



New insights into the origin of O–Hf–Os isotope signatures in arc lavas from Tonga–Kermadec

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ABSTRACT

O, Hf and Os isotope data are presented for lavas from the highly depleted Tonga–Kermadec arc. O isotope values overlap with those of MORB limiting the amount of interaction with the arc crust. $\delta^{18}\text{O}$ does not increase northwards as would be expected from the ~4 fold increase in subduction rate if slab-derived fluids had high $^{18}\text{O}/^{16}\text{O}$ ratios. Thus, the overall northward decrease in HFSE concentrations likely reflects depletion due to prior melt extraction, not increasing extents of melting. Hf isotopes are strongly negatively correlated with Be isotopes consistent with mixing of subducted pelagic sediment into the mantle wedge and do not require Hf to be fluid mobile. With the exception of a boninite from the north Tongan trench, the northern Tonga lavas do not overlap the Hf isotope composition of either the Samoan plume or the subducting Louisville volcanoclastic sediments. Thus, the Pb isotope signatures in these lavas must have been added by fluids and sediment melts derived from the Louisville volcanoclastics with minimal mobilisation of Hf. This suggests conservative behaviour for this element due to the formation of residual zircon during partial melting of the subducted sediments. $^{187}\text{Os}/^{188}\text{Os}$ ranges from 0.1275 to 0.4731 and the higher Os isotope ratios reflect the sensitivity of this system to even minor interaction with altered arc crust. Conversely, the lowest Os ratios are subchondritic and indicate that transfer of radiogenic Os from the slab is not all pervasive and provide an important constraint on the composition of the mantle wedge. Remarkably, the least radiogenic sample is a dacite demonstrating that evolved magmas can develop by fractionation from mantle-derived magmas with minimal interaction with the arc crust.

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1. Introduction

There has long been interest in element recycling at convergent plate margins and isotopes have been widely used to identify their different sources in the down-going plate and mantle wedge. O, Hf and Os have concentrations that range over 6 orders of magnitude in the mantle and exhibit very different geochemical behaviour to each other. Thus, the isotope systems of these elements have the potential to provide insights into oceanic arc magmatism that are not always available from the more commonly used Sr, Nd and Pb isotope systems. However, the origin of O, Hf and Os isotope signatures in arc lavas has been the subject of considerable debate.

O comprises ~50 wt.% of most rocks and minerals and its isotopes afford the opportunity to fingerprint the composition, and thus the source, of the fluids that facilitate mantle melting in this setting, yet the $\delta^{18}\text{O}$ values of the subduction fluid component in most arc lavas are poorly known. If these fluids are derived from subducted sediments or

the upper altered oceanic crust then high $\delta^{18}\text{O}$ values would be expected, but if they originate from the serpentinized interior of the slab, normal to low $\delta^{18}\text{O}$ values are predicted. O isotopes can also provide a means to distinguish between crustal additions that occur via sediment subduction and those that might result from via shallow-level assimilation because the curvature of the resultant mixing curves strongly differ (e.g. Davidson and Harmon, 1989). In a recent study of western Pacific arcs, Eiler et al. (2000) interpreted negative trends between $\delta^{18}\text{O}$ and high field strength elements (HFSE) to indicate that greater amounts of fluid addition lead to larger extents of melting (and thus lower HFSE concentrations) and, hence, that the fluid component had high $\delta^{18}\text{O}$.

Low concentrations of HFSE in arc lavas may equally result from prior depletion of the mantle wedge (e.g. Ewart and Hawkesworth, 1987; Woodhead et al., 1993; Caulfield et al., 2008). This interpretation assumes that these elements are minimally mobilised in fluids from the subducting slab (e.g. Keppler, 1996; Stalder et al., 1998) and thus largely controlled by the composition of the mantle wedge. Accordingly, Pearce et al. (1999, 2007) have employed isotopes of the HFSE Hf, as a unique tracer of the composition of the mantle wedge. In contrast, another study suggested that Hf might be significantly mobilised in subduction

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zone fluids (Woodhead et al., 2001). Therefore, ascertaining the source of elemental Hf in arc lavas remains an important outstanding problem.

In contrast to Hf, Os behaves as a compatible element during mantle melting and the demonstration of slab-derived Os isotope signatures (e.g. Alves et al., 2002) would require very rapid (kyr) melt ascent through the mantle wedge to minimise melt-wall rock interaction (Hauri, 1997; Bourdon et al., 2003). This could provide an independent test of models for rapid channelled melt ascent based on ^{226}Ra isotopes (Turner et al., 2001). However, the Os system is also probably the most

sensitive of all radiogenic isotopes to crustal contamination due to the high Re/Os ratios of the crust and many workers have argued that radiogenic Os isotope signatures reflect interaction with the overlying arc crust, especially in continental settings (Lassiter and Luhr, 2001; Chesley et al., 2002). Thus, there is a need for more Os isotope data from oceanic arc lavas that are less affected by contamination with old crust.

In light of these issues, we present here new O, Hf and Os isotope data from well-characterised samples from the oceanic Tonga–Kermadec arc (Fig. 1). This arc encompasses the largest variation in subduction rates (24

