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Osmium isotopes in Baffin Island and West Greenland picrites: Implications for the $^{187}Os/^{188}Os$ composition of the convecting mantle and the nature of high $^{3}He/^{4}He$ mantle

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ABSTRACT

Identifying the Os isotope composition of the prevalent, largely peridotitic, convecting mantle places important constraints on the Earth's accretion, differentiation and evolution and also has implications for the interpretation of Re-depletion ages in mantle peridotites. As partial melting preferentially samples mantle components with the lowest melting temperatures, large degree melts such as picrites should most closely reflect the peridotitic components within the source. Thus, Re–Os analyses of thirty picrites from Baffin Island and West Greenland are thought to provide a good estimate of the bulk $^{187}Os/^{188}Os$ composition of their convecting mantle source, which is indistinguishable from DMM in terms of lithophile isotopes and trace elements. In addition, the high $^{3}He/^{4}He$ of these rocks allows us to comment on the possible origins of high $^{3}He/^{4}He$ mantle. Ingrowth-corrected $^{187}Os/^{188}Os$ of the picrites ranges from 0.1267 to 0.1322. The higher $^{187}Os/^{188}Os$ samples have correspondingly lower $^{143}Nd/^{144}Nd$ which can be explained by contribution (~5%) from old recycled oceanic crust, including sediment. However, Baffin Island and the earliest West Greenland picrites are remarkably uniform in composition with $^{187}Os/^{188}Os$ between 0.1267 and 0.1280, and a mean and mode of 0.1272±0.0007. Such Os isotope compositions are less radiogenic than estimates of primitive upper mantle but are similar to the least radiogenic mid-ocean ridge basalts (MORB) and the most common composition of ophiolite-derived platinum-group alloys and chromites. These compositions appear to represent a source dominated by peridotite.

The picrites studied record the highest known $^{3}He/^{4}He$ in the silicate Earth (up to 50 R_a). For this signature to reflect isolated domains of ancient melt depletion would require significantly less radiogenic Os isotope compositions than observed ($^{187}Os/^{188}Os$: <0.115), unless radiogenic Os, but not He, has been subsequently added. Conversely, a bulk outer core contribution would impart a supra-chondritic $^{187}Os/^{188}Os$ signature to the picrites, and thus Os isotopes preclude the core as a source of high $^{3}He/^{4}He$, unless core–mantle transfer of Os and He is decoupled. It is possible to broadly account for the Os–He and Os–Nd isotope variations by mixing of depleted MORB mantle, recycled oceanic crust and high $^{3}He/^{4}He$ primitive mantle, but it is difficult to explain each individual sample composition in this way. Alternatively, as the high $^{3}He/^{4}He$ signature is found in samples with variable Os and Nd isotope compositions, it seems likely that He is decoupled from other isotopic tracers and is dominated by minor addition of a He-rich, high $^{3}He/^{4}He$ component probably of primordial nature, although the ultimate source is unclear from our data.

1. Introduction

Mantle rocks and mantle-derived melts display a broad range of Os isotope compositions, both depleted and enriched with respect to bulk Earth and primitive upper mantle (PUM) estimates. Due to the differential compatibility of Re and Os during mantle melting, crustal rocks typically have very high Re/Os ratios and, over time, evolve radiogenic $^{187}Os/^{188}Os$ compared to the mantle. Depleted mantle evolves complementary unradiogenic $^{187}Os/^{188}Os$ ratios, with the timing of Re depletion indicated by the extent to which $^{187}Os/^{188}Os$ deviates below a chondritic evolution curve. Therefore, the Re–Os system is a powerful tool with which to assess contributions from depleted mantle and enriched recycled materials to the source of mantle-derived melts (e.g. Shirey and Walker, 1998).

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Significant Os isotope heterogeneity exists in the mantle at a variety of length-scales from mineral- to vein- to slab-scale due to the recycling of enriched crustal materials and depletion of peridotite, melt percolation and metasomatism, and due to the highly siderophile nature of both Re and Os. Variable degrees of melting of such a heterogeneous mantle will lead to melts that vary in isotopic composition, where melts with the most radiogenic signature are typically derived from the smallest degrees of melting, and large-degree melts give the best estimate of the $^{187}Os/^{188}Os$ composition of the *bulk* mantle source. This study of North Atlantic (NA) picrites from Baffin Island (BI) and West Greenland (WG) should therefore provide a good estimate for the average Os isotope composition of the whole source volume. Given the lithophile isotope similarity of this source to depleted mid-ocean ridge basalt (MORB) mantle (DMM, e.g. Ellam and Stuart, 2004), this signature should also provide an estimate for the $^{187}Os/^{188}Os$ of typical convecting mantle without significant contribution from enriched components. Such an estimate is a valuable addition to current constraints on the Os isotope evolution of the Earth and peridotite melting ages (e.g. Meisel et al., 2001; Walker et al., 2002b).

The Baffin Island and West Greenland picrites define the high $^{3}He/^{4}He$ end-member of the mantle range (up to 50 Ra, Stuart et al., 2003; Starkey et al., 2009), which includes the canonical MORB range of 8±1 R_a (Graham, 2003; where $R_a = {}^{3}He/{}^{4}He_{atmosphere} = 1.39\times10^{-6}$). The picrites were erupted at about 61 Ma, probably due to the onset of the proto-Iceland plume (Saunders et al., 1997). This melting region continues to produce mantle melts with high $^{3}He/^{4}He$ in the Iceland region today (Macpherson et al., 2005). Due to the incompatibility of He, conventional wisdom posits that high $^{3}He/^{4}He$ mantle reservoirs are less degassed than the convecting upper mantle, and retain a component of the Earth's primordial volatile inventory (e.g. Kurz et al., 1982; Moreira et al., 2001; Porcelli et al., 2002). However, the observation that U and Th may be less compatible than He in an olivine-rich mantle assemblage has led to the suggestion that high $^{3}He/^{4}He$ may result from the greater loss of U and Th than He during ancient melt depletion (Graham et al., 1990; Class and Goldstein, 2005; Parman et al., 2005). The Re–Os isotope system has the ability to retain information about mantle melting events, even in the convecting mantle (e.g. Brandon et al., 2000; Meibom et al., 2002; Harvey et al., 2006; Pearson et al., 2007), and thus is the most suitable tracer to test whether high $^{3}He/^{4}He$ signatures can be directly linked to ancient depletion events.

In this study, Os isotope data for North Atlantic picrites from Baffin Island and West Greenland have been (i) used to gain an estimate of the average $^{187}Os/^{188}Os$ composition of the convecting mantle, and (ii) combined with existing He and Nd isotope data to re-assess the nature of the highest known $^{3}He/^{4}He$ mantle component.

2. Samples: setting and chemistry

The picrites in this study were collected from the eastern margin of Baffin Island (BI) at Cape Searle, Padloping Island and Durban Island and from Disko Island (Qeqertarsuaq) and the Nuussuaq peninsula in West Greenland (WG). The WG picrites were collected from the three members of the Vaigat formation, from oldest to youngest, the Anaanaa, Naujánguit and Ordlingassoq Members. Sampling focussed on olivine-rich samples, but is otherwise representative of the units sampled. The BI picrites are undifferentiated stratigraphically, but can be grouped chemically into the enriched (E-type) lavas (DUR-8, DI-23 and PAD-6) and normal (N-type) lavas (all others) first identified by Francis (1985). Sample CS-7 is from a cross-cutting dyke, and not from the picrite lava succession. Volcanism was largely contemporaneous on Baffin Island and in West Greenland and commenced ~61 Ma (Storey et al., 1998). Picrites from BI and the Anaanaa and lower Naujánguit Members of WG possess normal magnetisation whereas the subsequent WG melts are reversely magnetised (Pedersen et al., 2002). All members, and ~80% of the entire Paleocene volcanic sequence, were erupted within 1 million years (Storey et al., 1998). Petrography, major and trace element chemistry and Sr, Nd and Pb isotopes are described in more detail in previous studies (e.g. Francis, 1985; Holm et al., 1993; Graham et al., 1998; Larsen and Pedersen, 2000; Kent et al., 2004; Starkey et al., 2009).

