Tungsten isotopes as tracers of core–mantle interactions: The influence of subducted sediments

O. Nebel^{a,b,*}, P.Z. Vroon^a, D.F. Wiggers de Vries^a, F.E. Jenner^{b,1}, J.A. Mavrogenes^b

^a Faculty of Earth and Life Sciences, VU University Amsterdam, The Netherlands

^b Research School of Earth Sciences, The Australian National University, Canberra, Australia

Received 25 February 2009; accepted in revised form 7 October 2009; available online 14 October 2009

Abstract

The postulated difference in W isotopic composition of the Earth's core of $\sim 2 \epsilon_W$ units, compared to the bulk silicate earth (BSE) has previously been used to search for evidence of core–mantle interaction (CMI) in ocean island basalts (OIB). The absence of W isotope anomalies has thus been taken as evidence that CMI does not occur. However, the addition of subducted sediment with high W to the sources of OIB could obscure a core signature. This possibility brings into question the utility of W isotopes as tracers for CMI. To accurately consider the effects of sediment addition to mantle sources of OIB with respect to W requires improved constraints on the abundances of W in subducting sediment. Here, we present high-precision W abundance data (and other HFSE) for a suite of sediments from the Banda subduction regime in East Indonesia. Subducting East Indonesian sediments have trace element concentrations that resemble those of average upper continental crust (UCC), making these sediments valuable to consider as typical of subducted sediments. Average W abundances of 2.1 ppm, corrected for carbon content coupled with current models of 0.5% core addition and 1% sediment addition to EM1 or HIMU plume, suggest that a model hybrid source should exhibit values of $\epsilon_W = -0.24$ with ~ 25 ppb W. Prior studies have not reported such low W isotopic compositions or high estimated W concentrations present in the sources of either Hawaiian or French Polynesian lavas, so such large additions of core material to these plume sources seems unlikely. Given these constraints, core contributions to these source, if present, can be no more than $\sim 0.1\%$.

© 2009 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

Our knowledge of the geochemistry and mineralogy of the lower mantle, the core and the core–mantle boundary is limited, and mainly based on seismic interpretations and experiments (cf. review of Lay et al., 2008) that simulate the extreme conditions in these regions (Knittle and Jeanloz, 1991). The remote nature of these two reservoirs make it difficult to investigate interactions between the

outer core and the lowermost mantle (Carlson and Boyet, 2008) and the overall existence of interactions is highly debated (Brandon and Walker, 2005). Previous geochemical investigations of core–mantle interactions (CMI) have focused on ocean island basalts (OIB), derived from mantle plumes that are considered by some to originate deep in the mantle, potentially at the core–mantle boundary. Coupled Pt–Re–Os isotope systematics of OIB has been interpreted as evidence for CMI (Walker et al., 1995; Brandon et al., 1998). However, these interpretations have been challenged (Baker and Jensen, 2004; Brandon and Walker, 2005; Luguet et al., 2008) and definitive evidence is yet to be found.

An alternative to radiogenic $^{187}\text{Os}/^{188}\text{Os}$ and $^{186}\text{Os}/^{188}\text{Os}$ isotope systematics and a promising test to track CMI in OIB is provided by the extinct ^{182}Hf – ^{182}W isotope system.

* Corresponding author. Address: Research School of Earth Sciences, The Australian National University, 0200 ACT, Canberra, Australia. Tel.: +61 2 61253429.

E-mail address: oliver.nebel@anu.edu.au (O. Nebel).

¹ Present address: Institute for Study of the Earth's Interior, Okayama University at Misasa, Japan.

Tungsten is a moderately siderophile element under reducing conditions, whereas Hf is lithophile. The short-lived ^{182}Hf – ^{182}W isotope system (half life of ~ 9 Ma), coupled with the contrasting behaviour of Hf and W during silicate–metal differentiation results in the preferential storage of W in the metal core (~ 500 ppb) over the bulk silicate reservoir (<100 ppb) during core formation, whereas Hf will predominantly reside in the bulk silicate reservoir. Investigations of W isotopes in chondritic meteorites of known age showed a systematic offset of $\sim 2 \epsilon_{\text{W}}$ units relative to the silicate Earth (ϵ_{W} is defined as the deviation in $^{182}\text{W}/^{184}\text{W}$ over the chondritic value times 10,000, Kleine et al., 2002; Yin et al., 2002). This led to the conclusion that the bulk silicate Earth and the metallic core separated prior to final decay of ^{182}Hf , i.e., <5 myrs after solar system formation. As a consequence, the bulk silicate Earth (BSE) evolved to a radiogenic W isotopic composition until final decay of ^{182}Hf , whereas the core remained non-radiogenic (chondritic) in W isotopes. Hence, the BSE exhibits an elevated W isotope composition over the core of $\sim 2 \epsilon_{\text{W}}$ units. Chemical exchange of the outer core with the lower silicate portion of the mantle would potentially result in lower W isotopic compositions in this region compared to the ambient silicate Earth.

Previous investigations of W isotopes in OIB revealed an overall homogeneous, BSE-like W isotopic signature (Scherstén et al., 2004; Takamasa et al., 2009; Willbold et al., 2009), which has been taken as evidence against CMI. Other studies (Brandon and Walker, 2005; Arevalo and McDonough, 2008) have questioned whether CMI can be traced by W isotopic compositions of OIB. In these studies the authors have argued that a third, silicate component, which is possibly subducted material (Willbold et al., 2009), could have dominated the elemental and isotope composition of W in the source, or during ascent of plume material.

An important W-rich material that is subducted is the upper continental crust (Gao et al., 1998; Rudnick and Gao, 2003; Hawkesworth and Kemp, 2006). Because of the extreme enrichment in incompatible elements in upper continental crust (UCC), even the limited addition of UCC components, i.e., continentally derived sediments (McLennan, 2001), to mantle reservoirs could have a large effect on elemental abundances and isotope ratios (Plank and Langmuir, 1998; Rapp et al., 2008). To assess potential interaction between subducted UCC and mantle material, a detailed knowledge of the mixing end-members is required. So far, a limiting factor in investigating the potential effect of subducting sediment on tracing CMI with W isotopes is the poorly constrained abundance of W in subducting sediment (Takamasa et al., 2009). Although subducting ocean floor sediments are generally well mixed, large variations can exist in sediments due to the mixing of terrigenous material with carbonate, volcanoclastics and quartz.

This study aims to address this missing parameter by high-precision determinations of W and other HFSE concentrations in subducting East Indonesian sediment, which constitute a representative suite of UCC (Vroon et al., 1995). Combining our W data for subducting sediment with W data for other global reservoirs, we address the role that this sediment may have on the sources of OIBs, particularly

with respect to detecting potential core–mantle interactions via W isotopes.