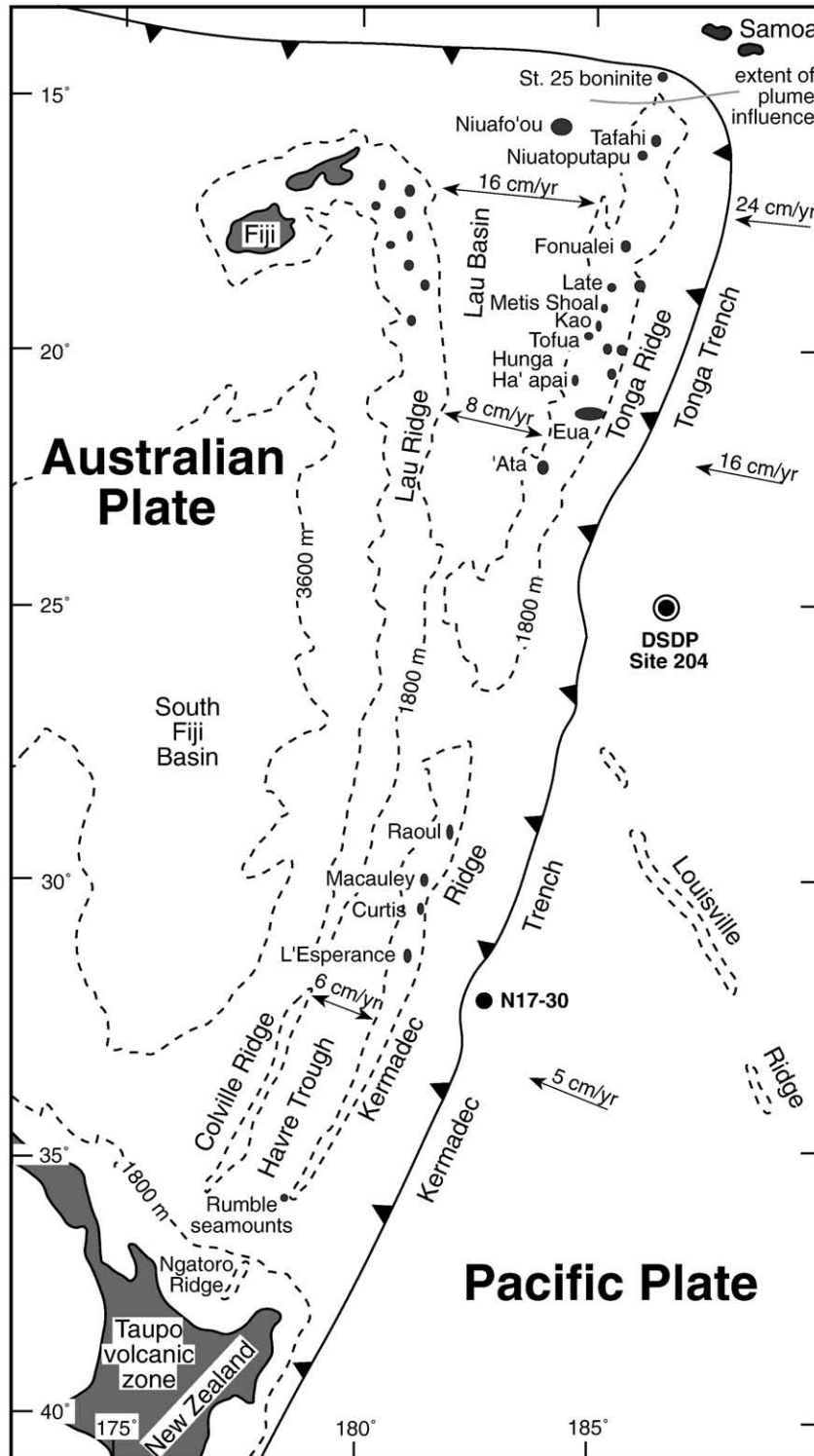


Fig. 1. Map of the Tonga–Kermadec arc showing localities of samples analysed and convergence and back-arc spreading rates from Bevis et al. (1995).

Table 1
Hf-, Os- and O isotope results for Tonga–Kermadec lavas.

Sample #	Location (north to south)	MgO (wt.%)	$\delta^{18}\text{O}$ (plog)	Hf (ng/g)	$^{176}\text{Hf}/^{177}\text{Hf}$	Re (pg/g)	Os (pg/g)	$^{187}\text{Re}/^{188}\text{Os}$	$\pm 2\sigma_m$	$^{187}\text{Os}/^{188}\text{Os}$	$\pm 2\sigma_m$
<i>Lavas</i>											
D7-17	Boninite (Station 25)	12.97	5.65 ^a	1.16	0.282997	233	53.6	20.9	1.1	0.1283	0.0007
T116	Tafahi	6.07	5.91	0.37	0.283257	407	7.2	273	1.5	0.1446	0.0014
NTT25/4	Niutoputapu	3.31	–	0.96	0.283393	504	6.8	358	1.8	0.1624	0.0026
Fon11	Fonualei	1.51	5.88	1.49	0.283201	557	47.0	57.1	0.3	0.1275	0.0005
Fon39	Fonualei	1.54	–	1.55	0.283180 ^b	915	5.4	822	5.6	0.1861	0.0037
Late2	Late	6.29	5.90	0.72	0.283121	97	7.9	59.1	0.1	0.1433	0.0020
26821	Tofua	3.85	5.79	1.20	0.283204	459	3.7	593	4.9	0.1446	0.0014
HHTop	Hunga Ha'apai	4.80	6.21	0.89	0.283210	143	7.6	90.5	0.3	0.1726	0.0043
482-8-12	Ata	6.72	5.92	0.88	0.283189	395	2.7	748	7.1	0.4731	0.0104
14807	Raoul	1.88	5.75	1.97	0.283167	447	2.2	983	12.6	0.3026	0.0074
45653	Macauley	5.45	5.93	1.06	0.283142	371	2.3	800	5.2	0.3133	0.0141
14868	Curtis	0.93	5.98	2.98	0.283150	327	3.6	444	5.3	0.2324	0.0050
37486	L'Esperance Rock	4.94	5.76	1.26	0.283135	770	2.2	1720	24.8	0.2271	0.0042
<i>Sediments</i>											
204 9-1 108-110	Louisville volcanoclastic	13.58	–	5.49	0.283024	35.7	251	0.690	0.002	0.1357	0.0004
204 4-1 75-76	Pelagic	2.91	–	3.66	0.282969	58.4	74.9	3.822	0.007	0.2565	0.0014

^a Calculated as $\delta^{18}\text{O}$ olivine + 0.5.^b Data from Hergt and Woodhead (2007).

to 6 cm/yr) worldwide (Bevis et al., 1995) and affords the opportunity to provide new insights into the debates outlined above because it erupts lavas which carry (1) a strong trace element (e.g. high Ba/Th, Sr/Th) fluid signature (Ewart et al., 1998; Turner et al., 2003), (2) very low HFSE concentrations indicative of a depleted wedge that is highly sensitive to slab contributions (Ewart and Hawkesworth, 1987; Caulfield et al., 2008), (3) ^{226}Ra evidence for rapid melt transport (Turner et al., 2000), (4) ^{10}Be evidence for pelagic sediment addition (George et al., 2005), and (5) a unique tracer of subducted sediment in the Louisville volcanoclastics (Regelous et al., 1997; Turner and Hawkesworth, 1997; Wendt et al., 1997).

2. Samples and analytical methods

The samples analysed include fresh basaltic-andesites, andesites and dacites containing 10–20% clinopyroxene and plagioclase phenocrysts as well as two representative subducted sediments from DSDP Site 204 (pelagic and Louisville volcanoclastic sediments). Locations are shown in Fig. 1 and full geochemical, radiogenic, short-lived and cosmogenic isotope data for these samples have been presented elsewhere (e.g. Turner and Hawkesworth, 1997; Turner et al., 2001; George et al., 2005). Also included is a boninite from the far north of the Tonga arc (see Fig. 1) that has been well characterised by Falloon and Crawford (1991, and references therein).

$^{18}\text{O}/^{16}\text{O}$ data were obtained on ~1 mg aliquots of separated phenocrysts which were determined by petrographic inspection to be unaltered. Analyses were performed by high precision CO_2 laser fluorination and mass spectrometry at the University of Oregon following techniques described in detail by Bindeman et al. (2004). The procedure used BrF_5 reagent and conversion to CO_2 gas following fluorination. Standards of garnet and mantle San Carlos olivine (Valley et al., 1995) were analysed at the same time as the unknowns and their precision is estimated to be $\pm 0.1\text{‰}$ (1 σ).