All North Atlantic (NA) picrites have high MgO contents compared to most mantle melts (up to 27 wt.% in this study) which, although in part a result of olivine accumulation, reflects the Mg-rich nature of parental melts. Estimates for the parental melts of WG picrites, based on Fo-rich olivine phenocrysts, vary between 18 and 21 wt.% MgO (Pedersen, 1985; Larsen and Pedersen, 2000; Herzberg and O'Hara, 2002). Such MgO contents indicate generation by a high degree of melting – 10–11% for a depleted source (Herzberg and O'Hara, 2002; twice as high as MORB melting) – of anomalously hot mantle (1540–1600 °C) at depths of 60–90 km (Pedersen, 1985; Gill et al., 1992; Herzberg and O'Hara, 2002). The high degree of melting generates Os-rich melts which are less susceptible to interactions with crust and lithospheric mantle – critical when looking at samples erupted through ancient continental crust and lithosphere.

The three West Greenland picrite members have similar major element characteristics. However, for a given MgO content, TiO_2 increases with time, possibly reflecting a changing contribution from enriched material in the picrite source (cf. Prytulak and Elliott, 2007), with the older WG picrites most closely resembling the Baffin picrites (Holm et al., 1993). Chondrite-normalised REE patterns are flattest in the Anaanaa and Naujánguit picrites, while the Ordlingassoq samples have higher LREE and incompatible element concentrations (Holm et al., 1993). Neodymium and Sr isotope compositions of the Ordlingassoq picrites resemble the least depleted Iceland picrites (Holm et al., 1993).

3. Analytical techniques

Approximately 1 g of each whole rock powder was digested and equilibrated with a mixed ^{190}Os–^{185}Re-enriched spike, using inverse aqua regia (2.5 mL 12 mol L^{-1} HCl and 5 mL 16 mol L^{-1} HNO_3) in a quartz high-pressure asher (HPA) vessel or borosilicate Carius tube. HPA vessels were placed in an Anton-Paar HPA at Durham University at 300 °C and >110 bars for at least 12 h, and Carius tubes were placed in an oven at 240 °C for at least 36 h. Osmium was extracted using CCl_4, back-extracted using HBr, and then microdistilled (Cohen and Waters, 1996). The aqua regia was dried, re-dissolved in 0.5 mol L^{-1} HCl, and Re was separated using AG1X-8 (100–200#) anion-exchange resin (Pearson and Woodland, 2000).

Osmium was loaded onto Pt filaments and measured as OsO_3^- ions by negative-thermal ionisation mass spectrometry (N-TIMS) using the ThermoFinnigan Triton at Durham University. All Os isotope beams and mass 233, corresponding to $^{185}ReO_3^-$, were measured sequentially using an axial secondary electron multiplier. Raw data were corrected offline for O isotope interference, mass fractionation (using $^{192}Os/^{188}Os = 3.08271$) and spike unmixing. Interference from $^{187}ReO_3^-$ was insignificant (<2 cps). Analyses of 170 pg aliquots of the University of Maryland Os standard solution (UMd, or UMCP) gave mean $^{187}Os/^{188}Os$ of 0.11384±16 (2σ, $n=19$) and 0.11379±14 (2σ, $n=39$) for the two periods of analysis, April–November 2002 and April 2006–May 2008, respectively. These values are in good agreement with a value of 0.113787±7 for 10–100 ng/g aliquots measured on the same mass spectrometer in Faraday cup mode (Luguet et al., 2008a). Rhenium was analysed by inductively-coupled plasma mass spectrometry (ICP-MS) on a ThermoFinnigan® Element 2. Solutions were introduced using a micro-concentric nebuliser and a dual-cyclonic quartz spray chamber. A standard Re solution (1 ng/g) was analysed at the start, middle and end of each session to determine mass fractionation.

Carius tube and HPA digestions gave, respectively, mean total procedural blanks of 0.43 and 0.32 pg Os, 2.5 and 1.9 pg Re, and $^{187}Os/^{188}Os$ of 0.143 and 0.192. Blank corrections relate to the appropriate

Table 1
Re–Os isotope data for Baffin Island and West Greenland picrites

	Dig. method	Os (ng/g)	Re (ng/g)	Re/Os	$^{187}Os/^{188}Os$	$^{187}Os/^{188}Os_i$	$^{187}Re/^{188}Os$	γOs	MgO (wt.%)	Ni (μg/g)	Yb (μg/g)
Baffin Island											
Padloping Island											
PI-23	CT	1.48	–	–	0.12849 (9)	–	–	–	24.5	1127	1.28
PI-24	HPA	1.83	0.173	0.095	0.12775 (7)	0.12729	0.457	0.10	26.1	1228	1.27
PI-25	HPA	2.56	0.101	0.040	0.12780 (5)	0.12761	0.191	0.35	27.7	1336	1.01
PI-26	HPA	2.03	0.251	0.124	0.12758 (7)	0.12698	0.596	−0.15	25.1	1190	1.24
dupl.	HPA	1.93	0.253	0.131	0.12775 (9)	0.12711	0.631	−0.04	–	–	–
dupl.	CT	1.97	–		0.12760 (9)	–	–	–	–	–	–
PI-27	HPA	1.37	0.336	0.245	0.12896 (6)	0.12775	1.17	0.46	23.2	1058	1.30
dupl.	CT	1.48	–		0.12849 (7)	–	–	–	–	–	–
PI-31	HPA	1.76	0.294	0.167	0.12816 (7)	0.12734	0.803	0.14	22.6	1027	1.48
PI-37	HPA	3.45	0.120	0.035	0.12692 (6)	0.12675	0.168	−0.32	26.6	1206	1.07
PI-43	HPA	2.11	0.295	0.140	0.12777 (8)	0.12708	0.674	−0.07	24.6	1081	1.37
PAD-6	HPA	1.08	0.419	0.387	0.12878 (7)	0.12689	1.86	−0.22	17.2	647	1.70
Durban Island											
DI-23	CT	2.55	0.097	0.038	0.12751 (5)	0.12732	0.182	0.12	24.1	1035	1.32
DI-26	HPA	0.91	0.286	0.315	0.12855 (8)	0.12701	1.52	−0.12	15.9	546	1.70
DUR-8	HPA	1.55	0.113	0.073	0.12714 (6)	0.12679	0.350	−0.30	22.9	856	1.28
Cape Searle											
CS-7*	HPA	0.484	0.506	1.044	0.13356 (12)	0.12844	5.03	1.00	20.2	831	1.47
dupl.	HPA	0.435	0.504	1.158	0.13442 (11)	0.12874	5.58	1.24	–	–	–
dupl.	CT	0.471	–	–	0.13369 (14)	–	–	–	–	–	–
W. Greenland											
Anaanaa Mb.											
400444	CT	1.91	0.259	0.136	0.12812 (8)	0.12746	0.655	0.23	20.8	769	1.53
400452	HPA	2.49	0.966	0.388	0.12922 (11)	0.12732	1.87	0.12	21.6	913	1.49
400457	CT	3.88	0.359	0.093	0.12765 (5)	0.12720	0.446	0.02	22.7	848	1.40
400492	CT	2.53	1.14	0.450	0.13024 (7)	0.12804	2.17	0.68	20.0	801	1.57
408001.233	CT	1.50	0.243	0.162	0.12824 (10)	0.12746	0.779	0.23	18.0	751	1.45
Naujánguit Mb.											
113210	CT	3.12	0.206	0.066	0.12725 (6)	0.12693	0.318	−0.19	20.9	920	1.67
264217	CT	2.79	0.472	0.169	0.12772 (8)	0.12689	0.816	−0.22	22.0	949	1.50
332771	CT	1.55	0.425	0.274	0.12837 (9)	0.12704	1.32	−0.10	20.1	824	1.57
362149	CT	2.81	0.291	0.103	0.12814 (8)	0.12759	0.550	0.33	23.5	1329	1.33
400485	HPA	4.02	0.316	0.079	0.12713 (8)	0.12674	0.378	−0.33	27.0	1184	1.17
Ordlingassoq Mb.											
113333	CT	2.26	0.063	0.028	0.12955 (7)	0.12942	0.134	1.77	20.5	935	1.45
138228	CT	1.52	0.330	0.216	0.13321 (8)	0.13216	1.04	3.93	17.2	850	1.52
332788	CT	2.03	0.180	0.089	0.13120 (7)	0.13094	0.427	2.97	25.6	1306	1.13
332828	CT	2.68	0.367	0.137	0.13060 (6)	0.12994	0.660	2.18	22.2	1098	1.35
332901	HPA	1.73	0.071	0.041	0.13123 (7)	0.13103	0.198	3.04	24.6	1098	1.22
354754	HPA	2.20	0.179	0.082	0.13254 (6)	0.13214	0.393	3.91	20.7	810	1.45
400230	HPA	2.77	0.335	0.121	0.13235 (6)	0.13175	0.584	3.61	21.8	935	1.43