1.1. Geological background and analytical procedures

Sediments analysed in this study were sampled in three tracks across the Banda subduction regime (Fig. 1; Vroon et al., 1995). The samples were obtained from eight piston and one box core from the north Australian shelf and the accretionary wedge of the East Sunda-Banda subduction zone. Samples show variable carbon concentrations (Table 1), isotopic systematics, in particular Pb, Sr, and Nd (Vroon et al., 1995; Vroon et al., 2001), and trace element systematics, e.g., Th/Sc. A detailed sample description is listed in Vroon et al. (1995). The change in radiogenic isotope tracer compositions is attributed to mixtures of juvenile island arc-derived debris and evolved crustal components, representing reworked crust from the northern Australian continental platform (dominantly track III), northern and southern New Guinea, and Timor (Tracks I and II). Thorium, U, and Pb concentrations have also been previously analysed using high-precision isotope dilution (Vroon et al., 1995), making this a well-characterized sediment suite. Previous trace element investigations showed that the overall geochemical signatures of these rocks are comparable to upper crustal trace element signatures world-wide (Vroon et al., 1995). Thus, the East Indonesia sediments constitute an ideal sample suite to investigate W abundances in subducting sediment representative of UCC. The behaviour of HFSE and W are geochemically similar, therefore HFSE constitute a first order proxy for W in sediments of the UCC. Consequently, in addition to the W, all sediments were analysed for their HFSE abundances, i.e., Zr, Hf, Nb and Ta to test the representative nature of the rocks for UCC.

For the isotope dilution analyses of HFSE including W, approximately 100 mg of each sample was weighed and de-

Fig. 1. Schematic sketch of the sample locality in the Arafura Sea-Banda Sea across the active Banda subduction regime (modified after Vroon et al. (1995)). Samples were collected along three tracks (see Table 1 for details).

Table 1
Concentrations of East Indonesian sediments and JG-2 standard reference material determined with isotope dilution.

Sample	Trough	Track	ppm Zr	ppm Hf	ppm Nb	ppm Ta	ppm W	ppm Lu	ppm U ^a	ppm Th ^a	CaCO ₃ wt.% ^a	org. C wt.% ^a
G5-1-2P	Banda Sea	I	88.85	2.502	7.11	0.4973	1.741	0.3036	0.26	9.25	13	1.02
G5-2-24B	Seram	I	185.7	5.267	12.4	0.8849	2.140	0.5411	2.64	12.3	0	0.72
G5-2-56P	Seram	I	156.7	4.347	10.6	0.7087	1.988	0.3619	3.30	11.3	8.6	1.32
G5-4-69P	Aru	II	239.3	6.371	10.1	0.7129	1.550	0.3310	3.32	11.7	8.8	1.19
G5-4-79P	Aru	II	139.1	4.007	12.1	0.8434	1.862	0.3603	4.03	10.9	8.2	1.02
G5-4-85P	Aru	II	119.5	3.460	9.92	0.6406	1.611	0.3340	5.15	10.4	15	1.40
G5-4-106P	Aru	II	143.4	4.091	11.2	0.7879	2.016	0.4091	4.58	9.59	2.3	0.96
G5-6-145P	Timor	III	109.7	3.100	12.7	0.6931	1.664	0.3455	3.50	8.98	1.6	0.38
G5-6-149P2	Timor	III	85.29	2.435	7.69	0.5060	1.268	0.2627	4.98	7.73	32.5	1.00
G5-6-157B	Timor	III	94.50	2.695	6.62	0.4954	1.084	0.2259	6.16	8.07	37.7	0.98
Average	–	–	136.2	3.830	10.05	0.6800	1.690	0.3500	3.79	10.02	–	–
σ UCC ^b	–	–	193.0	5.300	12.00	0.9000	1.900	0.3100	2.70	10.5	–	–
<i>Standard reference material JG2 (granite from the Geological survey of Japan)</i>												
JG2-1	–	–	124.5	5.854	17.9	2.269	23.7	1.284	–	–	–	–
JG2-2	–	–	88.95	4.227	16.9	2.004	22.5	1.196	–	–	–	–
JG2-3	–	–	125.3	5.885	16.5	2.093	24.5	1.232	–	–	–	–
JG2-4	–	–	107.9	4.984	16.7	1.961	22.0	1.321	–	–	–	–
JG2-5	–	–	113.5	5.445	18.6	2.095	24.1	1.248	–	–	–	–
JG2-6	–	–	109.3	5.016	17.3	1.998	25.0	1.289	–	–	–	–
JG2 ^c	–	–	97.6	4.73	14.7	2.76	23	1.22	–	–	–	–
JG2 ^d	–	–	82.6–114	2.51–5.81	12–18	1.9–2.6	29.6	0.92–1.96	–	–	–	–

Note that the reproducibility for granitic samples can be slightly worse due to sample inhomogeneity.

^a Data from Vroon et al. (1995).

^b Average upper continental crust values from Rudnick and Gao (2003).

^c Recommended by the Geological Survey of Japan.

^d Ranges of published values to be found under <http://georem.mpch-mainz.gwdg.de/>.

carbonated in 3 ml Savillex vials using 1 M HNO₃ and then dried. Samples were then covered in a HF–HNO₃ acid mixture and doped with a ⁹⁴Zr–¹⁷⁶Lu–¹⁷⁸Hf–¹⁸⁰Ta mixed spike and a ¹⁸³W enriched isotope tracer. All acids used in the analytical procedures were Teflon distilled. Samples were first placed on a hotplate at 130 °C for 1 day. After evaporation, concentrated HF–HNO₃ was added to each sample and the vials were placed inside Parr Teflon high-pressure autoclaves and heated to 200 °C for 3 days. Afterwards, the samples were dried and nitrated with concentrated HNO₃ to break calcium bonds until a clear solution was achieved. Finally, all samples were dried and equilibrated with HCl for chemical purification. Chromatographic extraction of HFSE and W were performed through a two-column chemistry using Eichrom Ln-resin and Biorad AG X-8 anion resin. Isotope dilution analyses follow the procedures of Münker et al. (2001) and Kleine et al. (2004). Isotope dilution analyses were performed on a ThermoFinnigan Neptune MC-ICPMS in Amsterdam. A detailed description of the chemical separation and mass spectrometric procedures, and additional international rock reference materials are given in Nebel et al. (2009). Analytical reproducibility (2 SD) for concentrations of HFSE are ±0.2% for Zr and Hf, ±1% for Ta and W, and ~±5% for the mono-isotopic Nb (calculated from Zr/Nb, after (Weyer et al., 2002). Analytical blanks were below a blank sample ratio of 1/1000, and thus negligible. Hafnium isotope analyses were carried out on a Finnigan Neptune MC-ICPMS in Amsterdam. Details of the instrumental set-

up and the analytical protocol are given in Morel et al. (2008) and Nebel et al. (2009). During the course of the study the in-house working standard solution (VU-01), which is isotopically indistinguishable from JMC-475, yield a ¹⁷⁶Hf/¹⁷⁷Hf = 0.282158 ± 9. Accordingly, all analysed samples were normalised to a ¹⁷⁶Hf/¹⁷⁷Hf value of 0.282160.

2. RESULTS

Results of the isotope dilution analyses of HFSE and W are listed in Table 1. A comparison with the best estimates of the HFSE, U, Th, and W in the upper continental crust (Rudnick and Gao, 2003; Fig. 2A and B) shows that the East Indonesian sediments exhibit slightly lower abundances for Zr–Hf–Nb–Ta and W, equal amounts of Th and elevated concentrations for U. Despite lower absolute abundances, there is only minor variation in the geochemically similar element pairs Nb/Ta (14.65 ± 0.86 , $r^2 = 0.995$, excluding one outlier) and Zr/Hf (35.38 ± 0.60 , $r^2 = 0.967$, Fig. 3A and B), and these ratios are in agreement with global UCC values (Fig. 2B, Rudnick and Gao, 2003; Hu and Gao, 2008).

