as well as accompanying heavy minerals and a small subset of grains from samples A-C is presented in Oberthür et al. (2016); these authors summarized that nearly 70% of the PGM grains are Ru-Os-Ir alloys, followed by Pt-Fe alloys (15%), sperrylite (9%) and other rare PGM including laurite-erlichmanite and tulameenite. The Ru-Os-Ir alloys formed a nearly complete solid solution between the three elements (Figure SI-1; Oberthür et al. 2016).

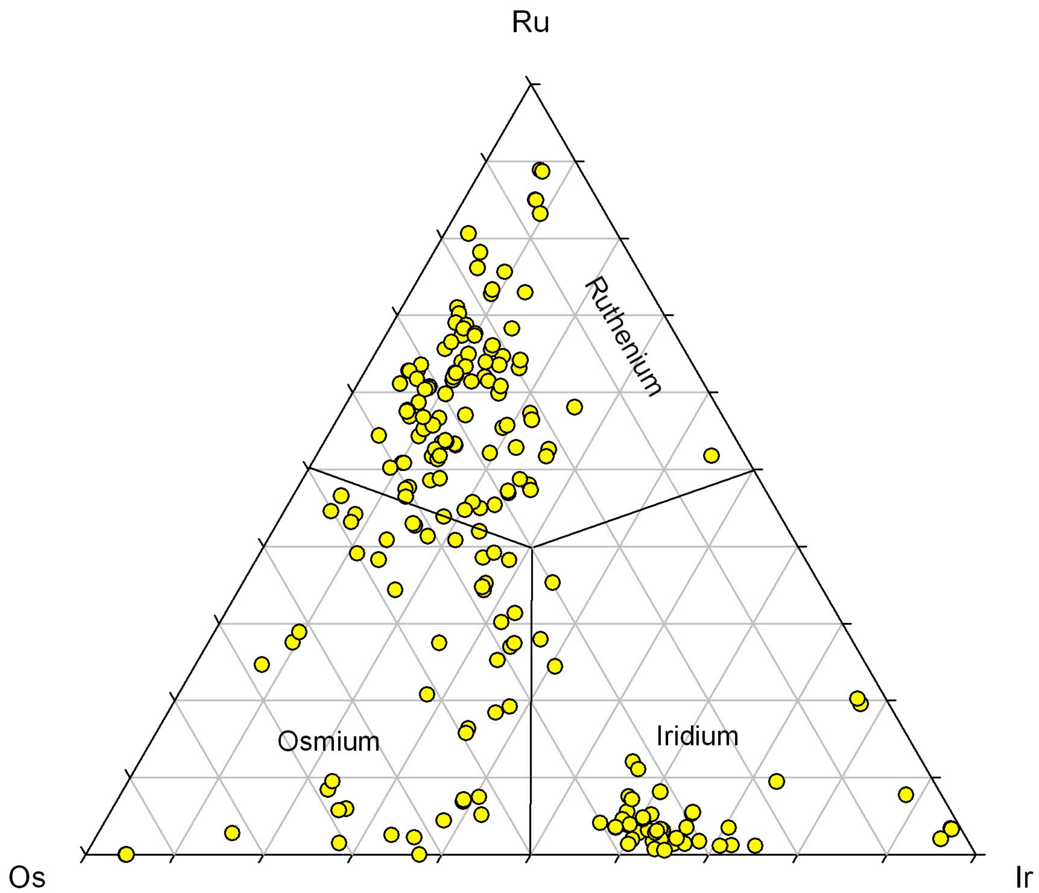


**Figure SI-1.** Compositional variation in a selection of Ru-Os-Ir alloys from the Rhine (atomic percentages) showing the nearly complete solid solution in the alloys. Modified from Oberthür at al (2016).