Notes:
For He isotope data see Graham et al. (1998), Stuart et al. (2003) and Starkey et al. (2009). Uncertainties on measured isotope ratios (given in brackets) are 2σ mean; $^{187}Os/^{188}Os$ ratios normalised using $^{192}Os/^{188}Os = 3.08271$ and corrected using $^{18}O/^{16}O$ and $^{17}O/^{16}O$ of 0.002045 and 0.000371 respectively; Given isotope ratios are blank corrected. $^{187}Os/^{188}Os_i$ – Os isotope composition corrected for ingrowth of ^{187}Os since the time of emplacement (61 Ma). γOs – deviation of $^{187}Os/^{188}Os_i$ from the chondrite evolution curve: $((^{187}Os/^{188}Os_i/^{187}Os/^{188}Os_{chondrite})-1)*100$. Digestion method: HPA – high-pressure asher, CT – Carius tube, both digestions in inverse aqua regia. Sample mass digested approx. 1 g in all cases. Reference materials analysed during the period of analysis (using HPA digestion) have been published previously in Dale et al. (2008) and Dale et al., (GCA, in press); MgO, Ni and Yb concentrations from Starkey et al. (2009; supp. online material); CS-7* taken from a dyke, all other samples from the picrite lava succession.

reagent batch rather than a long-term mean, but were always less than 0.1% for concentration and isotope composition.

3.1. Reproducibility of samples

Duplicate digestions of an Os-rich (~2 ng/g) and Os-poor sample (~0.5 ng/g) indicate $^{187}Os/^{188}Os$ reproducibility of 0.15% and 0.7% (2 RSD, $n=3$), respectively (Table 1). Os concentrations are reproducible to ~5% and 11% (2 RSD) for the two samples, respectively, and Re concentrations ($n=2$) vary by less than 1% (2 RSD) for both samples. The external accuracy of analyses is more difficult to evaluate, but reproducibility using two different digestion techniques for these samples and for reference materials (Dale et al., 2008; Dale et al., in press) suggests that incomplete digestion and/or sample-spike equilibration is unlikely to be a significant consideration.

4. Results

4.1. Re and Os elemental data

Osmium concentrations range from 1.50 to 4.02 ng/g in the West Greenland picrites and from 0.435 to 3.45 ng/g in the Baffin Island picrites (Table 1). The WG suite has a higher median of 2.49 ng/g Os compared to 1.66 ng/g for the Baffin suite. All samples have much greater Os concentrations than MORB, which range from <0.001 to 0.25 ng/g (Roy-Barman and Allegre, 1994; Gannoun et al., 2007). The highest Os concentrations are greater than approximate averages for primitive or depleted mantle (~3.1–3.7 ng/g, Morgan et al., 2001; Becker et al., 2006; Harvey et al., 2006). Rhenium concentrations vary from 0.113 to 0.506 ng/g in the BI picrites, with a median of 0.29 ng/g, while the WG samples have a larger range (0.063 to 1.14 ng/g) but a

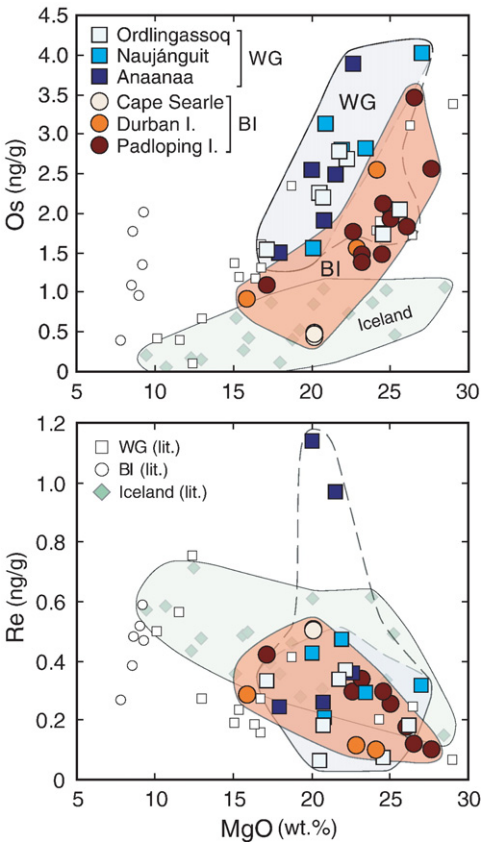

Fig. 1. Co-variation of Os and Re with MgO in picrites from West Greenland (WG) and Baffin Island (BI). Other WG, BI and Iceland picrite data from Schaefer et al. (2000), Kent et al. (2004) and Brandon et al. (2007), respectively.

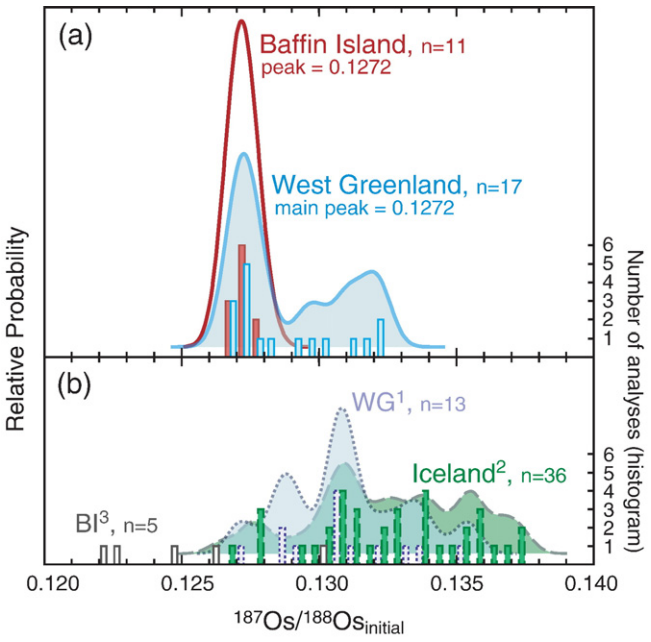

Fig. 2. Probability density plot for initial $^{187}Os/^{188}Os$ in (a) North Atlantic (NA: Baffin Island and West Greenland) picrites from this study and (b) NA and Iceland picrites from the literature (at same scale). Other data: [1] Schaefer et al. (2000), [2] Brandon et al. (2007) and Skovgaard et al. (2001), [3] Kent et al. (2004). NA picrite samples with <0.5 ng/g Os have been omitted due to potential crustal contamination. A probability curve for BI[3] data is omitted due to the very small sample number. For comparison, Iceland samples have been corrected to 61 Ma, based on chondritic evolution. A 'bandwidth' uncertainty of 0.001 was applied to the $^{187}Os/^{188}Os$ ratio of all samples (~0.8% relative uncertainty).

similar median of 0.32 ng/g. Such Re abundances are typically lower than MORB (0.34–2.28 ng/g, median ~1 ng/g, Sun et al., 2003; Gannoun et al., 2007).

Osmium concentrations decrease with decreasing MgO (Fig. 1) and Ni (not shown). For a given MgO content, WG picrites tend to be more Os-rich than BI picrites, which are both richer in Os than recent Iceland picrites (Brandon et al., 2007). Co-variation of MgO and Re is less systematic than with Os, but a negative co-variation exists in the BI samples and is well-defined in two regional sub-sets (Fig. 1). For the most part, Re/Os ratios increase with decreasing MgO content in all suites (see Fig. 1).