Hf purification involved decanting the supernatant from an HF dissolution and subsequent isolation using an anionic column followed by a cationic column according to methods described in Blichert-Toft et al. (1997). Hf isotopes were analysed statically on a Nu Instruments® multi-collector, inductively coupled plasma mass spectrometer at Macquarie University following methods described by Griffin et al. (2000). The data were normalised to a $^{179}\text{Hf}/^{177}\text{Hf}$ ratio of 0.7325 and analysis of the JMC475 and BHVO-2 standards during this period yielded $^{176}\text{Hf}/^{177}\text{Hf} = 0.282178$ and 0.283112 ± 16 (2 σ), respectively.

For the Os analyses, 2–3 g of sample powder was dissolved and equilibrated with ^{185}Re and ^{190}Os spikes using a modified Carius tube technique (Shirey and Walker, 1995). Os was separated using CCl_4 solvent extraction (Cohen and Waters, 1996) and further purified by

micro-distillation (Roy-Barman and Allegre, 1995). Re was separated using anionic exchange column chemistry. Both Re and Os were analysed on the IFREE (Institute for Frontier Research in Earth Evolution) Os-dedicated Triton® thermal ionization mass spectrometer in negative mode. Os was analysed on the SEM using standard peak hopping procedures, monitoring mass 233 for $^{185}\text{Re}^{16}\text{O}^{3-}$. Re was analysed on Faraday cups in static mode using a total emission procedure, which circumvents mass bias issues inherent in analysing two isotope elements and results in highly reproducible Re concentrations (Suzuki et al., 2004). Reported Re and Os data are blank subtracted. The Re blank was 1.5 pg and the Os blank ranged from 2 pg to 0.7 pg, with $^{187}\text{Os}/^{188}\text{Os} = 0.149$. Two blanks were processed with each batch of unknowns and the samples were blank subtracted using the blank values appropriate to each batch. Propagation of the blank uncertainty represents the largest component in the reported uncertainties for both the Os concentration and isotopic data.

3. Results

Our analytical results are presented in Tables 1 and 2. $\delta^{18}\text{O}$ values range from 4.82 to 5.15 in olivine, 4.68 to 5.28 in clinopyroxene, 4.98 to 5.34 in orthopyroxene, to 5.75 to 6.21 in plagioclase and 4.77 to 6.07 in the groundmass. The plagioclase and groundmass values are lower than data reported by Ewart and Hawkesworth (1987) from other samples from the same islands, but we suggest that this may reflect a general methodological difference between furnace and laser O isotope data (i.e. larger volume furnace samples contain more impurities such as altered glass), as noted by Eiler (2001) for mid-ocean ridge basalts (MORB).

Table 2
Additional $\delta^{18}\text{O}$ data.

Sample #	Island	Olivine	Clinopyroxene	Orthopyroxene	Glass
D7-17	Boninite (Station 25)	5.15			6.01
T116	Tafahi		4.77		
Fon11	Fonualei		5.17		
Late 2	Late		5.13	5.34	5.74
26821	Tofua		4.75	4.98	5.57, 5.66
482-8-3	Ata	4.82			6.07
14807	Raoul				5.26, 6.23
45653	Macauley		5.04		
14868	Curtis		5.12	5.17	
37486	L'Esperance Rock		4.89	5.26	
X162-1	Rumble IV	5, 4.96	4.68		
X451a	Clark		5.28		
L-2-5A	Valu Fa				4.77, 5.35

The $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of the lavas are mostly lower than average MORB (0.2833) and range from 0.28312 to 0.28329 with the exception of the boninite that has a distinctly lower ratio of 0.28300. The pelagic sediment has $^{176}\text{Hf}/^{177}\text{Hf}=0.28297$ and the Louisville volcanoclastic sediment has $^{176}\text{Hf}/^{177}\text{Hf}=0.28302$. These results are in excellent agreement with other recently published Hf isotope data from this arc (Woodhead et al., 2001; Pearce et al., 2007; Hergt and Woodhead, 2007).

Re and Os concentrations in the lavas vary from 97 to 915 pg/g and 2.2 to 53.6 pg/g, respectively. $^{187}\text{Os}/^{188}\text{Os}$ ratios range from slightly subchondritic at 0.1275 up to 0.1726 in the majority of the lavas but are very radiogenic in the Ata and some Kermadec lavas (0.2271 to 0.4731). The pelagic sediment has 75 pg/g Os and a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.2565, whereas the Louisville sediment has 251 pg/g Os and a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1357. Excepting the unusually radiogenic samples, the remaining Os data are broadly comparable to those reported from other southwest Pacific oceanic arcs such as the New Britain arc (Woodhead and Brauns, 2004).

4. O isotopes, crustal contamination and the source of subduction fluids

We decided to concentrate our O isotope interpretation on the plagioclase phenocryst data because this is an abundant phase in these

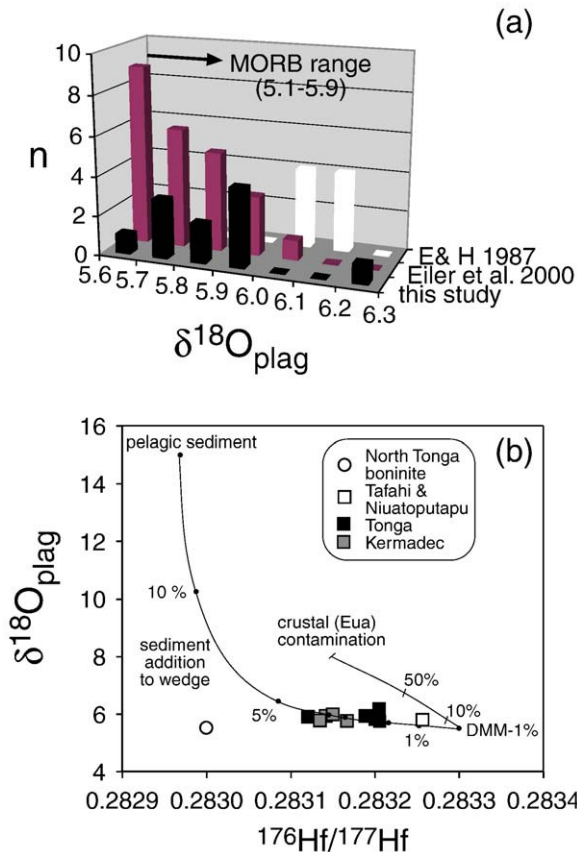


Fig. 2. (a) Histogram of $\delta^{18}\text{O}$ data from island arc plagioclases comparing Tonga-Kermadec data from this study with that reported by Ewart and Hawkesworth (1987) and data from the Mariana, South Sandwich and Vanuatu-Fiji arcs (from Eiler et al., 2000). Arrow indicates the overlap of MORB glass data obtained by laser methods (Eiler, 2000). (b) $\delta^{18}\text{O}$ versus $^{176}\text{Hf}/^{177}\text{Hf}$ with model curves for addition of pelagic sediment ($\delta^{18}\text{O}=15$, $\text{Hf}=2.9$ ppm, $^{176}\text{Hf}/^{177}\text{Hf}=0.283$) to a depleted MORB mantle (DMM-1%) from which a 1% partial melt had been previously extracted in the back-arc (Caulfield et al., 2008) ($\delta^{18}\text{O}=5.5$, $\text{Hf}=0.16$ ppm, $^{176}\text{Hf}/^{177}\text{Hf}=0.2833$) and crustal contamination ($\delta^{18}\text{O}=8$, $\text{Hf}=1$ ppm, $^{176}\text{Hf}/^{177}\text{Hf}=0.28315$) of a basaltic arc lava ($\delta^{18}\text{O}=5.5$, $\text{Hf}=1.3$ ppm, $^{176}\text{Hf}/^{177}\text{Hf}=0.2833$) for which the Hf data are based on data presented by Hergt and Woodhead (2007). Symbols: open circle = north Tonga boninite; open squares = Tafahi and Niuatoputapu; black squares = remaining Tongan islands; grey squares = Kermadec lavas.