**Methods of major element and isotope analysis**

The Os-bearing alloy and other PGM grains from samples A, B and C were hand-picked and mounted onto carbon tape stuck onto a 1 cm diameter circular SEM stub. The alloys were then imaged and semi-quantitatively analyzed for their major element composition to screen for Os-bearing PGM using EDS on a Philips XL30 SEM, operating at 20 KV at the University of Neuchâtel, Switzerland. All PGM grains from sample D, and a small subset from samples A-C, were cast in resin mounts and then polished. Subsequently, they were analyzed using an electron microprobe at the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) in Hannover, Germany. Details of the method and results are reported in Oberthür et al. (2016).

A total of 307 Os-bearing grains belonging to the (Os,Ir,Ru) alloy group were analysed for $^{187}Os/^{188}Os$ by laser ablation MC-ICPMS, using a New Wave UP 213 nm Nd:YAG laser system, coupled to a ThermoFinnigan Neptune MC-ICPMS at Durham Geochemistry Centre, Durham University. All isotopes of Os were analysed, together with the key elements which potentially cause isobaric interferences, $^{182}W$ and $^{185}Re$, in the configuration: $^{182}W$, $^{184}Os$, $^{185}Re$, $^{186}Os$, $^{187}Os$, $^{188}Os$, $^{189}Os$, $^{190}Os$, $^{192}Os$ in L4, L3, L2, L1, C, H1, H2, H3, H4 collectors, respectively. Due to the low Pt contents and relatively small size of the beams used, it was not necessary to omit $^{192}$Os from the analytical procedure, although we did not use this isotope for the correction of mass bias, to avoid the potential effects of Pt interference on $^{192}$Os. Instead, a normalization value of $^{189}$Os/$^{188}$Os = 1.21978 was used. Gain calibration, baselines, peak centering and peak shape were all measured and checked at the start of each analytical session, with greater detail given in Nowell et al. (2008a). Measurement consisted of 40 cycles each with 1-second integration time.

At the start of each session, during February 2010 and July-August 2011, a 1 ppm DROsS osmium standard solution was analyzed at least five times to assess instrumental accuracy and reproducibility. Two variably doped DROsS solutions were also analyzed to determine the factors required to correct for $^{184}$W, $^{186}$W and $^{187}$Re isobaric interferences during ablation analyses. These solutions had concentrations of W at 0.05 ppm and 0.1 ppm and Re at 0.01 and 0.05 ppm. Over the six sessions, the pure DROsS standards (n = 32) gave mean values of $^{187}$Os/$^{188}$Os = 0.160923 ± 06, $^{186}$Os/$^{188}$Os = 0.119922 ± 08 and $^{184}$Os/$^{188}$Os = 0.001301 ± 09, equating to relative reproducibilities of 40 ppm, 70 ppm and 7 ‰, respectively. Overall, including the two doped solutions, mean values were $^{187}$Os/$^{188}$Os = 0.160920, $^{186}$Os/$^{188}$Os = 0.119919 and $^{184}$Os/$^{188}$Os = 0.001296 with relative uncertainties of 145 ppm, 179 ppm and 12 ‰. Even with doping, these values remain in good agreement with previous values of $^{187}$Os/$^{188}$Os = 0.160916 ± 04, $^{186}$Os/$^{188}$Os = 0 0.119909 ± 04 and $^{184}$Os/$^{188}$Os = 0.001298 ± 02 for MC-ICP-MS analyses of >1 ppm pure DROsS solutions at Durham - when corrected with $^{189}$Os/$^{188}$Os = 1.21978 (Nowell et al., 2008a) However, the best fit $^{185}$Re/$^{187}$Re, $^{182}$W/$^{186}$W and $^{182}$W/$^{184}$W values used for interference correction did vary over the course of the six sessions by 23 ppm, 204 ppm and 102 ppm, respectively, with average values of 0.598154, 0.929224 and 0.863348. While these variations imply a higher degree of uncertainty than shown by the DROsS values alone - and in addition the conditions of analysis of the solutions (wet plasma) are not strictly identical to those of laser ablation - the $^{182}$W/$^{188}$Os and $^{185}$Re/$^{188}$Os ratios of the PGM grains included in this study are very minor compared to those of the doped standards: $^{182}$W/$^{188}$Os$_{\text{Rhine PGM}}$/$^{182}$W/$^{188}$Os$_{\text{doped standard}}$ is <0.5 for W in all cases and typically <<0.005; $^{185}$Re/$^{188}$Os$_{\text{Rhine PGM}}$/$^{185}$Re/$^{188}$Os$_{\text{doped standard}}$ is <0.09 for all PGM except one at 0.27. In addition, the uncertainties for both the interference correction and the mean DROsS value are lowest for the ratio of most importance in this study – $^{187}$Os/$^{188}$Os – and are far smaller than both the range of natural variation and the ~0.5% or greater uncertainty assigned to each data point in the probability density distribution plots.