4.2. Os isotope data

Baffin Island picrites have a range of $^{187}Os/^{188}Os$ from 0.1269 to 0.1344, which, when corrected for ingrowth of ^{187}Os since the time of emplacement (61 Ma), gives a narrow range of initial $^{187}Os/^{188}Os$ ratios from 0.1267 to 0.1287. The most radiogenic picrite has the lowest Os concentration (~0.45 ng/g, Fig. 3), consistent with a previous conclusion of crustal contamination for this sample (Stuart et al., 2003); this sample has been excluded from further discussion. Thus, the range of initial $^{187}Os/^{188}Os$ is considerably more limited, from 0.1267 to 0.1278. The WG picrites have a larger range of $^{187}Os/^{188}Os$ and $^{187}Os/^{188}Os_{initial}$ of 0.1271–0.1332 and 0.1267–0.1322, respectively. However, the least radiogenic WG samples define a peak on an initial $^{187}Os/^{188}Os$ probability density plot at 0.1272, which is identical to the BI peak (Fig. 2). The sub-chondritic to supra-chondritic range of Os isotope values observed in a different suite of BI picrites (Kent et al., 2004) was not found in this study. Source heterogeneity is a possible explanation for this difference but as the samples of Kent et al. (2004) have unusually high Os concentrations for their MgO content (Fig. 1), and Os co-varies with $^{187}Os/^{188}Os$, we contend that these samples may have been modified during interaction with an Os-rich, low $^{187}Os/^{188}Os$ lithospheric mantle component (cf. Larsen et al., 2003).

The WG picrites extend to more radiogenic Os isotope compositions than the BI picrites, and $^{187}Os/^{188}Os$ clearly varies with stratigraphy. Picrites from the Anaanaa and Naujánguit Members of the Vaigat formation possess largely uniform and unradiogenic $^{187}Os/^{188}Os$

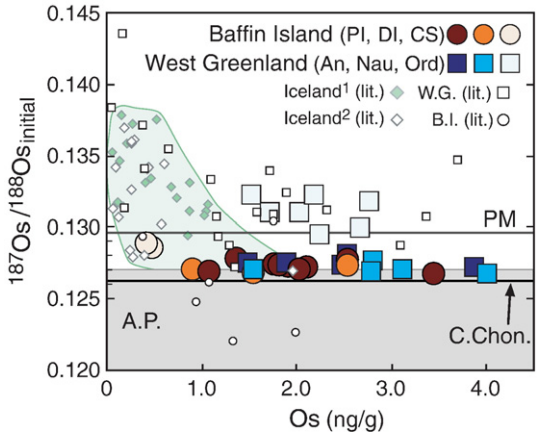

Fig. 3. Initial $^{187}Os/^{188}Os$ (at 61 Ma) plotted against Os concentration. PI, DI and CS are Padloping Island, Durban Island and Cape Searle. An, Nau and Ord are, oldest to youngest, Anaanaa, Naujánguit and Ordlingassoq Members of the Vaigat formation. A lack of co-variation suggests insignificant assimilation of radiogenic ancient crust or unradiogenic SCLM. Only the duplicated low Os CS sample has slightly more radiogenic Os than others from Baffin Island, consistent with a minor crustal contribution. Primitive mantle estimate (without uncertainty) from Meisel et al. (2001), abyssal peridotites (AP) from Snow and Reisberg (1995) and Harvey et al. (2006), carbonaceous chondrite (without uncertainty) from Walker et al. (2002a). Other data sources: WG: Schaefer et al. (2000), BI: Kent et al. (2004), Iceland[1]: Brandon et al. (2007), Iceland[2]: Skovgaard et al. (2001).

(Fig. 3). In contrast, all samples from the slightly younger Ordlingassoq Member have more radiogenic $^{187}Os/^{188}Os_{initial}$ ratios of 0.1294 to 0.1322. Such $^{187}Os/^{188}Os$ ratios range to more radiogenic values than estimates of putative present-day primitive mantle (0.1296±0.0008, Meisel et al., 2001) but do not extend as high as previous picrite data for the WG Vaigat formation (up to 0.1371, Schaefer et al., 2000) or recent picrites from Iceland erupted within the last 1 Ma (up to 0.1378, Brandon et al., 2007).

There is no co-variation of $^{187}Os/^{188}Os$ with Os concentration in either BI or WG picrites (Fig. 3, excluding CS-7, already discussed). Significant assimilation of crust or sub-continental lithospheric mantle (SCLM) would likely result in samples from the same parental melt falling on mixing lines towards either an Os-poor, ancient, extremely radiogenic crustal component or an Os-rich, ^{187}Os-depleted SCLM; such trends are not observed. Equally, different parental melts would be variably susceptible to contamination, according to their Os concentrations, and thus would display a range of isotope compositions. Most previously analysed WG samples with <0.5 ng/g Os have elevated $^{187}Os/^{188}Os$ (Schaefer et al., 2000), suggesting that Os-poor samples may be affected by crustal assimilation and/or preferential sampling of radiogenic material during mantle melting; these samples have been omitted from subsequent figures.

5. Discussion

5.1. Re–Os elemental behaviour

Olivine accumulation in the NA picrites studied is indicated by sample MgO contents of up to 27 wt.%, compared to an estimated parental magma of 18–21 wt.% MgO (Pedersen, 1985; Larsen and Pedersen, 2000; Herzberg and O'Hara, 2002). Osmium concentrations decrease with decreasing MgO (Fig. 1) and with Ni (not shown), reflecting the compatibility of Os within the olivine-rich crystallising assemblage, which probably includes significant co-precipitated sulphide (as in global MORB and OIB, e.g. Burton et al., 2002). Therefore, Os concentrations are likely controlled by olivine accumulation and fractionation. On the basis of the Os content at MgO=18 wt.%, BI and WG parental melts are estimated to contain ~1 and ~1.7 ng/g Os, respectively (Fig. 1). As Os has a high sulphide-silicate melt partition coefficient (e.g. ~10,000 at low pressure, Crocket et al., 1997), such high parental melt Os concentrations probably require complete consumption of sulphides in at least part of the melting column. The consumption of sulphide in a fertile upper mantle source is thought to occur at melt fractions of >20–25%, based on the sulphide content of the mantle and sulphur solubility in mafic melts (e.g. Mavrogenes and O'Neill, 1999; Lorand et al., 2003), or at lower melt fractions for a previously depleted mantle source as proposed for the NA picrites (e.g. Ellam and Stuart, 2004). These melt fractions are consistent with estimates based on MgO content: ~20–28% for a fertile source or 10–11% for a depleted source (Herzberg and O'Hara, 2002). In addition to sulphide-silicate partitioning, physical entrainment of liquid sulphide within a large degree silicate melt (Ballhaus et al., 2006) may, at least in part, account for the very high Os concentrations of the NA picrite parental melts.

Rhenium concentrations in the picrites are lower than MORB, consistent with the moderate incompatibility of Re during mantle melting and the higher melt fraction of picritic melts. Re/Yb ratios are comparable to MORB (~0.00025), illustrating that Re maintains similar compatibility to Yb at higher melt fractions than MORB. The preference of Re for olivine-poorer assemblages is illustrated by increasing Re and Re/Os ratios with decreasing MgO content in almost all the picrite units.

5.2. Osmium–neodymium isotope systematics

The majority of NA picrites analysed here have $^{143}Nd/^{144}Nd_{initial}$ of ~0.51307 (Graham et al., 1998; Starkey et al., 2009), consistent with a source dominated by a depleted mantle component, as previously noted by Holm et al. (1993). Such Nd isotope compositions are indistinguishable from the range of estimates for DMM corrected to 60 Ma (0.51304–0.51311, Salters and Stracke, 2004; Workman and Hart, 2005) and the proposed depleted end-member of the Iceland array (e.g. Taylor et al., 1997). There is considerable $^{143}Nd/^{144}Nd$ variation in BI and Anaanaa (WG) picrites, while $^{187}Os/^{188}Os$ is largely constant at around 0.127 (Fig. 4). The $^{143}Nd/^{144}Nd$ range may be partially due to crustal contamination (samples CS-7, 400444, Starkey et al., 2009; and by inference 408001.233) but still remains significant (0.512845–0.513072). In contrast, the younger Ordlingassoq Member of the WG suite displays a negative co-variation of Os and Nd isotopes with $^{143}Nd/^{144}Nd$ decreasing from 0.51308 to 0.51291 as $^{187}Os/^{188}Os$ increases from 0.1267 to 0.1322 (Fig. 4). Literature data for the Naujánguit and Ordlingassoq Members (Schaefer et al., 2000), possess similar systematics to the Ordlingassoq samples in this study, but display greater scatter, probably due to our careful screening during sample selection to avoid potential crustal contamination.

