

Rhenium–osmium isotope and elemental behaviour during subduction of oceanic crust and the implications for mantle recycling

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Abstract

This study presents major-, trace-element, and rhenium–osmium (Re–Os) isotope and elemental data for basalts and gabbros from the Zermatt-Saas ophiolite, metamorphosed to eclogite-facies conditions during the Alpine orogeny. Igneous crystallisation of the gabbros occurred at 163.5 ± 1.8 Ma and both gabbro and basalt were subject to ‘peak’ pressure–temperature (P – T) conditions of >2.0 GPa and ~ 600 °C at about 40.6 ± 2.6 Ma.

Despite such extreme P – T conditions, Re–Os isotope and abundance data for gabbroic rocks suggest that there has been no significant loss of either of these elements during eclogite-facies metamorphism. Indeed, ^{187}Re – ^{187}Os isotope data for both unaltered gabbros and gabbroic eclogites lie on the same best-fit line corresponding to an errorchron age of 160 ± 6 Ma, indistinguishable from the age of igneous crystallisation. In contrast, metamorphosed basalts do not yield age information; rather most possess $^{187}\text{Re}/^{188}\text{Os}$ ratios that cannot account for the measured $^{187}\text{Os}/^{188}\text{Os}$ ratios, given the time since igneous crystallisation. Taken with their low Re contents these data indicate that the basalts have experienced significant Re loss (~ 50 – 60%), probably during high-pressure metamorphism. Barium, Rb and K are depleted in both gabbroic and basaltic eclogites. In contrast, there is no evident depletion of U in either lithology.

Many ocean-island basalts (OIB) possess radiogenic Os and Pb isotope compositions that have been attributed to the presence of recycled oceanic crust in the mantle source. Published Re–Os data for high- P metabasaltic rocks alone (consistent with this study) have been taken to suggest that excessive amounts of oceanic crust are required to generate such signatures. However, this study shows that gabbro may exert a strong influence on the composition of recycled oceanic crust. Using both gabbro and basalt (i.e. a complete section of oceanic crust) calculations suggest that the presence of $\geq 40\%$ of 2 Ga oceanic crust can generate the radiogenic Os compositions seen in some OIB. Furthermore, lower U/Pb ratios in gabbro (compared to basalt) serve to limit the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios generated, while having a minimal effect on Os ratios. These results suggest that the incorporation of gabbro into recycling models provides a means of producing a range of OIB compositions having lower (and variable) $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, but still preserving $^{187}\text{Os}/^{188}\text{Os}$ compositions comparable to HIMU-type OIB.

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1. Introduction

Variations in the composition of the Earth's mantle are thought to reflect the processes of differentiation and recycling that have occurred throughout geological history, and this chemical heterogeneity of the mantle is sampled at the present-day by basaltic volcanism. Mid-ocean ridge basalts (MORB) sample mantle material that is depleted in incompatible elements, and this depletion is generally attributed to the extraction and generation of continental crust. In contrast, ocean-island basalts (OIB) are relatively enriched in many incompatible elements which is thought to reflect the presence of recycled crust or lithosphere in the mantle [1]. For example, radiogenic ^{206}Pb and ^{208}Pb in many OIB require source material that has experienced a long-term enrichment in U and Th relative to Pb, and this has been attributed to the presence of recycled, altered oceanic crust. HIMU-type OIB, in particular, possess very elevated Pb ratios and are thus thought to be generated by mantle containing ancient oceanic crust.

The rhenium–osmium (Re–Os) isotope system is an exceptional tracer of recycled crust or lithosphere in the mantle. This is because Os behaves as a compatible element during melting and is preferentially retained in the mantle, whereas Re is moderately incompatible and enters the melt. Consequently, both oceanic and continental crust possess high Re/Os (parent/daughter) ratios, and develop radiogenic Os isotope compositions over time, which can be readily traced as recycled material if mixed back into the convective mantle. Pioneering studies of Re–Os isotopes in OIB have revealed radiogenic Os isotope compositions that provide a strong support for the presence of recycled oceanic crust in the mantle, and have demonstrated the utility of this system as a tracer of mantle sources [2–5].

However, the interpretation of OIB data is complicated by the possibility of modification of the Re and Os budget of the oceanic crust during subduction. Previous work on basalts metamorphosed to high-pressure eclogite-facies indicates that significant Re loss may occur before oceanic crust is recycled back into the mantle [6]. Consequently, the Re/Os ratio is lowered, reducing the growth of radiogenic ^{187}Os in recycled oceanic crust, and its potential influence on mantle chemistry. Using these data, calculations suggest that between 70 and 90% of recycled oceanic crust is required in order to produce some of the observed OIB signatures; an estimate that is inconsistent with the major element abundances in alkaline OIB. For the most part, that study [6] considered only the recycling of basaltic rock types, whereas much of the oceanic crust, some 60% or more, comprises gabbroic lithologies. Although gabbros are often considered to simply represent the plutonic equivalent of contemporaneous basalt volcanism, there are

some notable differences in their mineralogy and hence Re and Os content. In particular, because of their differing geochemical behaviour, Os contents in gabbros are typically higher (and Re contents lower) than those of basalts (e.g. this study [7,8]), and this may have important global consequences for Re–Os isotope systematics. Moreover, gabbros and basalts potentially exhibit different behaviour during subduction because of their differing petrology (grain size, degree of hydration and rheology) and large scale structure.