The methods for ablation and analysis followed closely those detailed in Nowell et al. (2008b) Laser beam sizes of between 20 and 80 μm were used, depending on the grain size. The laser power and frequency were correspondingly adjusted to provide a stable beam, without rapidly ablating through the grain, but at the same time for small beam sizes the power of the laser beam was always kept at 80% or above to minimise any potential fractionation at the ablation site. Such fractionation is poorly understood and is mainly a consideration for inter-element fractionation, which is of secondary importance in this study because we use model age estimates rather than isochron dating methods. In any case, this inter-element fractionation is estimated to be 5 percent or less (Nowell et al., 2008b). After mass bias and interfering element corrections were applied to each measurement, the analyses were subject to a 2σ rejection. The method and corrections are discussed in greater detail by Nowell et al. (2008b).

**Statistical treatment**

To investigate the nature of the distribution of $^{187}Os/^{188}Os$ isotope ratios, Probability Density Distributions (also known as Kernel Density Estimates) were constructed for the Os isotope ratios of remaining Os-bearing grains using the <density> function in the R project software v. 3.0.1 (R Core Team, 2013). In this procedure, for each measurement a Gaussian distribution is constructed with the measured isotope ratio as the mean, with a constant half width (the so-called bandwidth), and with an integrated area of 1. The Probability Density Distribution diagram is derived by adding the Gaussian distributions for all the individual measurements together. The result is dependent on the choice of bandwidth: if the bandwidth is set too low, the diagram becomes spiky and shows spurious peaks without any statistical significance; if the bandwidth is set too large, the resulting distribution is over-smoothened and all the peaks merge into one broad asymmetric peak. In Figure 3 two statistically sound bandwidths were chosen: one based on 'Silverman's Rule of Thumb' (Silverman, 1986), and a second, smaller one, based on the method of Sheather & Jones (1991; see also Rudge, 2008). The first method produces a diagram with a broad peak and a distinct shoulder at lower $^{187}Os/^{188}Os$, whereas the second method resulted in a diagram with two reasonably clearly defined peaks – approximately corresponding to those of the larger bandwidth - and one minor shoulder at a less radiogenic value (Figure 3). We also calculated the 1st derivative of the probability density distributions using the <Kdde> function in R, selecting the bandwidth according to Silverman's Rule of Thumb. The positions of the zero-crossings in the 1st derivative mark the peak positions in the probability density function, and inflection points with shallow slopes produce troughs in the derivative. We have also applied 2-component Gaussian mixture modeling for the subchondritic part of the dataset ($^{187}Os/^{188}Os<0.1276$) using the <normalmixEM> function in the 'mixtools' package in R. Such parametric methods need fewer samples to resolve the peaks but require a-priori assumptions about the number of peaks in a distribution (see for instance: Pearson et al., 2007; Rudge, 2008).

**Source of the Ru-Os-Ir alloys: refractory mantle rocks or chromitites?**

Os-bearing alloys of 1-5 µm have been reported from refractory mantle rocks in the Lherz massif (Luguet et al., 2007). They are, however, much more abundant in podiform chromitites, typically hosted in dunites lenses or layers within refractory mantle rocks (e.g., Malitch, 2004). Therefore, we propose that while some of the Ru-Os-Ir alloys from the placer deposits in the Rhine could have been derived from harzburgitic rocks in the Alpine chain, it is likely that at least a significant proportion is derived from podiform mantle-hosted chromitites. These two models are visualized in supplementary figure SI-2.