5.2.1. Assessing the effects of post-melting crustal or lithospheric interaction

Assessment of the potential effects of continental crust assimilation is of particular importance due to the Proterozoic age of the crust through which the NA picrites were erupted. Careful screening has removed samples which appear obviously contaminated by crust, but

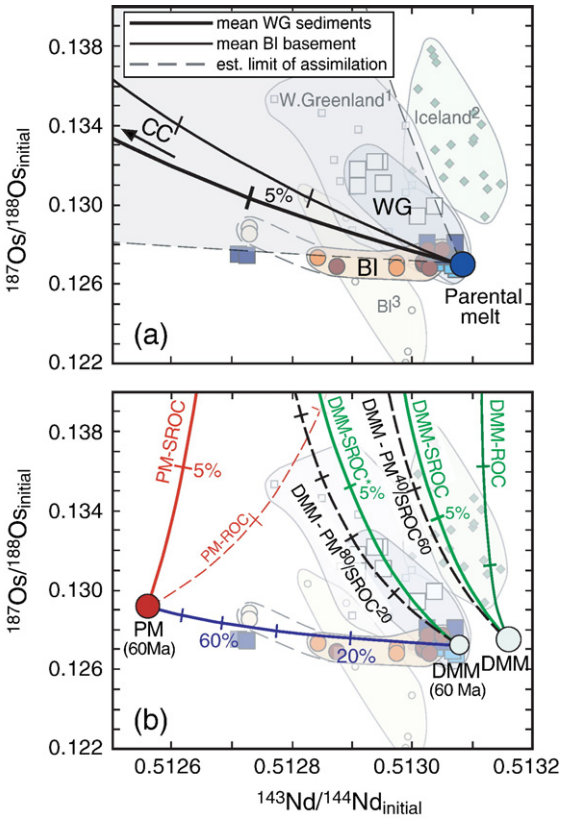

Fig. 4. $^{187}Os/^{188}Os$ vs. $^{143}Nd/^{144}Nd$ (corrected to 61 Ma) for NA picrites in this study (Nd data from Graham et al., 1998; Starkey et al., 2009) and published NA and Iceland picrites (Schaefer et al., 2000; Kent et al., 2004; Brandon et al., 2007). Symbols: see Fig. 1. (a) Best estimates for the effects of possible continental crust (CC) assimilation. (b) Mixing between possible mantle components: DMM, PM (primitive mantle), 2 Ga ROC (recycled oceanic crust; gabbro:basalt – 50:50), 2 Ga SROC (ROC:sediment – 95:5, except SROC*: 90:10), and mixing of PM/SROC hybrid component with DMM (superscript numbers refer to the relative proportions in the hybrid). Tick marks represent 10% proportion increments, except where stated. Displayed mantle mixing curves only represent a part of the large possible range due to parameter uncertainties and variable mixing proportions. Parameters – see Table 2.

Table 2
Os, Nd and He isotope and elemental modelling parameters

Component	[Os] (ng/g)	[Re][a] (ng/g)	$^{187}Os/^{188}Os$	[Nd] (μg/g)	$^{143}Nd/^{144}Nd$	[He] (μcm^3) (STP)/g	$^3He/^4He_{Ra}$
DMM	3.4	–	0.1276	0.581	0.51316	2.87	8.1
DMM at 60 Ma	3.4	–	0.1272	0.581	0.51308	2.87	8.1
PM	3.1	–	0.1296	1.250	0.512638	55	55
PM at 60 Ma	3.1	–	0.1292	1.250	0.51256	55	55
3.1 Ga depleted mantle	3.4	0.12	0.115	–	–	5.4	50
2 Ga ROC	0.024[b]	0.445	5.17	5.568	0.51310	49.6	5.94
2 Ga sediment	0.586[b]	16.0[c]	10.74	21.4	0.51151	454	0.01
WG sediments (mean)	0.031[b]	0.390	2.36	39	0.51110	–	–
BI Proterozoic basement (mean)	0.031[b]	0.390	2.36	24	0.51090	–	–
Possible crustal range	0.005–0.05	0.2–0.5	1.2–16.4	13–50	0.5102–0.5114	–	–
Parental melt	1.5	–	0.127	9.5	0.51308	–	–

Notes and references:
DMM data sources: Os – see text and this study, Nd – Salters and Stracke (2004), Workman and Hart (2005), He – Porcelli and Elliott (2008), Graham (2003). PM data sources: Os – see text, Meisel et al. (2001), Nd – Workman and Hart (2005) and refs therein, He –Porcelli and Elliott (2008). 3.1 Ga mantle data sources: Os – see text and Fig. 6 caption, He – Brandon et al. (2007), modified after Parman (2007) and Porcelli and Elliott (2008). Recycled oceanic crust (ROC) data sources: Os and Re – Gannoun et al. (2007), Dale et al. (2007), Brandon et al. (2007), Nd – Stracke et al. (2003), He – Brandon et al. (2007). 2 Ga sediment data sources: Os, Re and He – Brandon et al. (2007), Nd – Stracke et al. (2003). Continental crust data sources (for age of local crust, ~2 Ga): Os – Peucker-Ehrenbrink and Jahn (2001) and references therein, Nd – Goodrich and Patchett, 1991 and Larsen, unpubl. for West Greenland sediments and Theriault et al. (2001) for Baffin Island basement.
[a] ROC Re concentrations and calculated $^{187}Os/^{188}Os$ include ~60% Re loss from basalt (Dale et al., 2007). Similar Re loss is assumed for sediments based on (transferable?) behaviour of Re in basalts, but in any case, the values used are reasonable estimates for sediment, given the extremely large concentration range in different sediment types.
[b] Os data including ingrown ^{187}Os, original concentrations: 0.0145, 0.244 and 0.022 ng/g for ROC, sediment and continental crust, respectively.
[c] DMM-SROC* mixing uses a sediment Re concentration of 12 ng/g.

quantitative assessment of the isotopic effects of minor contamination by continental crust is not a simple task due to its marked heterogeneity, particularly in terms of Re–Os (e.g. Peucker-Ehrenbrink and Jahn, 2001). The Os isotope composition of local crust has not been measured, and measurements, even if numerous, are unlikely to provide a sufficiently well-constrained average due to the varied basement geology. Baffin Island Proterozoic basement rocks also display a considerable range of $^{143}Nd/^{144}Nd$ and Nd concentrations (Theriault et al., 2001), as do local Cretaceous West Greenland sediments, derived from Proterozoic basement, which are the most likely contaminants (Goodrich and Patchett, 1991, Larsen, unpubl.). Estimated Re and Os concentrations (Table 2) have been used to calculate the $^{187}Os/^{188}Os$ composition of 2 Ga basement or basement-derived sediment, which has then been combined with average measured Nd concentrations and isotope compositions (Table 2).

Mixing of average/best estimate 2 Ga basement or sedimentary cover with parental picritic melt does not generate the uniform $^{187}Os/^{188}Os$ BI array, nor the negative co-variation of Nd and Os isotopes observed in Ordlingassoq picrites. However, approximately 5% assimilation of two different extreme crustal components may be able to account for both the BI and Ordlingassoq co-variations (low Sm/Nd–low Re/Os and high Sm/Nd–high Re/Os crust, respectively, Fig. 4), but such very different and extreme contaminants are considered unlikely given the similar average composition of the country rock in the two regions. Crust-melt mixing may also result in co-variation of $^{187}Os/^{188}Os$ with Os concentration and this is not observed (Fig. 3).

Combining Nd isotopes and Nb/Zr ratios provides a further line of evidence that crustal assimilation is not a significant factor in controlling the isotope compositions of NA picrites (Starkey et al., 2009). Although very small amounts of crustal contamination can explain some of the spread in $^{143}Nd/^{144}Nd$, the broad array of increasing Nb/Zr with decreasing $^{143}Nd/^{144}Nd$ cannot be accounted for by assimilation of any low Sm/Nd crustal material. Thus, we conclude that Os and Nd isotopes predominantly reflect the mantle source.

