Earth and Planetary Science Letters 452 (2016) 115–122

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

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

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form 23 July 2016
Accepted 26 July 2016
Available online 11 August 2016
Editor: B. Marty

Keywords:
geodynamics
mantle melting
Ru–Os–Ir alloys
isotope geochemistry
mesoproterozoic

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 and Wittig, 2014); 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, Protero-

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http://dx.doi.org/10.1016/j.epsl.2016.07.047

zoic 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.

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 and 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 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 (Fig. 1). Details of the sample locations and sampling methods are found in the supplementary text. Some representative secondary electron images are shown in Fig. 2. Around 70% of PGM consisted of alloys of the Ru–Os–Ir system. A total of 307 Os-bearing grains were analyzed 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 analyzed 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 as-