The Hf isotopic composition of the samples analysed for this contribution show a strong crustal component with ε_{Hf} values ranging from –3.4 to –16.8 (Table 2). This finding is in agreement with previous radiogenic isotopic investigation of Sr, Pb and Nd isotopes for these sediments (Vroon et al., 1995). Although the sediments were sampled along

Fig. 2. (A) Average element concentration in the East Indonesian sediments normalised to primitive mantle (PM, dashed line). PM values for Zr, Hf, Nb, and U are from Hofmann (1988), Ta abundance is calculated from Nb abundances and an assumed Nb/Ta of 15, W from Arevalo and McDonough (2008). Zr–Hf, Nb–Ta, and W–Th exhibit similar abundances reflecting similar behaviours during crustal formation, U appears to be enriched compared to Th and W; (B) Nb/Ta vs. Zr/Hf of the sediments in comparison with global reservoirs (after Pfänder et al., 2007) showing the general overlap with continental crust.

three different tracks in the fore-arc front of the Banda subduction regime, with only limited influence of continental crust in the northern portion (Track I) and a much stronger input of continental debris from Australia in the South (Track II and III), most Hf isotopic compositions cluster in a narrow range between -3.4 and $-9.2 \epsilon_{\text{Hf}}$. Ergo, there is little or no variation in sedimentary Hf and Nd isotopic composition along the arc. In addition, there is no correlation between elemental concentrations between coarser arc-derived debris, and fine-grained continentally derived material. In a Hf–Nd isotopic co-variation diagram (Fig. 4), the samples plot in the centre of the field for continental crust and cluster around the terrestrial array, defined by global sediments (Vervoort et al., 1999).

2.1. Th, W and U abundance in the East Indonesian sediments

Very few high-precision W and HFSE concentration data are available for sediments (Takamasa et al., 2009). To assess if the East Indonesian sediments are representative of global sediments the abundances and geochemical

behaviour of HFSE, W, Th and U were compared with each other to investigate systematic variations. Tungsten, Th, and U show similar geochemical behaviour during igneous processes (i.e., partial melting and fractional crystallization) and are used here to assess decoupling during sedimentary processes. As expected, W and Th concentrations in the sediments show a broad positive correlation, with an average Th/W = 5.81 (Fig. 3D), in the range of typical UCC (Rudnick and Gao, 2003). In contrast, W and U are negatively correlated (Fig. 3C), which is contrary to the positive correlation observed in igneous rock suites (Newson et al., 1996; Arevalo and McDonough, 2008).

It is unclear how W-rich carbonates are, but their enrichment in U is clearly established (Jones et al., 1995; Ortega et al., 2005). This can potentially account for the decoupling of W from U in the East Indonesian sediments. Niobium–uranium correlations of global reservoirs are well constrained (Sun et al., 2008), and Nb is incompatible in sedimentary carbonates, therefore we use the Nb/U of the Indonesian sediments to monitor variations in U concentrations with increasing carbon content (sum of CaCO_3 and organic carbon) of the Indonesian sediments (Fig. 5).

The Nb/U of the East Indonesian sediments decreases with increasing carbonate content, in agreement with the UCC Nb/U at ~ 0 wt.% carbon content (Fig. 5A). This correlation demonstrates that the proportion of carbonate controls the Nb/U of the sediment. In contrast, the concentration of W decreases with increasing carbon content (Fig. 5B). It is important to correct for this ‘dilution effect’ because (i) carbonate-free rocks represent the majority of the UCC, and (ii) during subduction of the sediments, decarbonisation with progressive depth of the slab will mask the dilution effect of surface exposed sediments. The intercept of W at a carbon content of 0 is 2.1 ppm (i.e., the average abundance of W in the silicate portion of the rocks). This value is slightly higher than the average calculated W abundance of 1.7 ppm for the East Indonesian sediments (without correcting for the carbon concentrations), and the concentration determined from global loess (1.5 ppm, (Taylor et al., 1983). Similarly, the slightly lower concentrations of other HFSE in the Indonesian sediments compared to the UCC (Rudnick and Gao, 2003) is also attributable to the dilution by carbonate. To circumvent the effects of carbonate contribution to the U/W, we initially chose the Th/W (Fig. 5C) and the W concentrations corrected for the carbonate dilution effect for investigating the effects of sediment contribution via subduction into the mantle.

3. DISCUSSION

Scherstén et al. (2004) were the first to search for variable (non-radiogenic) W isotope compositions in a series of OIB from the Hawaii Emperor Seamount chain, in order to test if core material contributed to the source of the Hawaiian basalts. All analysed rocks exhibited uniform, BSE-like W isotopic signatures, which is at odds with CMI in the source of the Hawaiian magmas. However, the study by Scherstén and co-workers was based on the assumption that the Earth’s core and lower mantle form a

Fig. 3. Correlation of selective element pairs (in ppm) from the East Indonesian sediments analysed in this study. The r^2 reflects the correlation coefficient of the best-fit line. Mean ratios give the weighted average of the sample suite. Samples in grey are excluded for r^2 calculation. Notably, U and W are anti-correlated, in disagreement with their suggested behaviour.

Table 2

Hafnium isotope composition of the East Indonesian sediments and JG-2 standard reference material.

Sample	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf} \pm 2\text{SE}$	$^{143}\text{Nd}/^{144}\text{Nd}^a$	ϵ_{Nd}^a	ϵ_{Hf}	$T_{\text{DM}} (\text{Hf})$
G5-1-2P	0.01664	0.282670 (4)	0.512257	-7.4	-3.6	1370
G5-2-24B	0.01409	0.282572 (4)	0.512172	-9.1	-7.1	1441
G5-2-56P	0.01142	0.282513 (5)	0.512151	-9.5	-9.2	1413
G5-2-69P	0.007125	0.282298 (5)	0.512058	-11.3	-16.8	1583
G5-4-79P	0.01234	0.282590 (3)	0.512138	-9.8	-6.4	1306
G5-4-85P	0.01324	0.282607 (5)	0.512158	-9.4	-5.8	1318
G5-4-106B	0.01372	0.282646 (4)	0.512167	-9.2	-4.4	1258
G5-6-145P	0.01529	0.282675 (4)	0.512192	-8.7	-3.4	1278
G5-6-149P2	0.01480	0.282588 (4)	0.512128	-9.9	-6.5	1448
G5-6-157P	0.01150	0.282395 (3)	0.511959	-13.2	-13.3	1649
<i>Standard reference material (JG-2 Granite Std., Geological survey of Japan)</i>						
JG2-1	0.03009	0.282558 (4)	—	—	-7.6	—
JG2-2	0.03882	0.282550 (5)	—	—	-7.8	—
JG2-3	0.02872	0.282559 (5)	—	—	-7.5	—
JG2-4	0.03635	0.282555 (5)	—	—	-7.7	—
JG2-5	0.03144	0.282560 (5)	—	—	-7.5	—
JG2-6	0.03525	0.282546 (3)	—	—	-8.0	—
Average	0.0327	0.282554 (4)	—	—	-7.7	—

2SE is the in-run precision of the individual analysis and refers to the 6th significant digit; chondritic values for the epsilon notation after Jacobsen and Wasserburg (1980) for Nd, and Blichert-Toft and Albarède (1997) for Hf. Depleted mantle (DM) model ages in Ma, value for model age calculation after Vervoort and Blichert-Toft (1999). The average for JG2 is the weighted average of all six analyses using a Lu/Hf of $\pm 1\%$ and a $^{176}\text{Hf}/^{177}\text{Hf}$ of ± 0.000014 .