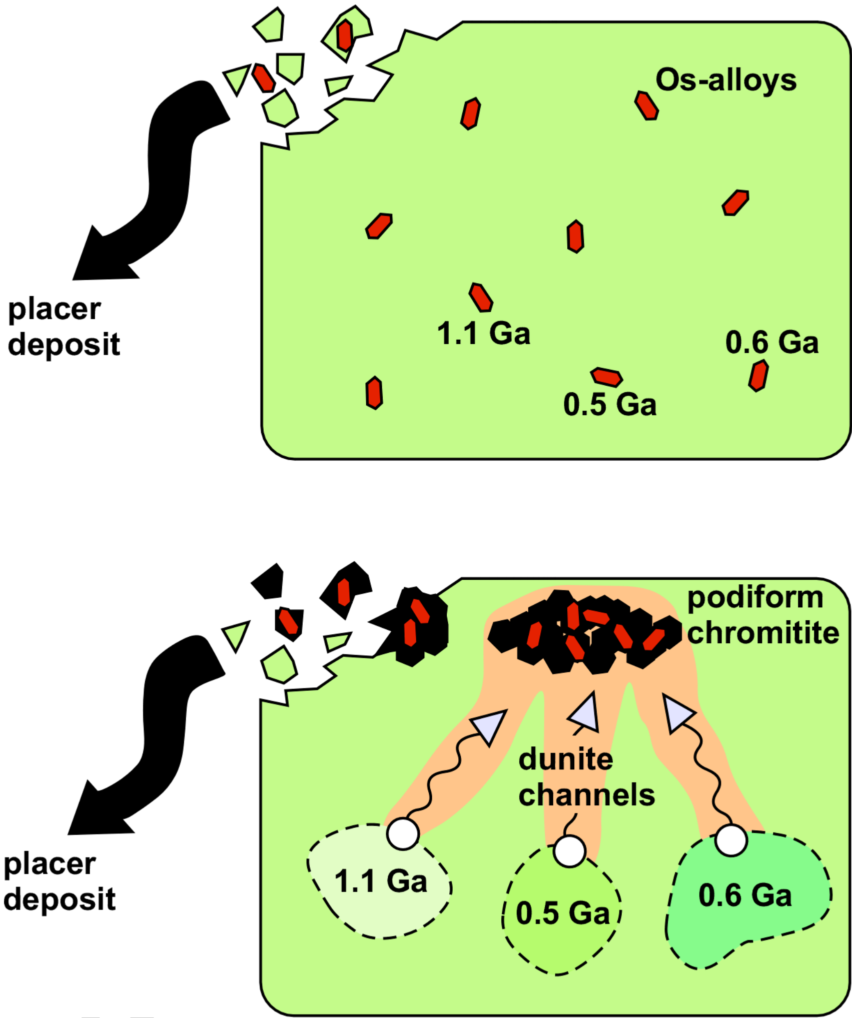


**Figure SI-2.** Two models for the origin of the sampled alloys. In the first model (upper diagram), Ru-Os-Ir with different ages produced during several melting events are present in refractory mantle rocks such as harzburgites (model based on Luguet et al., 2007; Fonseca et al., 2012). In the second model (lower diagram), the alloys are derived from podiform chromitites in dunite lenses within refractory mantle rocks (e.g., Pearson et al., 2007). They were either transported in water bubbles in silicate melts from their mantle source, where they formed during high degree mantle melting, and deposited in podiform chromitites (e.g., Matveev & Ballhaus, 2002; Fonseca et al., 2012), or they may have crystallized from the sulfide melt droplets within silicate melt fractions derived from unhomogenized Re-depleted mante domains (e.g., Büchl et al., 2004). In either case, the $^{187}Os/^{188}Os$ model ages of the sulfides reflect the age of Re-depletion during high-degree mantle melting events.

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