5.2.2. Generation of the osmium and neodymium isotope variations in the mantle source

The upper part of the Vaigat formation (WG) records increasing $^{187}Os/^{188}Os$ combined with decreasing $^{143}Nd/^{144}Nd$. If this is unlikely to result from melt–crust interaction, such a shift in Os and Nd isotope compositions may reflect an increased source input from an enriched component. For instance, modelled mixing of DMM with 2 Ga recycled oceanic crust and associated sediment can produce the negative array in Os–Nd isotope space (Fig. 4, e.g. up to 5% recycled component containing ~10% sediment). However, this model is non-unique and it is possible that other enriched material such as metasomatised oceanic lithosphere (e.g. Niu and O'Hara, 2003) could produce the negative array. Equally, mixtures of a hybrid putative primitive mantle – recycled oceanic crust component with DMM can also explain the arrays of both the Ordlingassoq and Iceland picrites, by varying the proportions of primitive mantle and recycled crust in the hybrid component (Fig. 4).

The variation of $^{143}Nd/^{144}Nd$, with no complementary change in $^{187}Os/^{188}Os$, seen in Baffin and Anaanaa picrites is more difficult to explain because old recycled oceanic crust (plus sediment), and old continental crust, are both likely to possess complementary high $^{187}Os/^{188}Os$ and low $^{143}Nd/^{144}Nd$. Mixing of primitive mantle and DMM may be able to account for such an array (Fig. 4). Alternatively, such a signature may reflect a mantle source containing a minor (sulphide-poor?) pyroxenite component that, due to its high Nd content and low Os content, significantly affected the Nd isotope composition of the melt without noticeably affecting Os. Regardless of the ultimate source of Nd isotope heterogeneity, the uniform $^{187}Os/^{188}Os$ of BI and early WG picrites indicates that any enriched component has had little influence on Os isotope compositions.

5.3. Summarised evolution of the Iceland plume: Os, Nd and He evidence

Volcanism associated with the onset of the proto-Iceland plume was derived from high degree melting and was characterised by approximately chondritic Os isotope compositions, the highest known $^3He/^4He$ ratios and variable, but fairly radiogenic $^{143}Nd/^{144}Nd$ ratios. Osmium isotope compositions are consistent with a source more depleted than estimates of PUM (e.g. Meisel et al., 2001), with no significant contribution from any enriched component including, based on current models, the outer core (e.g. Walker et al., 1995; Brandon et al., 1998) or metasomatic sulphide (Luguet et al., 2008b). Subsequent melts (Ordlingassoq Member), erupted within 1 Ma of the earliest picrites, have elevated $^{187}Os/^{188}Os$ indicating a contribution from enriched material, possibly old recycled oceanic crust plus sediment, which was not tapped in the first phase of plume melting, but was soon brought into the zone of melting presumably by continued upwelling. Crustal and lithospheric interactions appear to mask the source composition of 58 Ma East Greenland samples (e.g.

Peate et al., 2003), but $^{3}He/^{4}He$ up to 21 R_a has been measured (Marty et al., 1998).

Elevated $^{187}Os/^{188}Os$ ratios and low $^{143}Nd/^{144}Nd$ isotope data, relative to DMM, in recent Iceland picrites (Brandon et al., 2007) can be explained by mixing of a similar recycled crustal component, including ~5% sediment, with a DMM component (Fig. 4). The absence of ^{186}Os enrichment in these picrites, relative to DMM (Brandon et al., 2007), combined with the NA picrite Os data, suggests no bulk core contribution to the plume over its history. High $^{3}He/^{4}He$ ratios persist in the Iceland plume today (>30 R_a, Macpherson et al., 2005) and, intriguingly, $^{3}He/^{4}He$ increases with $^{187}Os/^{188}Os$ in recent picrites (Brandon et al., 2007; Fig. 6b), despite the proposed involvement of recycled oceanic crust which would possess very low $^{3}He/^{4}He$ (~4, Brandon et al., 2007).

5.4. The $^{187}Os/^{188}Os$ composition of shallow convecting mantle

Trace element and Nd–Sr isotope evidence (Holm et al., 1993; Stuart et al., 2003; Ellam and Stuart, 2004; Kent et al., 2004) indicates that the early NA picrite source is typically depleted with respect to putative primitive mantle (e.g. Zindler and Hart, 1986), and is indistinguishable from the MORB source mantle (DMM, e.g. Salters and Stracke, 2004; Workman and Hart, 2005). The $^{187}Os/^{188}Os$ compositions of the earliest NA picrites (0.1267 to 0.1280) are consistent with a depleted mantle source containing no significant contribution from recycled crust, pyroxenite, sediment, recycled SCLM, metasomatised peridotite or outer core, nor any isolated ancient depleted domains.

Global ocean island basalts have variable reference TiO_2 concentrations (defined as the TiO_2 concentration on the olivine control line at the estimated parental MgO content). This has been interpreted to reflect variable source contributions from enriched components, primarily recycled oceanic crust (Prytulak and Elliott, 2007). The reference TiO_2 content for the early NA picrites is ≤1% (at ~18 wt.% MgO), lower than all OIB suites compiled by Prytulak and Elliott (2007), and comparable to Iceland. By this measure the NA picrites define the least enriched end-member for within plate magmas, i.e. their sources are dominated by peridotite, with minimal 'enriched' component. This conclusion is also supported by the low Ni/Mg ratios of Fo-rich picritic olivines (0.74–0.94, Fo: 89–91, respectively; Larsen and Pedersen, 2000) which are comparable to MORB and peridotite but lower than most within-plate magmas (Sobolev et al., 2007). Although Ni/Mg in olivine may simply reflect the depth of melting, with which it appears positively correlated (Niu and O'Hara, 2007), low Ni/Mg ratios combined with relatively deep melting definitely suggests an insignificant pyroxenite source contribution.

Due to the large degree of melting during the generation of the NA picrites, their Os isotope composition will closely reflect the composition of the bulk mantle source. This, coupled with the chemical similarity to DMM and insignificance of enriched components, gives the potential for providing an estimate of the bulk $^{187}Os/^{188}Os$ composition of the peridotitic convecting upper mantle/DMM sampled by these magmas. The dominance of the DMM signature in a proposed plume-head has probably arisen from extensive entrainment during the latter stages of plume upwelling, and a disproportionate contribution due to melting in the shallower part of the melting column. To facilitate comparison with other data such as those for MORB, initial $^{187}Os/^{188}Os$ for picrites, platinum-group alloys and chromites have been recalculated to the present day by assuming chondritic evolution of their sources since the time of mantle melting. Strictly speaking, post-melting evolution of Os isotopes will be depressed relative to chondrite, due to Re depletion. Thus, for a depleted NA picrite mantle source, with 0.12 ng/g Re (Sun et al., 2003), the present day $^{187}Os/^{188}Os$ would be lower by 0.0002 than the values discussed below.

On the basis of the probability peak for the NA picrites (Fig. 5), or the mean for the BI and older WG members, the $^{187}Os/^{188}Os$ composition of present-day convecting mantle underlying this region is estimated to be 0.1276±0.0007 (2 SD of data contributing to peak). This value is indistinguishable from the least radiogenic recent Iceland melts (<0.5 Ma, Skovgaard et al., 2001, Figs. 2 and 3) and from the largest platinum-group alloy peak (0.1276, Fig. 5), derived mainly from Tibetan ophiolites (Pearson et al., 2007; Shi et al., 2007). Phanerozoic ophiolite-derived chromites define a peak $^{187}Os/^{188}Os$ of 0.1283, while regression of $^{187}Os/^{188}Os$ versus time gives a lower intercept of 0.1281 (Walker et al., 2002b). Subduction-related enrichment of Re (see Becker, 2000; Dale et al., 2007) or radiogenic Os (e.g. Brandon et al., 1996) has the potential to elevate this value, although this must also be considered for the ophiolite-derived platinum-group alloys. The $^{187}Os/^{188}Os$ estimate defined by NA picrites and platinum-group alloys is intermediate between averages for carbonaceous, enstatite and ordinary chondrites (0.1262, 0.1281, 0.1283, respectively, Walker et al., 2002a). It is, however, significantly lower than the proposed $^{187}Os/^{188}Os$ of 0.1296±0.0008 for putative PUM, based on co-variation of Al_2O_3 and $^{187}Os/^{188}Os$ in mantle xenoliths (Meisel et al., 2001). This difference is presumably due to the effect of time-integrated mantle Re depletion through the generation of continental crust and/or generation and isolation of subducted oceanic crust, although the potential effects of coupled metasomatic increases in Al_2O_3 (e.g. Pearson et al., 2003) and $^{187}Os/^{188}Os$ (e.g. Alard et al., 2005) may also need to be considered. The similarity between the modal NA picrite Os isotope composition and other estimates of convecting mantle indicate that a $^{187}Os/^{188}Os$ value somewhere between 0.1274 and 0.1281 might be an appropriate estimate for ambient shallow convecting mantle.