rocks, encompasses a restricted compositional range (An_{90-65}) and $\Delta^{18}\text{O}_{\text{melt/plagioclase}}$ is close to $0\pm 0.2\%$ for the studied SiO_2 range (Bindeman et al., 2004), such that plagioclase values can be used as a proxy for melt $\delta^{18}\text{O}$. Moreover, they are in generally good agreement with $^{18}\text{O}/^{16}\text{O}$ ratios measured in groundmass glass, and with fractionation-corrected values for olivine and pyroxene (Table 2). Fig. 2a shows that the plagioclase $\delta^{18}\text{O}$ values (5.75–5.98) define normal MORB-like values and are lower than plagioclase data reported earlier by Ewart and Hawkesworth (1987) but overlap with those from other western Pacific oceanic arc lavas (Eiler et al., 2000).

In assessing the isotopic signature of arc lavas it is important to distinguish between contributions from subducted components and crustal interaction (e.g. Davidson et al., 2007), although this should, in principle, be minimised in oceanic arcs. In Tonga, the island of Eua is comprised of mid-Eocene MORB and arc basalts inferred to have rifted off the Lau Ridge during opening of the Lau Basin (see Fig. 1) and it is anticipated that the northern Kermadec and Tongan arcs are built upon similar material. Hydrothermal alteration of such material frequently leads to elevated $\delta^{18}\text{O}$ and interaction between ascending magma and this crust should lead to increases in $\delta^{18}\text{O}$. However, as noted by Davidson and Harmon (1989), the contrasting incompatible element (e.g. Hf) concentrations of the mantle wedge and arc lavas lead to very different curvatures for model vectors simulating addition of sediment to the wedge and crustal contamination. Fig. 2b shows the $\delta^{18}\text{O}$ – $^{176}\text{Hf}/^{177}\text{Hf}$ covariation for the Tonga-Kermadec lavas along with model mixing curves for sediment addition to the mantle wedge and crustal contamination. As can be seen, the flat array is consistent with $<5\%$ sediment addition to the source dominating the signature of these two isotope systems. However, it is important to note that whilst this provides encouragement that isotope systems such as ^{176}Lu – ^{176}Hf reflect source composition, it does not preclude even more sensitive systems, such as Os, from having been affected by some crustal interaction as we discuss below.

The O isotope data also shed light upon the possible source of fluids beneath the Tonga-Kermadec. Since the rate of subduction decreases dramatically from north to south along this arc this should, in principle, result in a decrease in fluid addition to the wedge per unit time. Additionally, there is strong evidence that the Tongan wedge is more depleted than that beneath the Kermadec arc (Ewart and Hawkesworth, 1987; Woodhead et al., 1993; Caulfield et al., 2008) making it more sensitive to additions from the slab. This is consistent with the observation that fluid-sensitive trace element ratios like Sr/Th are highest (up to 2000) in the Tongan sector of the arc. If these large relative fluid contributions lead to higher $\delta^{18}\text{O}$ and greater extents of melting, $\delta^{18}\text{O}$ should decrease southwards. However, the lavas we have analysed show no clear correlation between $\delta^{18}\text{O}$ and indices of slab fluid input (e.g. Ba/La, Sr/Th) and there is no systematic decrease in $\delta^{18}\text{O}$ southwards along the arc (from top to bottom in Table 1) as would be expected if the subduction fluids had high $\delta^{18}\text{O}$. We also found no correlation between $\delta^{18}\text{O}$ and ^{226}Ra excesses that have been interpreted to reflect recent fluid addition (Turner et al., 2000). Rather, our new O isotope data overlap the upper end of the range of MORB glasses (see Fig. 2a) and are most consistent with models in which subduction fluids (at least in Tonga-Kermadec) have “normal” or MORB-like $\delta^{18}\text{O}$ suggesting derivation of fluids from the serpentinized interior of the slab.

5. Hf isotopes, Hf mobility and the geographic distribution of Samoan mantle

Although most studies have concluded that the $^{143}\text{Nd}/^{144}\text{Nd}$ isotope variations in Tonga-Kermadec arc lavas are controlled by additions from the subducted sediments (e.g. Ewart and Hawkesworth, 1987; Turner and Hawkesworth, 1997; Ewart et al., 1998), the situation for Hf isotopes has been one of more debate (Hergt and Woodhead, 2007; Pearce et al., 2007). Our new data are consistent with the Hf isotope variations reflecting source composition (cf. Fig. 2a) and provide important observations pertinent to these discussions.

First, there is a negative trend between $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{10}\text{Be}/^9\text{Be}$ as shown in Fig. 3a. ^{10}Be provides an unambiguous tracer of subducted pelagic sediments (Morris et al., 1990) thus this correlation strongly suggests that the variation in Hf isotopes in these arc lavas reflect sediment contributions as well (see also Hergt and Woodhead, 2007; Pearce et al., 2007). In detail, the $^{176}\text{Hf}/^{177}\text{Hf}$ – $^{10}\text{Be}/^9\text{Be}$ array could be linear but this would require the end-members have identical Be/Hf ratios. This is unlikely because depleted mantle has a Be/Hf ratio of ~ 0.13 (Salters and Stracke, 2004) whereas the average pelagic sediments have a Be/Hf ratio of 0.66 (George et al., 2005) and, because Be is more incompatible than Hf during melting, depletion of the mantle wedge and/or partial melting of the sediments will only exacerbate this contrast. Note that since the Louisville volcanoclastics do not carry ^{10}Be (George et al., 2005), addition of this material alone cannot account for the array (see Fig. 3a). Simple binary mixing models are strongly convex upwards and Fig. 3a shows that addition of pelagic sediment with a $^{10}\text{Be}/^9\text{Be}$ ratio of 198 (George et al., 2005) cannot replicate the $^{176}\text{Hf}/^{177}\text{Hf}$ – $^{10}\text{Be}/^9\text{Be}$ array. However, a reasonably acceptable fit to the data can be achieved if the pelagic sediment has a $^{10}\text{Be}/^9\text{Be}$ ratio closer ~ 7.4 . This is significantly lower than the integrated ^{10}Be signal entering the trench but could result either from aging of this component during transfer to the wedge or because