^a Neodymium data from Vroon et al. (1995).

simple two-component mixture. In contrast to this assumption, most OIB sample a source that experienced contamination with a (presumably old) crustal component. For example, radiogenic isotopic tracers (e.g., Pb, or Sr) can be used to demonstrate that the source of OIB end-members (enriched mantle one and two, EM1, EM2), such as

the Hawaiian (EM1) or the Samoan Plume (EM2), have been enriched by contributions from recycled crustal components (Hawkesworth et al., 1979; Cohen and Onions, 1982; Weaver, 1991; Hofmann, 1997; Hoffman, 2003; Jackson et al., 2007). Based on O isotope investigations, the amount of subducted sediment in the source of EM2 OIBs

Fig. 4. Hafnium–Neodymium isotope correlation (expressed in the epsilon notation defined as the deviation from the chondritic reservoir times 10,000). The gray line shows the terrestrial array as defined by analyses of global occurring rocks (Vervoort et al., 1999).

might be as high as 6%, whereas EM1 and HIMU sources may contain $\sim 1\%$ (Eiler et al., 1997) of subducted sediment. Because W is strongly depleted in the lower mantle compared to Earth's core with a $[W]_{\text{core}}/[W]_{\text{lower mantle}}$ of >20 (Arevalo and McDonough, 2008), even small amounts of core contribution, on the order of 0.5% (Brandon et al., 1998) should be evident from W isotopes. However, the overall high abundance of W in the UCC (>1 ppm) is suggestive of addition of reworked, subducted UCC to the source of OIB with respect to W isotopes. All attempts so far have failed to show W isotope anomalies in the OIB source, which has been interpreted as evidence against core mantle interaction (e.g., Scherstén et al., 2004). However, the mixing of W-rich sediments to OIB source regions may mask a subtle core signature such as depleted $^{182}\text{W}/^{184}\text{W}$ relative to the BSE, and may account for elevated W concentrations in the source of OIB as well. Hence, the possible influence of a sediment component on the W budget in OIB is assessed here.

3.1. Tungsten loss in sediments during subduction zone processes?

Before the effect of sediment contamination on OIB sources can be evaluated, the potential reflux of sedimentary W during the subduction process needs to be established. Tungsten and Th have similar (within 10%) partition coefficients (K_D) during partial melting of the mantle (Münker et al., 2007). Consequently, Th/W of a broad range of terrestrial rocks (Newsom et al., 1996; Arevalo and McDonough, 2008) show only minor variations, including island arc basalts (IAB). However, rock types representing major global silicate reservoirs such as IAB or mid ocean ridge basalts (MORB) span a range in Th/W (~ 2 – 12), independent of the degree of melting or differentiation (Arevalo and McDonough, 2008). Thus, decoupling of both elements (exceeding 10% variation) occurs in different tectonic environments. Under oxidizing conditions in silicate reservoirs, W behaves similar to other highly incompatible elements, such as Th, U or Ba (Newsom et al., 1996; Arevalo and McDonough, 2008). In contrast to large ion lithophile elements (e.g., Ba), W and Th are considered to be immobile during fluid-transport and dehydration in subduction zones. However, recent investigations of Th/W systematics in subduction-related settings have revealed a potential decoupling of Th and W due to small differences in their mobility in slab-derived fluids (König et al., 2008). Thus, Th/W is a potential tracer of fluid mobility in subduction zones, which may in turn influence the re-mixing budget of recycled/subducted W back into the mantle reservoir (see discussion in Ireland et al., 2009).

Although there is a narrow range in Th/W for most igneous rocks, the absolute abundances of these elements show large variations, resulting from the overall low $^{182}\text{W}/^{184}\text{W}$ of both elements during melting. The continental crust and the depleted mantle show large differences in their W abundances with average concentrations in the continental crust of ~ 1 – 2 ppm (Rudnick and Gao, 2003), compared to the depleted mantle reservoir of ~ 0.003 ppm (Arevalo and McDonough, 2008). Therefore, comparison of absolute W concentrations in arc rocks coupled with Th/W may consti-

Fig. 5. Nb/U, concentrations and Th/W vs. total C content of the samples. (A) Reflects the deviation towards lower Nb/U due to high U contents in carbonates and organic carbon. An intercept though the data with zero carbon contents overlaps with the Nb/U value for UCC given in (Sun et al., 2008). (B) Shows the opposite effect for W, indicating the lithophile nature of W, and a 'dilution' effect with increasing C content. (C) Demonstrates that Th/W are not affected by the 'carbon dilution effect'.

tute a valuable indicator of the extent of W mobility in slab-derived fluids and the effect this has on the W budget of subducting sediment.

To assess if W is mobilised during subduction in global island arc systems, Th/W vs. W concentrations and Sr/Nd vs. W/Nb for a global range of island arc rocks were plotted ($n = 270$, GEOROC database, ICPMS and ID data only). As expected from the similar behaviour of Th and W during differentiation, most of the igneous rocks plot in a range of Th/W between around zero and 12, with a few outliers exceeding Th/W = 12 (not shown). Variations in W concentrations show no correlation with Th/W. To investigate the effect of sediment subduction on the distribution, rocks were subdivided into Th/La < 0.18, and > 0.18 (cf. Plank, 2005) with the latter indicating elevated sediment contribution to the arc rocks. Rocks with Th/La ≥ 0.18 have the highest W abundance, which may have resulted from the preferential loss of W from the subducting sedimentary pile (Fig. 6A). The samples with the high Th/La also have elevated W/Nb (Fig. 6B), which can account for preferential loss of the incompatible W during partial sediment melting. The majority of rocks with elevated Sr/Nd (indicative of dehydration) show low W concentration and low W/Nb. This indicates that W is predominantly fluid-immobile during dehydration of subducting components, whereas it is

incompatible (mobile) during melting of subducted sediment. Thus, some W might be mobilised by melting of sediment but the majority of W is retained in the subducting sediment.

It is worth noting that W concentrations in most IAB, in particular those with Th/La < 0.18, are higher than those observed in MORB (<100 ppb W) by a factor of 2–3. However, because the overall concentrations of W are generally less than ~300 ppb in arc rocks, the loss of W by fluid mobility during slab dehydration appears to be negligible as the W concentration in the sediments are often >2000 ppb. This may reflect variable degrees of melting between MORB ($F = 0.15$) and IAB ($F = < 0.1$), with respect to the incompatible nature of W during melting.

An alternate way to constrain the mobility of W during dehydration of subducted sediments is to investigate the behaviour of W in fluids (Ireland et al., 2009). For example, the concentration of W in groundwaters (<100 °C) that are percolating through Icelandic basaltic rocks increase with increasing water temperatures (Arnorsson and Oskarsson, 2007). Notably, W concentrations in these fluids hardly exceed 20 ppb. In contrast, high-temperature (up to 360 °C) fluid veins in samples collected from the ocean floor show W concentrations ranging from ppt levels to <10 ppb W (Kishida et al., 2004). Overall, increasing W with increasing temperature possibly indicates an enhanced fluid mobility of W with increasing temperature. However, the overall low concentrations of W in these fluids compared to concentration in arc rocks do not support significant W transport by dehydration. Although slab-surface sub-solidus temperatures reach ~600–800 °C, well in excess of the aforementioned studies, the temperature versus W concentration correlations do not support mobility of W, which probably does not exceed 100 ppb in slab-derived fluids.