The least radiogenic MORB ($^{187}Os/^{188}Os$ of 0.1261–0.1272) are isotopically similar to the NA picrite $^{187}Os/^{188}Os$ peak of 0.1276, and therefore support this proposal. Most MORB are significantly more

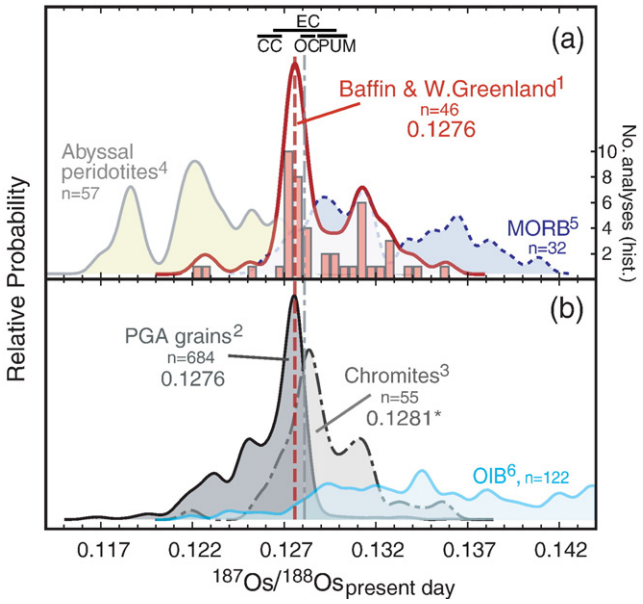

Fig. 5. Probability density plot for $^{187}Os/^{188}Os$ of NA picrites and other direct and indirect indicators of mantle composition. $^{187}Os/^{188}Os_{present\,day}$ denotes that data, where appropriate, has been corrected for ingrowth since emplacement and then recalculated to a present day mantle composition assuming chondritic evolution. NA picrites with <0.5 ng/g Os have been omitted due to potential crustal contamination. A 'bandwidth' uncertainty of 0.001 was applied to the $^{187}Os/^{188}Os$ ratio of all samples (~0.8% relative uncertainty). Data sources: [1] This study, Schaefer et al. (2000) and Kent et al. (2004), [2] Pearson et al. (2007) and Shi et al. (2007), [3] Walker et al. (2002b; * average (intermittent dashed grey line) from the authors' regression using $^{187}Os/^{188}Os$ vs. time), [4] Roy-Barman and Allegre (1994), Snow and Reisberg (1995), Brandon et al. (2000) and Harvey et al. (2006), [5] Gannoun et al. (2007), [6] global OIB data from samples with >30 pg/g Os from: Martin (1991), Hauri and Hart (1993), Reisberg et al. (1993), Martin et al. (1994), Marcantonio et al. (1995), Bennett et al. (1996), Hauri et al. (1996), Widom and Shirey (1996), Widom et al. (1999). EC, OC and CC are enstatite, ordinary and carbonaceous chondrites, respectively (Walker et al., 2002a), PUM is primitive upper mantle (Meisel et al., 2001).

radiogenic with $^{187}Os/^{188}Os$ ratios up to 0.148 (Gannoun et al., 2007). This probably reflects preferential sampling of enriched components and/or ^{187}Os-rich metasomatic sulphides within the DMM, by MORB melts of smaller degree than the NA picrites (e.g. Alard et al., 2005; Escrig et al., 2005). If such enriched components are present in the initial NA picrite source (as suggested by the Nd isotope data), their Os isotope signature is greatly diluted compared to the contribution from depleted peridotite.

5.5. Implications for high $^{3}He/^{4}He$ in the mantle

Based on the possibility of greater compatibility of He than U and Th during mantle melting (Graham et al., 1990; Parman et al., 2005; Heber et al., 2007), it has been proposed that ancient melt depletion will lead to the retention of high $^{3}He/^{4}He$ in the residue, through reduced ingrowth of ^{4}He (Class and Goldstein, 2005; Parman et al., 2005). The timing of this depletion event, for $^{3}He/^{4}He$ as high as 50 R_a, has been variously estimated at 3.7 and 3.1 Ga (Parman, 2007; Porcelli and Elliott, 2008). Preservation of high $^{3}He/^{4}He$ through depletion probably requires a large degree of melting (Parman et al., 2005; Porcelli and Elliott, 2008) and this would likely result in near complete Re depletion. Such Re depletion of the mantle will lead, over time, to $^{187}Os/^{188}Os$ ratios which deviate well below the chondrite evolution curve. Thus, in contrast to the broadly chondritic $^{187}Os/^{188}Os$ of the NA picrites, a source entirely depleted in Re at 3.7 or 3.1 Ga (T_{RD}), and subsequently isolated, would have $^{187}Os/^{188}Os$ of ~0.102 or ~0.107, respectively. Even partial Re depletion of the source at these ages would reduce $^{187}Os/^{188}Os$ evolution to between 0.113 and 0.115 (if Re was reduced to 0.12 ng/g, equal to an estimate of the DMM (Sun et al., 2003), Fig. 6). The lowest initial $^{187}Os/^{188}Os$ for the NA picrites corresponds to a T_{RD} of only ~0.4 Ga, and therefore Os isotopes are not consistent with ancient depletion as a mechanism for the preservation of the highest known mantle $^{3}He/^{4}He$ ratios. Equally, mixing of high $^{3}He/^{4}He$ depleted mantle and DMM entrained in the plume, cannot explain the range of $^{3}He/^{4}He$ at a near constant $^{187}Os/^{188}Os$ as the former is unlikely to have a sufficiently high He content (Fig. 6, Table 2). Alternative models, such as a sub-continental lithospheric mantle source for the high $^{3}He/^{4}He$ are also not supported by the Os isotope data, because they too demand significantly sub-chondritic $^{187}Os/^{188}Os$ (see Larsen et al., 2003 for WG lithosphere). Furthermore, high $^{3}He/^{4}He$ has not been found in sub-continental mantle xenoliths or melts (Dunai and Baur, 1995; Day et al., 2005). For the NA picrites considered here, only subsequent addition of radiogenic Os, without He, could reconcile the Os data with an ancient depleted source for the high $^{3}He/^{4}He$. Such a specific flux seems unlikely as fluid-mobile or incompatible elements, including both U and Th, and probably He, would also presumably be involved.

The core has been proposed as a possible source of He enriched in ^{3}He (e.g. Macpherson et al., 1998; Porcelli and Halliday, 2001). The proposed partitioning behaviour of Re and Os between the inner and outer core has led to the hypothesis that the outer core possesses supra-chondritic Re/Os ratios (Walker et al., 1995). Based on this model, the approximately chondritic $^{187}Os/^{188}Os$ of high $^{3}He/^{4}He$ NA picrites precludes a bulk contribution from core material, as much less than 1% Fe-rich core input would impart a radiogenic signature due to its much greater Os concentration. However, decoupled transfer of He and Os across the core–mantle boundary, for instance by diffusion, could produce high $^{3}He/^{4}He$ without correspondingly high $^{187}Os/^{188}Os$.

In an attempt to account for the Os–He isotope data, mixing calculations for various possible mantle components have been performed (Fig. 6). However, constraints on He abundances are poor and can be varied in order to better fit the data. We find such flexibility unsatisfactory in that it leads to non-uniquely constrained models, thus we have cautious conclusions from our modelling. Furthermore, such modelling implicitly assumes that source contributions of He and Os are coupled, while the parameters are not sufficiently constrained to allow assessment of this assumption.