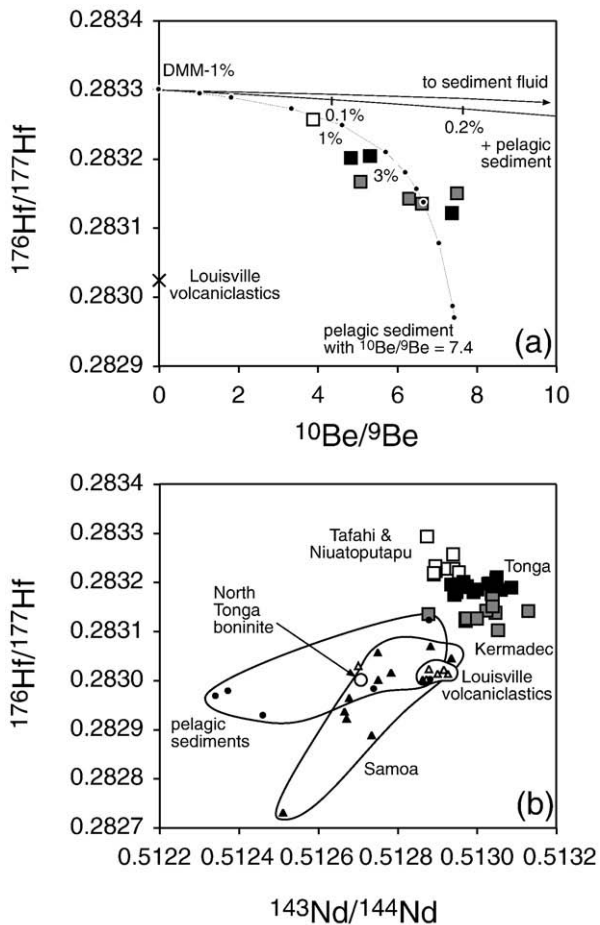


Fig. 3. Plots of (a) $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{10}\text{Be}/^9\text{Be}$ (data from this study and George et al., 2005), and (b) $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ (data from this study; Workman et al., 2004; Pearce et al., 2007; Hergt and Woodhead, 2007; Pfänder et al., 2007). Mixing models in (a) assume a 1% depleted MORB mantle (DMM–1%) with 0.16 ppm Hf, 0.012 ppm Be, $^{176}\text{Hf}/^{177}\text{Hf} = 0.2833$, $^{10}\text{Be}/^9\text{Be} = 0$ and pelagic sediment from Table 1 with Be data from George et al. (2005) or assuming a $^{10}\text{Be}/^9\text{Be}$ ratio of 7.4 (see text for discussion). Sediment fluid was calculated as a 10% Rayleigh distillation of the pelagic sediment assuming fluid/rock partition coefficients of 0.25 and 0.18 for Be and Hf, respectively, which were based on those reported for Sm and Hf by Stalder et al. (1998). Symbols same as Fig. 2b.

some of the upper, and most ^{10}Be enriched, sediment was scraped off during subduction. Both scenarios have been advocated previously (Turner and Hawkesworth, 1997; George et al., 2005).

Although it has been argued that the sediment and fluid components were added separately in space and time beneath the Tonga–Kermadec arc (Turner and Hawkesworth, 1997), the suggestion that Hf might be fluid mobile (Woodhead et al., 2001) makes it important nevertheless to assess whether the $^{176}\text{Hf}/^{177}\text{Hf}$ – $^{10}\text{Be}/^9\text{Be}$ array could reflect addition of a sediment fluid. Few fluid–rock partitioning data are available for Be and Hf and so we use data for Sm and Zr as analogues for Be and Hf (Be is generally thought to behave like Nd but here we use Sm). As might be anticipated, the fluid/rock partitioning ratio for Sm/Zr is ≥ 1 (Stalder et al., 1998) and the predicted Be/Hf ratios of a sediment-derived fluid are higher than that of the bulk sediment. As a consequence, mantle wedge–sediment–fluid mixing curves are even more strongly convex upwards than bulk sediment addition curves on Fig. 3a and provide an even poorer fit to the data. George et al. (2005) also found no evidence for a sediment–fluid signature in the Th/Be–Li/Be variations in these Tonga–Kermadec lavas. Thus, we conclude that the Hf budget is dominated by sediment (or sediment melt) addition in this arc and that there is no compelling evidence for fluid mobility of Hf. More fluid mobile elements like Sr and Pb do become mobilised from the sediments (see below).

Second, on a Hf–Nd isotope plot, the arc lavas can be subdivided into three geographic groups that have distinct average $^{176}\text{Hf}/^{177}\text{Hf}$ ratios but largely overlapping $^{143}\text{Nd}/^{144}\text{Nd}$ ratios (Fig. 3b). In detail, the $^{176}\text{Hf}/^{177}\text{Hf}$ ratios increase northwards along the arc and the lavas from the northernmost islands of Tafahi and Niuaotupapu do not overlap the field for erupted Samoan lavas, conflicting with hypotheses that the elevated Nb/Zr ratios in these lavas reflect the presence of Samoan plume mantle in the wedge beneath these islands (Wendt et al., 1997; Pearce et al., 2007; Regelous et al., 2008). In contrast, the boninite does have low $^{176}\text{Hf}/^{177}\text{Hf}$ and plots well within the Samoan field on Fig. 3b. Therefore, we propose that the extent of influence of Samoan mantle does not reach as far south as the island of Tafahi and that the boundary between Samoan and Indian mantle must lie somewhere between this island and the boninite locality near the north Tongan trench (see Fig. 1).

Notwithstanding the preceding discussion, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the Tafahi and Niuaotupapu lavas do require a Pb contribution from the subducting Louisville volcanoclastic sediments and this is likely to have been added by fluids derived from these sediments (Turner and Hawkesworth, 1997; Wendt et al., 1997). Additionally, the presence of ^{10}Be in these lavas and their low $^{143}\text{Nd}/^{144}\text{Nd}$ ratios on Fig. 3b also requires a pelagic sediment contribution of both Be and Nd. Yet it is clear from Fig. 3a that these lavas cannot contain significant contributions of Hf from either the volcanoclastic or the pelagic sediments. This dichotomy can seemingly only be explained if the pelagic sediment contribution to the Tafahi and Niuaotupapu lavas carried Be and Nd but minimal Hf. This is possible if the sediment component was added in the form of a partial melt (cf. Turner and Hawkesworth, 1997; George et al., 2005) that was formed in the presence of zircon that retained the majority of the Hf in the residue. Such a suggestion is consistent with the observation of negative Zr–Hf anomalies in the Tafahi and Niuaotupapu lavas (e.g. Turner et al., 1997) and the formation of zircon during partial melting experiments on the Tonga pelagic sediments (Johnson and Plank, 1999). Note that the ^{10}Be and Hf isotope data from the remaining islands do permit a small amount of pelagic sediment Hf addition (cf. Fig. 3a). It may be that the apparent change from zircon being present to zircon being absent in the sediment melting residue provides information on changes in the thermal state of the upper surface of the subducting plate as the rate of subduction decreases southwards.