Because W concentrations in most IAB are <200 ppb W (Fig. 6A), we suggest that only a small proportion of the W in erupted rocks was carried in slab fluids. The majority of the W in the arc rocks is derived from the mantle wedge during partial melting. The high concentrations of W in subducting sediment, i.e., >2000 ppb (this study) would not be greatly affected by fluid-transport and the associated depletion of W in sediments which would have little effect on the total amount of subducted W that resides in the mantle.

Having said this, sediment melts most likely mobilise W (see Fig. 6). So far, there are no W data available for sediment melting during subduction. Sediment melting may significantly recycle W back to the crust, and deplete W in deeply subducted sediments. This should be taken into account when studying sediment–OIB interactions.

3.2. W–Th–U in global ocean island basalts

Previous studies of W abundances in OIB and the depleted mantle reservoir have focused on W–Th–U elemental co-variations to identify possible heterogeneities (Newsom and Palme, 1984; Newsom et al., 1996; Arevalo and McDonough, 2008). In order to search for W contamination from subducted sediment in OIB, we use a compilation of published W–Th–U data for OIBs (EM1 and HIMU-type,

Fig. 6. Th/W and Sr/Nd vs. ppb W of global IAB, indicating that W is rather fluid immobile, which argues against substantial W loss during dehydration processes in subduction zones. Th/La > 0.18 indicate the presence (and probably melting) of large amounts of subducting sediment (cf. Plank, 2005), which has potentially the largest impact on W mobility in subduction zones. Data source: <http://georoc.mpch-mainz.gwdg.de/georoc/>. GEOROC database. MPI Mainz.

$n = 190$). In Fig. 7 it is shown that global OIB tend towards elevated W concentrations when compared to IAB. This is best explained by low $K_D^{\text{solid-melt}}$ of W during melting coupled with the low degree of melting of OIB. Thus, because different processes are responsible for elevated W concentration in different tectonic settings, we acknowledge that interpretations based on trends of W–Th–U from different global reservoirs need to be treated with caution. However, as indicated in the figure, the majority of OIB have $\text{Th}/\text{W} > 5$ similar to East Indonesian sediments, whereas many of the IAB have $\text{Th}/\text{W} < 5$. Because the Th/W is independent of the degree of melting, this may indicate a mixing of plume and sediment material for some OIB on the basis of this co-variation. Conversely, it can be argued that those OIB that show elevated Th/W significantly higher than the EIS are the least contaminated by sediment. This might be a useful discriminator for sample selection in future studies aiming to identify CMI with W isotopes. A trend similar to Th/W vs. W can be observed in U/W vs. W space. Here EM1-type OIB form a broad mixing line with East Indonesian sediment. Notably, the variations in U/W as observed in the sediments from East Indonesia as a function of carbon content, appears to be minor compared to the overall spread in U/W vs. W observed for global OIB. In summary, we speculate that

Th/W and U/W possibly indicate the addition of sedimentary W to OIB, as argued on the basis of other elements such as stable isotopes of Tl (Nielsen et al., 2006), or Mo (Willbold et al., 2009), or radiogenic Hf isotopes (Blichert-Toft et al., 1999).

3.3. Sediment contamination to ascending plumes

Subducted sediment has ~ 1000 times higher concentrations of W compared to the mantle source of OIBs, and the majority of this sedimentary W is dragged into the mantle. Since there is abundant evidence for a crustal component such as e.g., subducting sediment being admixed to OIB, sedimentary W can have a considerable effect on the W budget of OIB. There is currently no direct evidence for subducted sediment in the OIB source as deep as the core–mantle boundary. In the absence of such deep subduction of sediments, incorporation of sedimentary W from the ambient mantle during plume ascent is the most likely mechanism for contamination. Notably, the residence of sedimentary components in the convecting mantle is not well known. A possible mineral hosting sedimentary derived W in the mantle is (post-) hollandite (Rapp et al., 2008), where W can potentially substitute for Ba or Mn. Alternatively, because W is moderately siderophile under reducing conditions, and because the asthenosphere < 250 km below the surface may be metal saturated (Rohrbach et al., 2007), iron-rich nuggets could be an alternative phase to host subducted W in the mantle. In both cases, the addition of sedimentary W to plumes can potentially obscure W isotope signatures that may point to a core component in OIB (Brandon and Walker, 2005; Arevalo and McDonough, 2008; Takamasa et al., 2009). Possible core contribution to the source of OIB has been constrained to a maximum of $\sim 1\%$ based on Pt–Re–Os isotope systematics, but if it occurs, it is most likely in the range of 0.5% or lower (e.g., Brandon et al., 1999). The new W data on subducting sediments presented here can help to clarify this issue. To investigate the addition of sediment to a hypothetical mantle source that experienced core addition, we modelled mixtures of an OIB source with 0.5% and 1% core addition, and variable amounts of sediment (using the average composition of the East Indonesian sediments (with 5% W loss during subduction resulting in 2 ppm W). In addition to our preferred model, we consider two different W abundances consistent with the potential loss of sedimentary W to subducted sediment melts, or the change in sedimentary composition towards more mafic sediments. A composition of 1 ppm of W ($\sim 50\%$ W loss) in the sediment is shown for comparison to establish how these abundances affect W isotopic signatures (Fig. 8).

Importantly, in addition to the effect of sediment contamination on the W isotope composition of OIB, the addition of a crustal component to the mantle source of OIB can also lead to an increase in the W concentration of the OIB, depending on the amount of sediment being added during plume ascent. The best estimate of subducting sediment addition to the OIB sources is in the range of 1% for most OIB types based on O isotopes, except for the EM2 OIB component with up to 6% sediment (Eiler et al.,

Fig. 7. Th/W vs. ppb W (A) and U/W vs. ppb W (B) of the East Indonesian sediments (EIS) in comparison with global HIMU and EM1-type OIB (taken from, <http://georoc.mpch-mainz.gwdg.de/georoc/>, the GEOROC database) N-MORB and E-MORB = normal and enriched mid ocean ridge basalts taken from Arevalo and McDonough (2008).

Fig. 8. Effect on W isotope compositions of OIB with sedimentary admixture (in%) (concentrations given in ppm) to a core–mantle mixture with variable core addition (given in%), assuming a difference of $2\epsilon_W$ (defined as the deviation of an isotope composition from the chondritic reservoir times 1000) between core and lower mantle. Composition of the depleted mantle component is 0.003 ppm W, and the core 0.5 ppm (Arevalo and McDonough, 2008). Note that higher W concentrations in the mantle would lower the effect of core contribution. The grey shaded field reflects current estimates of sediment addition to OIB based on O isotopes (Eiler et al., 1997, excluding EM2 with up to 6% sediment contribution). The grey line shows the current external reproducibility of W isotope analyses using state-of-the-art MC-ICPMS, i.e., $\pm 2\epsilon_W$ units. The absence of W isotope anomalies in OIB in the presence of CMI can only be explained by very limited CMI $< 0.1\%$.