This study presents major and trace element, and Re–Os isotope and elemental data for contemporaneous basalts and gabbros from the Zermatt-Saas ophiolite, metamorphosed to eclogite-facies conditions during the Alpine orogeny. The aim of this work is to quantify the behaviour of Re and Os in both basalt and gabbro (that is, a representative section of the entire oceanic crust). These results illustrate the differential behaviour of the Re–Os system in basalt and gabbro lithologies, and serve as a means to assess the role of recycling a complete section of oceanic crust in generating the isotope compositions observed in many oceanic basalts.

2. Geological setting and samples

Samples have been collected from the Zermatt-Saas Fee ophiolite (ZSO), Switzerland (Fig. 1), which comprises structurally duplicated fragments of Mesozoic Tethyan oceanic crust that formed the Piemonte basin which lay between Europe and the micro-continent of Apulia prior to the Alpine collision. At the present-day, the ZSO lies between the Monte Rosa nappe (structurally below), which is part of the Briançonnais zone

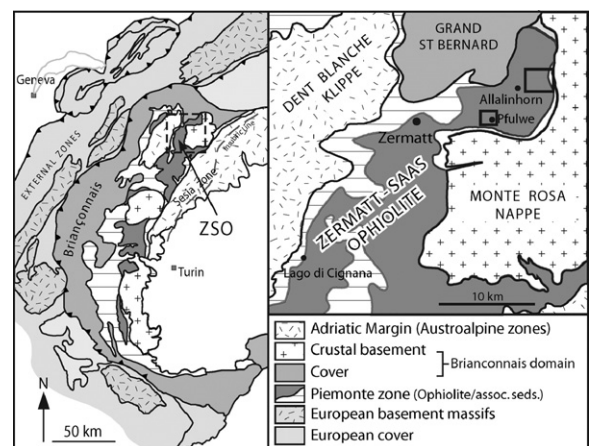


Fig. 1. Geological map of the Western Alps (left) and larger scale map of Zermatt-Saas ophiolite (ZSO) showing sampling areas in black boxes (right).

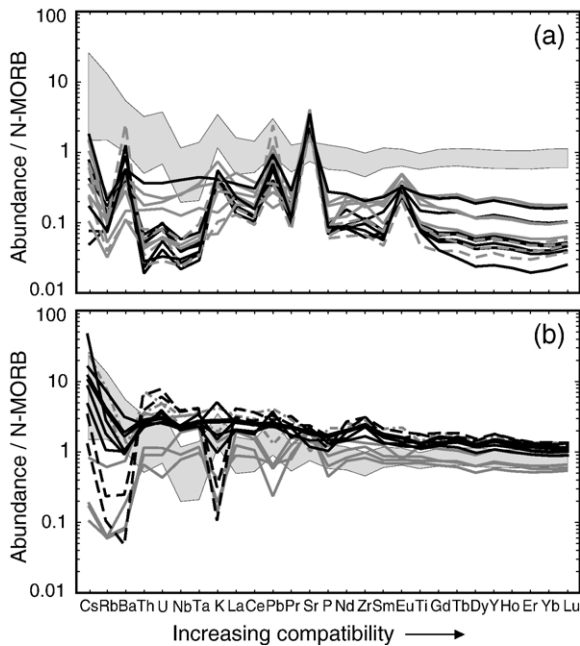


Fig. 2. N-MORB normalised spidergram for (a) Allalin gabbroic lithologies (black lines — gabbros, grey lines — gabbroic eclogites, broken lines — transitional) and (b) ZSO basaltic eclogites (black lines — pillows, broken lines — undifferentiated, grey lines — Allalin). Gabbroic samples display marked positive anomalies for Ba, Sr and Eu, thought to reflect plagioclase accumulation. ZSO basaltic eclogites contain concentrations of incompatible elements which range from N-MORB to four-times N-MORB to four-times N-MORB for the ‘mobile’ elements Cs, Rb, Ba, K and Pb are all lower than expected when compared to similarly compatible less mobile elements (Th, Nb, Ta, La), suggesting some loss of these elements. However, U does not display depletion with respect to Th.

representing European continental crust, and the Dent Blanche Klippe (structurally above) which comprises continental material from the Apulian plate.

The ZSO contains a nearly complete range of ophiolitic lithologies including serpentinized ultramafics, metagabbros, metabasalts and associated metasediments. Samples were collected from the gabbroic unit of the Allalin Gabbro and basaltic units close to Pfulwe pass (see Fig. 1). The crystallisation age of the ophiolite has been determined from U–Pb dating of magmatic zircon from two gabbro bodies. Zircons from both the Allalin and Mellichen metagabbros give ages of 163.5 ± 1.8 Ma and 164.0 ± 2.7 Ma, respectively [9], consistent with a 153–154 Ma maximum age for deposition of the sedimentary cover in the Allalin area [9].