6. Os isotopes and interaction with the mantle wedge and arc crust

Our new data show that the Tonga–Kermadec lavas have some of the lowest $^{187}\text{Os}/^{188}\text{Os}$ ratios yet reported from arc lavas and two are

similar or lower than currently accepted values for the primitive upper mantle, within the range of depleted upper mantle as represented by abyssal peridotites. The boninite has a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1283, whilst the $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1275 observed in one of the Fonualei samples (Fon 11) represents the first time a subchondritic Os isotope ratio has been measured in any arc lava. More intriguingly, this latter sample is dacitic, which has important implications for the formation of felsic magmas in the oceanic arc setting. Recently, a number of workers have argued that felsic magmas in oceanic arcs form by crustal anatexis rather than by crystal fractionation from a mantle-derived melt. For example, Smith et al. (2003) advocate melting of amphibole-bearing metabasaltic crust for silicic lavas in the northern Kermadec arc. The northern Kermadec–Tonga arc crust is likely comprised of mid-Eocene MORB with accretion of progressively larger volumes of arc-like magmas over time (Smith et al., 2003, and references therein). Taking conservative Re/Os values for MORB and arc lavas from the Kermadec arc, this crustal material is likely to have radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values up to >1.0 (for mid-Eocene MORB), and anatexis of metabasalt would have to involve only very young arc material (less than a few Myr) to be able to preserve a subchondritic Os isotopic composition. The Fon 11 dacite's mantle-like Os composition is therefore more consistent with a model of direct fractional crystallisation of a mantle-derived magma than crustal anatexis.

A corollary is that, if any equilibration with a mantle wedge of chondritic Os isotopic composition or assimilation of the Eocene arc crust occurred during ascent and fractionation of the magma parental to the

Fon 11 dacite, this would require that its source was even more unradiogenic with respect to Os isotopes, and a $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.1275 can be taken as a maximum value for the sub-Tongan mantle wedge. This value is consistent with subchondritic Os isotopic ratios that have been measured in arc peridotite samples (e.g. Brandon et al., 1996; Parkinson et al., 1999) and suggests that a subchondritic mantle may be a more appropriate pre-subduction baseline for evaluating possible Os fluxes in subduction zones than that of associated back-arc basin basalts, which appear to have moderately radiogenic $^{187}\text{Os}/^{188}\text{Os}$ values (Woodhead and Brauns, 2004).

On Fig. 4a the Fon 11 dacite and three other samples lie broadly parallel to a pelagic sediment mixing model based on the one used for Fig. 3a, whilst the remainder is significantly displaced to higher $^{187}\text{Os}/^{188}\text{Os}$ values. The boninite also lies on the mixing curve but this is probably fortuitous and more likely reflects the Os isotope signature of the Samoan plume. Unfortunately, there are as yet no Samoan basalts for which both Hf and Os isotopes have been measured in order to assess this further. Nevertheless, it is possible that the Hf–Os isotope signature of four of the arc lavas is largely derived from sediment-modified wedge followed by relatively minor modification in the arc crust (see below). If so, this might restrict the amount of melt–wall rock interaction during ascent through the mantle wedge and support models for rapid channelled ascent consistent with recent inferences from ^{226}Ra data and numerical modelling (Turner et al., 2000; Bourdon et al., 2003; Petford et al., 2008).

The remaining lavas, including the second Fonualei dacite (Fon 39), a dacite from Raoul and a rhyolite from Curtis Island, appear to be distinct from those just described and form a trend towards high $^{187}\text{Os}/^{188}\text{Os}$ and Sr/Os (Fig. 4b). With the possible exception of the Tofua sample, seawater interaction cannot generate this trend as the extreme Sr/Os ratio of seawater ($\sim 10^7$) would produce a horizontal mixing line on Fig. 4b. Therefore, we attribute them to interaction with the arc crust and the array on Fig. 4b is consistent with the inferences made above for the Os isotope composition of the crustal contaminant (note that more complex, AFC processes, could result in curved, rather than linear, mixing arrays). The absence of Re–Os data for the Eocene crust precludes quantitative modelling of such contamination but the relationships on Fig. 4 both highlight the sensitivity of Os to crustal interaction and underline the significance of the Fon 11 result. Because the pelagic sediment has a low Os concentration but very radiogenic $^{187}\text{Os}/^{188}\text{Os}$, it is possible that the binary arrays observed from a number of arc lava suites (Alves et al., 2002) reflect addition of sediment to a subchondritic mantle wedge followed by crustal contamination.

7. Conclusions

The combination of O, Hf and Os isotope data from Tonga–Kermadec lavas permit the following observations, not all of which were apparent from earlier work based on Sr–Nd–Pb isotopes. It seems likely that further multi-isotope studies will continue to provide insights into the origins of the signatures observed in oceanic island arc lavas:

- (1) O isotopes are largely MORB-like and preclude a major role for crustal contamination or high $\delta^{18}\text{O}$ fluids from the subducting slab.
- (2) Hf behaves conservatively in north Tonga and does not appear to be significantly mobilised by either fluid (cf. Woodhead et al., 2001) or even sediment melts; further south larger amounts of Hf are added by the sediment (?melt) contributions.
- (3) Hf isotopes indicate a mantle source similar to that of erupted Samoan lavas for the north Tongan boninite but preclude it for the Tafahi and Niuatoputapu arc lavas, placing a tighter constraint upon the extent of influence of the Samoan plume.
- (4) Some Os isotope ratios may reflect subduction signatures that would require very rapid melt ascent through the mantle wedge and overlying lithosphere. However, most are overprinted by subsequent interaction with the arc crust.