1997). The latter extreme is consistent with Sr and Pb isotope mixtures in OIB (e.g., Hoffman, 2003; Jackson et al., 2007). Although there are no data for W concentrations available for EM2-type OIB to date, the sediment component in EM2-type lavas on the order of 4–6% can safely be assumed to mask any core contribution even in the range of the most extreme case of 1% core addition to the lower mantle. For EM1 and/or HIMU OIB with less sediment contamination, concentration estimates for their source has been calculated to be in the range of 2–15 ppb (Hawkesworth and Schersten, 2007; Arevalo and McDonough, 2008; Takamasa et al., 2009). The effect of sediment addition on W concentrations in plume-derived magmas, or their mantle sources, can be significant because of their large differences in W concentrations. Thus, a W isotope composition of a potential core–lower mantle mix that is masked by sedimentary W will also exhibit elevated W abundances, which should be mirrored in W estimates of OIB sources. Thus, in a modelling approach, W abundances need to be in the range of suggested W concentrations for the source of the OIB in order to constitute a reasonable scenario. Conversely, if it is assumed that OIB sources are representative of the lower mantle and have W concentrations of ~ 3 ppb, estimations for W abundances for OIB sources may provide an additional proxy to quantify the amount of sediment contamination.

The relatively low postulated abundances of W in the sources of EM1 and HIMU systems do not necessarily conflict with the assumption of the presence of recycled sediments in these sources. Hawkesworth and Schersten (2007) recalculated the concentration of the host reservoir

of Hawaiian basalts and estimated a concentration of ~ 8 –12 ppb W, which exceeds the recent estimates of depleted mantle W concentration of 3 ppb (Arevalo and McDonough, 2008). Further calculations of W abundances in OIB from French Polynesia (Takamasa et al., 2009) yield OIB source concentrations of 2–15 ppb W. Accordingly, samples with the lowest W concentration may represent a ‘pure’ depleted mantle source. Notably, these estimates potentially host large uncertainties, because the calculations are either based on W concentrations deduced for Th/W and Th concentrations for the Hawaiian basalts, or on low precision W concentration determinations. Furthermore, corrections of fractionation effects and degrees of melting provide further sources of uncertainty. Although assumptions required in the calculations, as e.g., degree of melting, make these values highly imprecise, the overall agreement of reported concentrations (Arevalo and McDonough, 2008; Hawkesworth and Schersten, 2007; Takamasa et al., 2009) of ~ 2 –15 ppb W indicates that for most OIB, this range is probably a reasonable estimate.

3.4. Mixing models for core–lower mantle–sediment end-members

Using an extreme of 1% core addition to the lower mantle (assuming 500 ppb concentration in the core) will result in an increase in W concentration of only 5 ppb from 3 to 8 ppb in the source of OIB. However, the W isotope composition will be lowered to $\epsilon_W = -1.25$, an isotope composition that should be easy to trace in erupting OIB. To alter the isotope signature of the erupting OIB lava by sediment addition towards $\epsilon_W = 0 \pm 0.2$, the addition of 2% sediment is required, elevating the W concentration to 48 ppb. In a more likely scenario, with 0.5% core addition to a lower depleted mantle (yielding a core–mantle mix of 5.5 ppb W and $\epsilon_W = -0.91$), the source W concentration for OIB with 1% sediment addition will be 25 ppb, with a source W isotope composition of $\epsilon_W = -0.19$. Given the reproducibility of W isotopic measurements of $\sim 0.2\epsilon_W$ (± 20 ppm), using state-of-the-art MC-ICPMS, a core contribution is not likely to be resolvable, in agreement with the suggestion of Brandon and Walker (2005). However, the high W concentration for OIB sources almost doubles the estimates for initial OIB sources from Hawaii and French Polynesia, even considering the large uncertainties for these initial concentration estimates. In order to match the approximate W concentration values for OIB sources given in Takamasa et al. (2009) and Arevalo and McDonough (2008) of 2–15 ppb, $\sim 0.5\%$ sediment addition is required and would result in 15.5 ppb W with $\epsilon_W = -0.31$ (or alternatively 50% W loss during subduction, i.e., 1 ppm W in the sediment component). This isotope value, however, should be resolvable by W isotope analyses. To validate the assumption that core–mantle interaction occurs but is masked by sediment addition and to meet the requirements of W isotope signatures $> 0.2\epsilon_W$ and $W < 10$ ppb, our modelling only offers the option of less core material added to the lower mantle. As demonstrated in Fig. 7, CMI need to be on the order of 0.1–0.05% or less.

3.5. Towards tracing core-mantle interactions

Sediment contamination of some OIB may account for some elevated W concentrations, but it is not sufficient to eliminate the W isotope signal resulting from core–mantle interaction of the order of 0.5% core addition. Hence, with the given parameters of our modelling CMI with respect to W isotope signatures needs to be lower than 0.5% in order to explain the absence of W isotope anomalies in OIB. For future investigations tracing possible W core contributions to OIB sources in the per mill range, the investigation of samples with the lowest estimates for source W concentrations of <5–10 ppb are the most promising. This is because sediment contamination can most likely be ruled out for samples with calculated low W concentration (i.e., <10 ppb) in OIB sources based on the high W abundance of subducting sediment and thus high W abundances in an OIB–sediment mix. However, core–mantle mixing with 0.05% core addition to the mantle will only have a minor effect on the overall W abundance (200 ppb elevation) but shifts the W isotope composition to $-0.15 \epsilon_W$ units. To resolve this isotope signal, high-precision analyses in the range of 5–10 ppm reproducibility are required, potentially using the negative TIMS technique (Becker et al., 2007) or more sensitive MC-ICPMS instruments (Willbold et al., 2009). Future studies should ideally be accompanied by additional geochemical proxies such as Pt–Re–Os isotope analyses, or possibly $^3\text{He}/^4\text{He}$. Coupled investigations with other radiogenic isotope tracers may further be used to constrain the presence of a sedimentary component in the OIB.

Notably, the identification of ancient plume material may yet be another possibility, as sediment subduction and reflux to the early mantle may have played a less important role in the Hadean and early Archean eons. Accordingly, W isotope anomalies found in 3.8 Ga old rocks in Greenland may well be remnants of an early plume component with signatures from core–mantle interaction rather than heavy meteorite bombardment (Schoenberg et al., 2002). If this can be confirmed, the presence of CMI in the early Earth may possibly place further constraints on thermodynamics in the core–mantle boundary region.