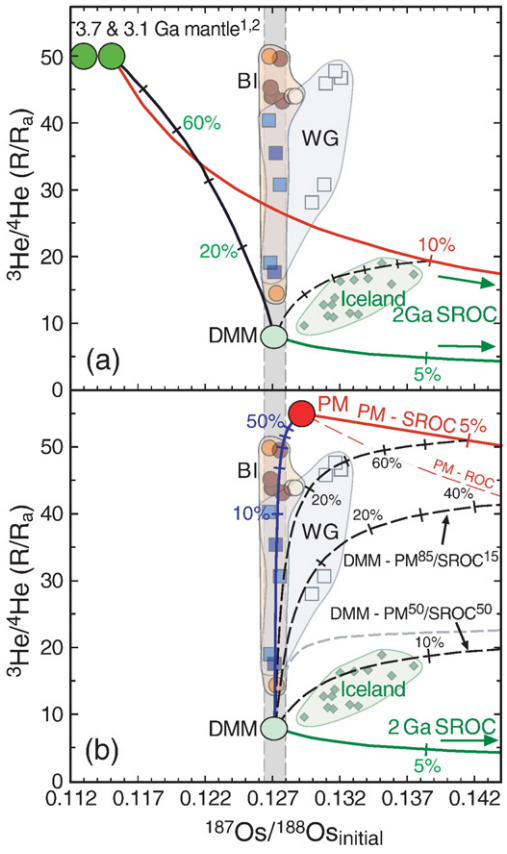

Fig. 6. He isotope composition against $^{187}Os/^{188}Os$ at the time of eruption (61 Ma) for NA picrites (this study, He data from Graham et al., 1998; Stuart et al., 2003; Starkey et al., 2009) and recent Icelandic picrites (Brandon et al., 2007). Symbols: see Fig. 1. (a) Mixing of isolated depleted 3.1 Ga mantle and 2 Ga recycled oceanic crust plus sediment (SROC, ROC:sediment 90:10) and mixing of this hybrid with DMM. Isolated depleted mantle compositions are based on the He evolution models of [1] Parman (2007), [2] Porcelli and Elliott (2008) and Os isotope evolution assuming a residual [Re] of 0.12 ng/g, similar to an estimate for the DMM (Sun et al., 2003). As relatively high degree melting is required to generate sufficiently high $^{3}He/^{4}He$ depleted domains (Parman et al., 2005; Porcelli and Elliott, 2008) such a Re content, and therefore the evolved $^{187}Os/^{188}Os$, is considered an upper limit. (b) Mixing of primitive mantle, DMM, SROC (ROC:sediment 90:10), and PM/SROC hybrid (superscript numbers refer to the relative proportions in the hybrid). Parameters: see Table 2. Note that there are poor constraints on all He concentrations, and Re–Os abundances in ancient recycled sediment are likely to be extremely heterogeneous. Grey dashed curve in (b) is DMM – $PM^{50}/SROC^{50}$ mixing modelled with a DMM [He] of 0.269 μcm^3(STP)/g used in Brandon et al. (2007).

Mixing between DMM and a subsidiary primitive mantle component (up to 25% in this model) can broadly explain the Os–He array for the picrites with constant, approximately chondritic $^{187}Os/^{188}Os$ (Fig. 6). A primitive high $^{3}He/^{4}He$ source of >50 with sufficient He, would permit a small contribution derived from 2 Ga recycled oceanic crust, while retaining $^{3}He/^{4}He$ of >45 as observed in some WG Ordlingassoq picrites (also proposed for Iceland, Brandon et al., 2007). However, the difference in He concentration between a proposed primitive mantle-recycled oceanic crust end-member and DMM gives rise to convex-up mixing curves which means that Ordlingassoq samples require unique proportions of primitive mantle, recycled oceanic crust and DMM, rather than variable contributions along a single mixing line. Convex-up mixing lines are also problematic for the quasi-linear Icelandic array, although use of a higher He concentration for the DMM than that used by Brandon et al. (2007) (Table 2), generates mixing lines that more closely approach linearity (Fig. 6). Mixing of DMM, PM and recycled oceanic crust plus sediment can also broadly explain the NA and Iceland picrite Os–Nd variations

(Fig. 4), but such mixing requires somewhat different component proportions in Os–He and Os–Nd isotope space and does not easily account for each individual sample.

It has been proposed that a high $^3He/^4He$ component could be widespread in the upper mantle (Meibom et al., 2003), and such a component with MORB-like $^{187}Os/^{188}Os$ of ~0.1276 cannot be ruled out on the basis of these data, as long as it contains sufficient He to retain high $^3He/^4He$ despite mixing of a minor recycled oceanic crust component. However, while the mechanisms for such a scenario are not well understood, it seems unlikely that this material would only be sampled during episodes of large degree melting of hot mantle (as opposed to MORB melting) and even if so, that it would not also impart an ancient depleted Os isotope signature, complementary to the unradiogenic high $^3He/^4He$ signature.

Given that high $^3He/^4He$ ratios (>45) in NA picrites are not restricted to samples with a specific Os isotope signature and mixing models do not satisfactorily explain isotope co-variations in detail, it seems most likely that Os and He are decoupled (and Nd–He, Starkey et al., 2009). Diffusion or mixing of high $^3He/^4He$ from a He-rich primordial reservoir could impart the necessary He signature without significantly changing the previously established Os and Nd isotope heterogeneity. Constraining the ultimate source of this high $^3He/^4He$ component is difficult, but as it was tapped most efficiently during melting of a plume-head and persists in Icelandic volcanism today, it seems most plausible that it diffused across, or was entrained at, a deep boundary layer.

6. Concluding remarks

Osmium concentrations in NA picrites are high for mantle melts (1–1.7 ng/g parental Os content) suggesting complete consumption of sulphide in at least part of the source due to a large degree of melting. This is consistent with previous evaluations of the degree of melting based on MgO-rich olivines: 10–11% for depleted mantle (Herzberg and O'Hara, 2002). Initial Os isotope compositions in the earliest picrite melts from West Greenland (early Vaigat formation) and Baffin Island are uniform and broadly chondritic (mean $^{187}Os/^{188}Os$ = 0.1272 ± 0.0007). In terms of Os isotope mass balance, this initial volcanism cannot contain any significant contribution from the outer core or from old recycled crustal material, as both would impart a radiogenic $^{187}Os/^{188}Os$ signature. In addition, the minimal presence of enriched pyroxenitic components in the source of NA picrites is suggested by various parameters such as Ni content of olivine and bulk-rock TiO_2 content. The absence of enriched components, coupled with a large degree of melting and Nd isotope compositions which are indistinguishable from DMM, means that the average $^{187}Os/^{188}Os$ may reflect the bulk $^{187}Os/^{188}Os$ of convecting mantle. This value (0.1276 when corrected to the present day) is similar to the least radiogenic MORB (e.g. Gannoun et al., 2007) and the most common $^{187}Os/^{188}Os$ ratios found in platinum-group alloys from Tibetan ophiolites (Pearson et al., 2007; Shi et al., 2007). Subsequent melts sampled from the upper Vaigat formation, erupted within 1 Ma of the earliest melts (Storey et al., 1998), possess supra-chondritic initial $^{187}Os/^{188}Os$ ratios of up to 0.1322. Such ratios, also seen in recent Iceland plume melts (Brandon et al., 2007), can be accounted for (though not uniquely) by a greater contribution from recycled oceanic crust.

Models seeking to explain high mantle $^3He/^4He$ ratios by ancient depletion (Class and Goldstein, 2005; Parman, 2007) are not supported by the uniform and largely chondritic $^{187}Os/^{188}Os$ ratios of NA picrites. Ancient melting and isolation would lead to significantly sub-chondritic $^{187}Os/^{188}Os$ in the NA picrite source, which possesses the highest known mantle-derived $^3He/^4He$ ratios (up to 50 R_a, Stuart et al., 2003). Outer core material would nominally impart radiogenic Os to the plume, and so core material is also not supported as a source of high $^3He/^4He$, unless the mechanism of He transfer to the plume (diffusion?) is decoupled from Os. Therefore, three possible explanations for the high $^3He/^4He$ signature are: (i) it is present in a typical upper mantle source, entrained in the plume-head, but is only tapped during episodes of high-degree melting of hot mantle; (ii) it is derived from a primitive mantle component which has been mixed with recycled oceanic crust and DMM thus broadly explaining the Os, He and Nd isotope variations or, (iii) He is largely decoupled from Os and Nd and is dominated by addition of a He-rich, high $^3He/^4He$ component, probably primordial in nature, without complementary addition of other elements. The difficulties presented above for (i) and (ii) and the fact that high $^3He/^4He$ is not restricted to a source with a particular Os (or Nd) isotope composition make the latter our favoured model, although our data do not identify the ultimate source.

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