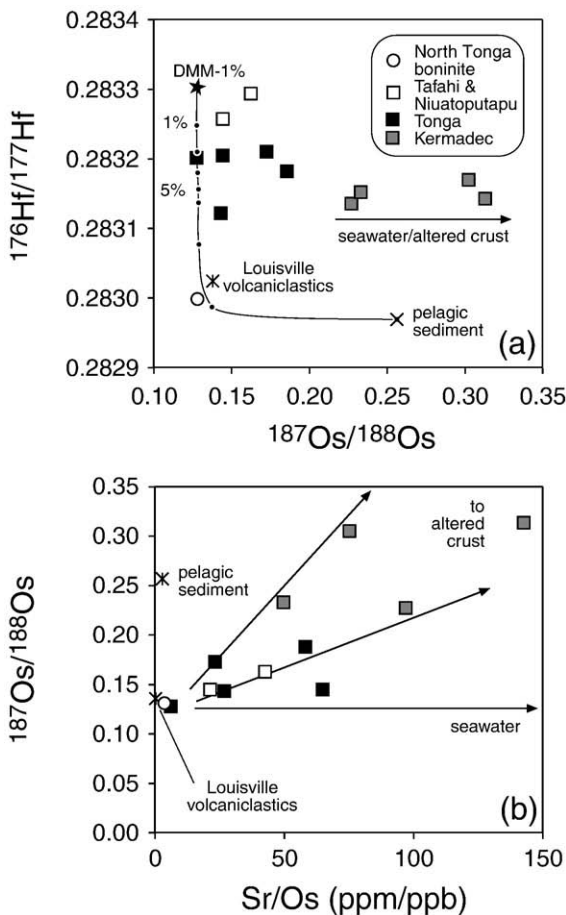


Fig. 4. Plots of (a) $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{187}\text{Os}/^{188}\text{Os}$, and (b) $^{187}\text{Os}/^{188}\text{Os}$ versus Sr/Os. Mixing model in (a) is between DMM–1% with 1000 ppt Os (Brandon et al., 1996; McInnes et al., 1999; Widom et al., 2003), $^{187}\text{Os}/^{188}\text{Os} = 0.128$ and the pelagic sediment from Table 1. Mixing to seawater in (b) is horizontal because seawater has a Sr/Os ratio of $\sim 10^7$ and $^{187}\text{Os}/^{188}\text{Os} \sim 1.05$ so samples with elevated Sr/Os and $^{187}\text{Os}/^{188}\text{Os}$ are inferred to have interacted with altered arc crust. Symbols as indicated on Figs. 2 and 3.

- (5) Some evolved magmas can develop by crystal fractionation with little or no interaction with the arc crust.