4. CONCLUSION

From our isotope dilution analyses of HFSE and W on a set of East Indonesian sediments, we draw the following conclusions:

- (i) Tungsten and U are decoupled in sediments with elevated carbonate contents. The carbonate portion creates a dilution effect for W concentrations and other HFSE, whereas U contents are almost doubled for samples that contain a third of carbonate/organic carbon. This might be a useful tracer for future investigations of carbonate–melt–rock interaction studies. Notably, this feature appears not to affect the use of U/W as a tracer for sediment contamination to OIB, such that the U/W is a valuable ratio in studying OIB sources, in agreement with previously suggestions (Arevalo and McDonough, 2008; Ireland et al., 2009)

- (ii) The abundance of W in carbonate-free, subducting East Indonesian sediments as a representative for UCC is 2.1 ppm. Addition of such a deep subducted sediment component, either to the source of HIMU/EM1 OIB or to mantle regions where ascending plume material is in contact with post-sediment phases, can significantly elevate W concentration in OIB. Mixing models show that in a scenario of 1% sediment addition with 2 ppm W and a 0.5% core addition to the plume source, as based on recent models of the core–mantle boundary, the expected source of HIMU/EM1 OIB have 25 ppb W. This value exceeds current estimates, suggesting that sediment contamination of, e.g., Hawaiian OIB is smaller than 1%. Only 0.5% of sediment addition equals 16 ppb W in their source, which is within the range of calculated W abundances. Alternatively, larger amounts of W were lost during subduction (~50%), probably due to sediment melting.
- (iii) Based on the mixing models presented in this contribution and the absence of ^{182}W isotope anomalies in OIB that have been analysed to date, the core addition component to plume sources does not exceed 0.5%, but, if present at all, is more likely in the range of 0.1% or even below. Accordingly, for future investigations on core–mantle interactions using W isotopes, analytical limits of $\sim \pm 0.2 \epsilon_W$ units are probably not sufficient.

ACKNOWLEDGMENTS

O.N. thank Richard Smeets and Bas van der Wagt for keeping the clean lab and the Neptune in Amsterdam in shape. The authors thank Bob Rapp for discussion on subducting sediment, and Yona Nebel-Jacobsen for comments on an early ms version. We kindly acknowledge funding of this study by an NWO (Dutch Science Organisation) grant to P.Z.V. The MC-ICPMS facility at VU University Amsterdam was supported by a Grant (175.107.404.01) from NWO-ALW. Constructive and detailed journal reviews by Thomas Ireland, Ambret Luguët, and an anonymous reviewer are kindly appreciated. Finally, we thank Rich Walker for his editorial handling and comments that helped to improved the clarity of this study.

REFERENCES

- Arevalo R. and McDonough W. F. (2008) Tungsten geochemistry and implications for understanding the Earth's interior. *Earth Planet. Sci. Lett.* **272**, 656–665.
- Arnorsson S. and Oskarsson N. (2007) Molybdenum and tungsten in volcanic rocks and in surface and <100 degrees C ground waters in Iceland. *Geochim. Cosmochim. Acta* **71**, 284–304.
- Baker J. A. and Jensen K. K. (2004) Coupled Os-186–Os-187 enrichments in the Earth's mantle – core–mantle interaction or recycling of ferromanganese crusts and nodules? *Earth Planet. Sci. Lett.* **220**, 277–286.
- Becker H., Brandon A. D. and Walker R. J. (2007) Geochemical tracing of core–mantle interaction: high-precision W isotopic data on komatiites using TIMS. *Geochim. Cosmochim. Acta* **71**–supplement, A71.
- Blichert-Toft J. and Albarède F. (1997) The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle crust system. *Earth Planet. Sci. Lett.* **148**, 243–258.

- Blichert-Toft J., Frey F. A. and Albarede F. (1999) Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts. *Science* **285**, 879–882.
- Brandon A. D., Norman M. D., Walker R. J. and Morgan J. W. (1999) ^{186}Os – ^{187}Os systematics of Hawaiian picrites. *Earth Planet. Sci. Lett.* **174**, 25–42.
- Brandon A. D. and Walker R. J. (2005) The debate over core–mantle interaction. *Earth Planet. Sci. Lett.* **232**, 211–225.
- Brandon A. D., Walker R. J., Morgan J. W., Norman M. D. and Prichard H. M. (1998) Coupled Os-186 and Os-187 evidence for core–mantle interaction. *Science* **280**, 1570–1573.
- Carlson R. W. and Boyet M. (2008) Composition of the Earth's interior: the importance of early events. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **366**, 4077–4103.
- Cohen R. S. and Onions R. K. (1982) Identification of recycled continental material in the mantle from Sr, Nd and Pb isotope investigations. *Earth Planet. Sci. Lett.* **61**, 73–84.
- Eiler J. M., Farley K. A., Valley J. W., Hauri E., Craig H., Hart S. R. and Stolper E. M. (1997) Oxygen isotope variations in ocean island basalt phenocrysts. *Geochim. Cosmochim. Acta* **61**, 2281–2293.
- Gao S., Luo T. C., Zhang B. R., Zhang H. F., Han Y. W., Zhao Z. D. and Hu Y. K. (1998) Chemical composition of the continental crust as revealed by studies in East China. *Geochim. Cosmochim. Acta* **62**, 1959–1975.
- Hawkesworth C. and Schersten A. (2007) Mantle plumes and geochemistry. *Chem. Geol.* **241**, 319–331.
- Hawkesworth C. J. and Kemp A. I. S. (2006) Evolution of the continental crust. *Nature* **443**, 811–817.
- Hawkesworth C. J., Norry M. J., Roddick J. C. and Vollmer R. (1979) Nd-143–Nd-144 and Sr-87–Sr-86 ratios from the azores and their significance in Lil-element enriched mantle. *Nature* **280**, 28–31.
- Hoffman A. W. (2003) Sampling mantle heterogeneity through oceanic basalts: isotopes and trace elements. *Treatise Geochem.* **2**.
- Hofmann A. W. (1988) Chemical differentiation of the Earth – the relationship between mantle, continental-crust, and oceanic-crust. *Earth Planet. Sci. Lett.* **90**, 297–314.
- Hofmann A. W. (1997) Mantle geochemistry: the message from oceanic volcanism. *Nature* **385**, 219–229.
- Hu Z. C. and Gao S. (2008) Upper crustal abundances of trace elements: a revision and update. *Chem. Geol.* **253**, 205–221.
- Ireland T. J., Arevalo, Jr., R., Walker R. J. and McDonough W. F. (2009) Tungsten in Hawaiian picrites: a compositional model for the source of Hawaiian lavas. *Geochim. Cosmochim. Acta* **73**, 4517–4530.
- Jackson M. G., Hart S. R., Koppers A. A. P., Staudigel H., Konter J., Blusztajn J., Kurz M. and Russell J. A. (2007) The return of subducted continental crust in Samoan lavas. *Nature* **448**, 684–687.
- Jacobsen S. B. and Wasserburg G. J. (1980) Sm–Nd isotopic evolution of chondrites. *Earth Planet. Sci. Lett.* **50**, 139–155.
- Jones C. E., Halliday A. N. and Lohmann K. C. (1995) The impact of diagenesis on high-precision U–Pb dating of ancient carbonates – an example from the late Permian of New-Mexico. *Earth Planet. Sci. Lett.* **134**, 409–423.
- Kishida K., Sohrin Y., Okamura K. and Ishibachi J. (2004) Tungsten enriched in submarine hydrothermal fluids. *Earth Planet. Sci. Lett.* **222**, 819–827.
- Kleine T., Mezger K., Palme H. and Münker C. (2004) The W isotope evolution of the bulk silicate Earth: constraints on the timing and mechanisms of core formation and accretion. *Earth Planet. Sci. Lett.* **228**, 109–123.
- Kleine T., Münker C., Mezger K. and Palme H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf–W chronometry. *Nature* **418**, 952–955.
- Knittle E. and Jeanloz R. (1991) Earth's core–mantle boundary – results of experiments at high-pressures and temperatures. *Science* **251**, 1438–1443.
- König S., Münker C., Schuth S. and Garbe-Schönberg D. (2008) Mobility of tungsten in subduction zones. *Earth Planet. Sci. Lett.* **274**, 82–92.
- Lay T., Hernlund J. and Buffett B. A. (2008) Core–mantle boundary heat flow. *Nat. Geosci.* **1**.
- Luguet A., Pearson D. G., Nowell G. M., Dreher S. T., Coggon J. A., Spetsius Z. V. and Parman S. W. (2008) Enriched Pt–Re–Os isotope systematics in plume lavas explained by metasomatic sulfides. *Science* **319**, 453–456.
- McLennan S. M. (2001) Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophys. Geosyst.* **2**, art. no.-2000GC000109.
- Morel M. L. A., Nebel O., Nebel-Jacobsen Y. J., Miller J. S. and Vroon P. Z. (2008) Hafnium isotope characterization of the GJ-1 zircon reference material by solution and laser-ablation MC-ICPMS. *Chem. Geol.* **255**, 231–235.
- Münker C., Paulick H. and König S. (2007) The geochemical behaviour of W, Nb–Ta, and Zr–Hf during mid ocean ridge melting. *Geochim. Cosmochim. Acta* **71**, A696.
- Münker C., Weyer S., Scherer E. E. and Mezger K. (2001) Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICPMS measurements. *Geochemistry Geophys. Geosyst.* **2**. doi:10.1029/2001GC000183.
- Nebel O., Morel M. L. A. and Vroon P. Z. (2009) Isotope dilution analyses of Lu, Hf, Zr, Ta and W, and Hf-isotope compositions of NIST SRM-610 and SRM-612 glass wafers. *Geostandards Geanal. Res.* **33**(4), 446–459.
- Newsom H. E. and Palme H. (1984) The depletion of siderophile elements in the Earth's mantle – new evidence from molybdenum and tungsten. *Earth Planet. Sci. Lett.* **69**, 354–364.
- Newsom H. E., Sims K. W. W., Noll P. D., Jaeger W. L., Maehr S. A. and Beserra T. B. (1996) The depletion of tungsten in the bulk silicate Earth: constraints on core formation. *Geochim. Cosmochim. Acta* **60**, 1155–1169.
- Nielsen S. G., Rehkamper M., Norman M. D., Halliday A. N. and Harrison D. (2006) Thallium isotopic evidence for ferromanganese sediments in the mantle source of Hawaiian basalts. *Nature* **439**, 314–317.
- Ortega R., Maire R., Deves G. and Quinif Y. (2005) High-resolution mapping of uranium and other trace elements in recrystallized aragonite-calcite speleothems from caves in the Pyrenees (France): implication for U-series dating. *Earth Planet. Sci. Lett.* **237**, 911–923.
- Pfänder J. A., Münker C., Stracke A. and Mezger K. (2007) Nb/Ta and Zr/Hf in ocean island basalts – implications for crust–mantle differentiation and the fate of Niobium. *Earth Planet. Sci. Lett.* **254**, 158–172.
- Plank T. (2005) Constraints from thorium/lanthanum on sediment recycling at subduction zones and the evolution of the continents. *J. Petrol.* **46**, 921–944.
- Plank T. and Langmuir C. H. (1998) The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* **145**, 325–394.
- Rapp R. P., Irifune T., Shimizu N., Nishiyama N., Norman M. D. and Inoue J. (2008) Subduction recycling of continental sediments and the origin of geochemically enriched reservoirs in the deep mantle. *Earth Planet. Sci. Lett.* **271**, 14–23.
- Rohrbach A., Ballhaus C., Golla-Schindler U., Ulmer P., Kamenetsky V. S. and Kuzmin D. V. (2007) Metal saturation in the upper mantle. *Nature* **449**, 456–458.