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References

- Alves, S., Schiano, P., Capmas, F., Allegre, C.J., 2002. Osmium isotope binary mixing arrays in arc volcanism. *Earth and Planetary Science Letters* 198, 355–369.
- Bevis, M., Taylor, F.W., Schutz, B.E., Recy, J., Isacks, B.L., Helu, S., Singh, R., Kendrick, E., Stowell, J., Taylor, B., Calmant, S., 1995. Geodetic observations of very rapid convergence and back-arc extension at the Tonga arc. *Nature* 374, 249–251.
- Bindeman, I.N., Ponomareva, V.V., Bailey, J.C., Valley, J.W., 2004. Volcanic arc of Kamchatka: a province with high- $\delta^{18}\text{O}$ magma sources and large-scale $^{18}\text{O}/^{16}\text{O}$ depletion of the upper crust. *Geochimica et Cosmochimica Acta* 68, 841–865.
- Blichert-Toft, J., Chauvel, C., Albarede, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS. *Contributions to Mineralogy and Petrology* 127, 248–260.
- Bourdon, B., Turner, S., Dosseto, A., 2003. Dehydration and partial melting in subduction zones: constraints from U-series disequilibria. *Journal of Geophysical Research* 108. doi:10.1029/2002JB001839.
- Brandon, A.D., Creaser, R.A., Shirey, S.B., Carlson, R.W., 1996. Osmium recycling in subduction zones. *Science* 272, 861–864.
- Caulfield, J.T., Turner, S.P., Dosseto, A., Pearson, N.J., Beier, C., 2008. Source depletion and extent of melting in the Tongan sub-arc mantle. *Earth and Planetary Science Letters* 273, 279–288.
- Chesley, J., Ruiz, J., Richter, K., Ferrari, L., Gomez-Tuena, A., 2002. Source contamination versus assimilation: an example from the Trans-Mexican volcanic arc. *Earth and Planetary Science Letters* 195, 211–221.
- Cohen, A.S., Waters, F.G., 1996. Separation of osmium from geologic materials by solvent extraction for analysis by TIMS. *Analytica Chimica Acta* 332, 269–275.
- Davidson, J.P., Harmon, R.S., 1989. Oxygen isotope constraints on the petrogenesis of volcanic arc magmas from Martinique, Lesser Antilles. *Earth and Planetary Science Letters* 95, 255–270.
- Davidson, J.P., Morgan, D.J., Charlier, B.L.A., Harlou, R., Hora, J.M., 2007. Microsampling and isotopic analysis of igneous rocks: implications for the study of magmatic systems. *Annual Reviews of Earth and Planetary Sciences* 35, 273–311.
- Eiler, J.M., 2001. Oxygen isotope variations of basaltic lavas and upper mantle rocks. *Reviews in Mineralogy and Geochemistry* 43, 319–364.
- Eiler, J.M., Crawford, A., Elliott, T., Farley, K.A., Valley, J.W., Stolper, E.M., 2000. Oxygen isotope geochemistry of oceanic-arc lavas. *Journal of Petrology* 41, 229–256.
- Ewart, A., Hawkesworth, C.J., 1987. The Pleistocene–Recent Tonga–Kermadec arc lavas: interpretation of new isotopic and rare earth data in terms of a depleted mantle source model. *Journal of Petrology* 28, 495–530.
- Ewart, A., Collerson, K.D., Regelous, M., Wendt, J.L., Niu, Y., 1998. Geochemical evolution within the Tonga–Kermadec–Lau arc–back–arc systems: the role of varying mantle wedge composition in space and time. *Journal of Petrology* 39, 331–368.
- Falloon, T.J., Crawford, A.J., 1991. The petrogenesis of high-calcium boninite lavas dredged from the northern Tonga ridge. *Earth and Planetary Science Letters* 102, 375–394.
- George, R., Turner, S., Morris, J., Plank, T., Hawkesworth, C., Ryan, J., 2005. Pressure–temperature–time paths of sediment recycling beneath the Tonga–Kermadec arc. *Earth and Planetary Science Letters* 233, 195–211.
- Griffin, W.L., Pearson, N.J., Belousova, E., Jackson, S.E., O'Reilly, S.Y., van Acherberg, E., Shee, S.R., 2000. The Hf isotope composition of cratonic mantle: LAM–MC–ICPMS analysis of zircon megacrysts in kimberlites. *Geochimica et Cosmochimica Acta* 64, 133–147.
- Hauri, E.H., 1997. Melt migration and mantle chromatography, 1: simplified theory and conditions for chemical and isotopic decoupling. *Earth and Planetary Science Letters* 153, 1–19.
- Hergt, J.M., Woodhead, J.D., 2007. A critical evaluation of recent models for Lau–Tonga arc–backarc basin magmatic evolution. *Chemical Geology* 245, 9–44.
- Johnson, M., Plank, T., 1999. Dehydration and melting experiments constrain the fate of subducted sediments. *Geochemistry, Geophysics, Geosystems* 1. doi:10.1029/1999GC000014.
- Kepler, H., 1996. Constraints from partitioning experiments on the composition of subduction-zone fluids. *Nature* 380, 237–240.
- Lassiter, J.C., Luhr, J.F., 2001. Osmium abundance and isotope variations in mafic Mexican volcanic rocks: evidence for crustal contamination and constraints on the geochemical behavior of osmium during partial melting and fractional crystallization. *Geochemistry, Geophysics, Geosystems* 2 2000GC000116.
- McInnes, B.I.A., McBride, J.S., Evans, N.J., Lambert, D.D., Andrew, A.S., 1999. Osmium isotope constraints on ore metal recycling in subduction zones. *Science* 286, 512–515.
- Morris, J.D., Leeman, B.W., Tera, F., 1990. The subducted component in island arc lavas: constraints from Be isotopes and B–Be systematics. *Nature* 344, 31–36.
- Parkinson, I.J., Hawkesworth, C.H., Cohen, A.S., 1999. Ancient mantle in a modern arc: osmium isotopes in izu–Bonin–Mariana forearc peridotites. *Science* 281, 2011–2013.
- Pearce, J.A., Kempton, P.D., Nowell, G.M., Noble, S.R., 1999. Hf–Nd element and isotope perspective on the nature and provenance of mantle and subduction components in western Pacific arc-basin systems. *Journal of Petrology* 40, 1579–1611.
- Pearce, J.A., Kempton, P.D., Gill, J.B., 2007. Hf–Nd evidence for the origin and distribution of mantle domains in the SW Pacific. *Earth and Planetary Science Letters* 260, 98–114.
- Petford, N., Koenders, M.A., Turner, S., 2008. Channelised melt flow in downwelling mantle: implications for ^{226}Ra – ^{210}Pb disequilibria in arc magmas. *Journal of Geophysical Research* 113. doi:10.1029/2007JB005563.
- Pfänder, J.A., Münker, C., Stracke, A., Mezger, K., 2007. Nb/Ta and Zr/Hf in ocean island basalts – implications for crust–mantle differentiation and the fate of Niobium. *Earth and Planetary Science Letters* 254, 158–172.
- Regelous, M., Collerson, K.D., Ewart, A., Wendt, J.L., 1997. Trace element transport rates in subduction zones: evidence from Th, Sr and Pb isotope data for Tonga–Kermadec arc lavas. *Earth and Planetary Science Letters* 150, 291–302.
- Regelous, M., Turner, S., Falloon, T.J., Taylor, P., Gamble, J., Green, T., 2008. Mantle dynamics and mantle melting beneath Niuafo'ou Island and the northern Lau back-arc basin. *Contributions to Mineralogy and Petrology* 156, 103–118.
- Roy-Barman, M., Allegre, C.J., 1995. $^{187}\text{Os}/^{186}\text{Os}$ in oceanic island basalts: tracing oceanic crust recycling in the mantle. *Earth and Planetary Science Letters* 129, 145–161.
- Salters, V.J.M., Stracke, A., 2004. Composition of the depleted mantle. *Geochemistry, Geophysics, Geosystems* 5. doi:10.1029/2003GC000597.
- Shirey, S.B., Walker, R.W., 1995. Carius tube digestions for low-blank rhenium–osmium analysis. *Analytical Chemistry* 67, 2136–2141.
- Smith, I.E.M., Worthington, T.J., Stewart, R.B., Price, R.C., Gamble, J.A., 2003. Felsic volcanism in the Kermadec arc, SW Pacific: crustal recycling in an oceanic setting. *Geological Society of London Special Publication* 219, 99–118.
- Stalder, R., Foley, S.F., Brey, G.P., Horn, I., 1998. Mineral–aqueous fluid partitioning of trace elements at 900–1200 °C and 3.0–5.7 GPa: new experimental data for garnet, clinopyroxene, and rutile, and implications for mantle metasomatism. *Geochimica et Cosmochimica Acta* 62, 1781–1801.
- Suzuki, K., Miyata, Y., Kanazawa, N., 2004. Precise Re isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS) using total evaporation technique. *International Journal of Mass Spectrometry* 235, 97–101.
- Turner, S., Hawkesworth, C., 1997. Constraints on flux rates and mantle dynamics beneath island arcs from Tonga–Kermadec lava geochemistry. *Nature* 389, 568–573.
- Turner, S., Hawkesworth, C., Rogers, N., Bartlett, J., Worthington, T., Hergt, J., Pearce, J., Smith, I., 1997. ^{238}U – ^{230}Th disequilibria, magma petrogenesis and flux rates beneath the depleted Tonga–Kermadec island arc. *Geochimica et Cosmochimica Acta* 61, 4855–4884.
- Turner, S., Bourdon, B., Hawkesworth, C., Evans, P., 2000. ^{226}Ra – ^{230}Th evidence for multiple dehydration events, rapid melt ascent and the time scales of differentiation beneath the Tonga–Kermadec island arc. *Earth and Planetary Science Letters* 179, 581–593.
- Turner, S., Evans, P., Hawkesworth, C.J., 2001. Ultrafast source-to-surface movement of melt at island arcs from ^{226}Ra – ^{230}Th systematics. *Science* 292, 1363–1366.
- Turner, S., Bourdon, B., Gill, J., 2003. Insights into magma genesis at convergent margins from U-series isotopes. In: Bourdon, B., Henderson, G., Lundstrom, C., Turner, S. (Eds.), *Uranium series geochemistry: Reviews in Mineralogy and Geochemistry*, vol. 52, pp. 255–315.
- Valley, J.W., Kitchen, N., Kohn, M.J., Niendorf, C.R., Spicuzza, M.J., 1995. UWG-2, a garnet standard for oxygen isotope ratio: strategies for high precision and accuracy with laser heating. *Geochimica et Cosmochimica Acta* 59, 5223–5231.
- Wendt, J.L., Regelous, M., Collerson, K.D., Ewart, A., 1997. Evidence for a contribution from two mantle plumes to island arc lavas from northern Tonga. *Geology* 25, 611–614.
- Widom, E., Kepezhinskas, P., Defant, M., 2003. The nature of metasomatism in the sub-arc mantle wedge: evidence from Re–Os isotopes in Kamchatka peridotite xenoliths. *Chemical Geology* 196, 283–306.
- Woodhead, J., Brauns, M., 2004. Current limitations to the understanding of Re–Os behaviour in subduction systems, with an example from New Britain. *Earth and Planetary Science Letters* 221, 309–323.
- Woodhead, J., Eggins, S., Gamble, J., 1993. High field strength and transition element systematics in island arc and back-arc basin basalts: evidence for multi-phase melt extraction and a depleted mantle wedge. *Earth and Planetary Science Letters* 114, 491–504.
- Woodhead, J.D., Hergt, J.M., Davidson, J.P., Eggins, S.M., 2001. Hafnium isotope evidence for 'conservative' element mobility during subduction zone processes. *Earth and Planetary Science Letters* 192, 331–346.
- Workman, R.K., Hart, S.R., Jackson, M., Regelous, M., Farley, K.A., Blusztajn, J., Kurz, M., Staudigel, H., 2004. Recycled metasomatized lithosphere as the origin of the enriched mantle II (EM2) end-member: evidence from the Samoan volcanic chain. *Geochemistry, Geophysics, Geosystems* 5. doi:10.1029/2003GC000623.