- Rudnick R. L. and Gao S. (2003) The composition of the continental crust. *Treatise Geochem.* **3**, 1–64.
- Scherstén A., Elliott T., Hawkesworth C. and Norman M. (2004) Tungsten isotope evidence that mantle plumes contain no contribution from the Earth's core. *Nature* **427**, 234–237.
- Schoenberg R., Kamber B. S., Collerson K. D. and Moorbath S. (2002) Tungsten isotope evidence from similar to 3.8-Gyr metamorphosed sediments for early meteorite bombardment of the Earth. *Nature* **418**, 403–405.
- Sun W. D., Hu Y. H., Kamenetsky V. S., Eggins S. M., Chen M. and Arculus R. J. (2008) Constancy of Nb/U in the mantle revisited. *Geochim. Cosmochim. Acta* **72**, 3542–3549.
- Takamasa A., Nakai S., Sahoo Y. V., Hanyu T. and Tatsumi Y. (2009) W isotope composition of ocean islands basalts from French Polynesia and their meaning for core–mantle interactions. *Chem. Geol.* **260**, 37–46.
- Taylor S. R., McLennan S. M. and McCulloch M. T. (1983) Geochemistry of loess, continental crustal composition, and crustal model ages. *Geochim. Cosmochim. Acta* **47**, 1897–1905.
- Vervoort J. D. and Blichert-Toft J. (1999) Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. *Geochim. et Cosmochim. Acta* **63**, 533–556.
- Vervoort J. D., Patchett P. J., Blichert-Toft J. and Albarede F. (1999) Relationships between Lu–Hf and Sm–Nd isotopic systems in the global sedimentary system. *Earth Planet. Sci. Lett.* **168**, 79–99.
- Vroon P. Z., Lowry D., Van Bergen M. J., Boyce A. J. and Matthey D. P. (2001) Oxygen isotope systematics of the Banda Arc: low delta O-18 despite involvement of subducted continental material in magma genesis. *Geochim. Cosmochim. Acta* **65**, 589–609.
- Vroon P. Z., Vanbergen M. J., Klaver G. J. and White W. M. (1995) Strontium, neodymium, and lead isotopic and trace-element signatures of the East Indonesian sediments – provenance and implications for Banda Arc magma genesis. *Geochim. Cosmochim. Acta* **59**, 2573–2598.
- Walker R. J., Morgan J. W. and Horan M. F. (1995) Os-187 enrichment in some plumes – evidence for core–mantle interaction. *Science* **269**, 819–822.
- Weaver B. L. (1991) The origin of ocean Island basalt end-member compositions – trace-element and isotopic constraints. *Earth Planet. Sci. Lett.* **104**, 381–397.
- Weyer S., Münker C., Rehkämper M. and Mezger K. (2002) Determination of ultra-low Nb, Ta, Zr and Hf concentrations and the chondritic Zr/Hf and Nb/Ta ratios by isotope dilution analyses with multiple collector ICP-MS. *Chem. Geol.* **187**, 295–313.
- Willbold M., Elliot T. and Archer C. (2009) $\epsilon^{182}\text{W}$ in ocean island basalts and the role of core–mantle interaction Goldschmidt conference. *Geochimica et Cosmochimica Acta*, Suppl. **vol. 73**, Davos, Switzerland, p. A1444.
- Yin Q. Z., Jacobsen S. B., Yamashita K., Blichert-Toft J., Telouk P. and Albarede F. (2002) A short timescale for terrestrial planet formation from Hf–W chronometry of meteorites. *Nature* **418**, 949–952.

Associate editor: Richard J. Walker