The ZSO underwent high- to ultra-high-pressure (UHP) metamorphism during south-easterly directed partial subduction and the subsequent continental collision that formed the Alpine mountain belt. Peak pressures and temperatures recorded in the Lago di Cignana area (about 20 km south-west of Zermatt) are in the range of 2.7–

2.9 GPa and 600–630 °C [10], while to the north-east of Zermatt, assemblages in the Allalin Gabbro and Täschalp (Pfulwe) areas are estimated to have formed at ≥ 2.0 GPa and 550–600 °C [11,12]. More recently it has been suggested that peak metamorphic pressures for the Allalin Gabbro may have reached 3.5 GPa [13]. The ‘peak’ of metamorphism in the ZSO is thought to have occurred at 40.6 ± 2.6 Ma from a Sm–Nd mineral isochron for a metabasite in the Lago di Cignana area [14], consistent with a U–Pb age of 44.1 ± 0.7 Ma for zircons from a metabasite and metasediments in the same area [9].

The sample suite from the ZSO comprises eclogitic metabasalts and variably recrystallised eclogite-facies cumulate gabbros from the Allalin Gabbro. The samples were chosen so as to be representative of upper and lower oceanic crustal material, respectively, metamorphosed under conditions similar to those experienced by subducting slab material. The gabbroic samples span a range of *apparent* metamorphic conditions although field (and hand specimen) evidence precludes metamorphism under significantly different peak *P–T* conditions. Some gabbros have completely retained their original magmatic mineralogy (principally olivine, clinopyroxene and plagioclase) in a metastable state, possibly due to their anhydrous mineralogy, the local absence of fluid infiltration, and relatively low peak temperatures. At the same time, other samples from the same body comprise an eclogitic mineralogy (that includes garnet, omphacite, zoisite, paragonite, talc and glaucophane). Several samples from the Allalin Gabbro display the transition from gabbro to eclogite on the scale of an individual hand specimen (referred to as transitional gabbroic samples). The utility of such samples is that they provide the opportunity to directly compare the geochemistry of unmodified gabbros and genetically related metamorphosed eclogites, without the uncertainties that typically arise in comparing igneous material which has a differing source and magmatic history. Little or no greenschist-facies retrogression is evident in the gabbros. However, some of the metabasalts (particularly those from the Allalin locality) display some greenschist retrogression (<20%), although in all cases eclogitic mineralogy predominates and it is unlikely that the samples have been extensively modified during exhumation.

3. Analytical techniques

Major element analyses were obtained by wavelength dispersive XRF, where the reproducibility deduced from replicate analyses was typically better than 0.2 wt.%. Trace element concentrations were determined by ICP-MS, after dissolution in Teflon® vials using HF, HNO₃ and HCl. All analyses were externally standardised

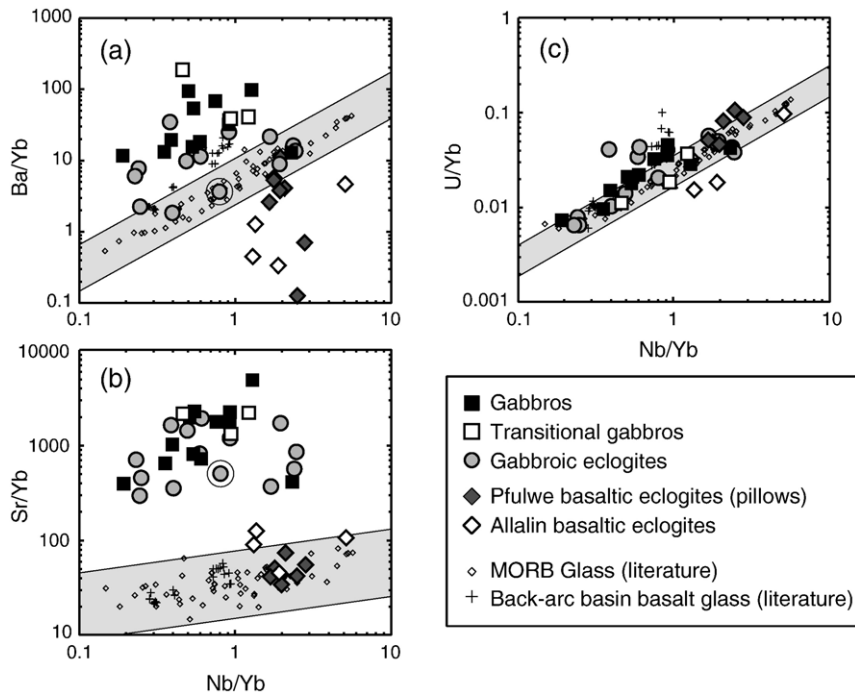


Fig. 3. Non-conservative element discrimination plots (after [18], see text). MORB forms well-defined positive trends on all plots, against which the basalt data can be compared (MORB data [21], A. Gannoun personal communication; back-arc basin glass [21]). The gabbros are cumulates and are therefore probably not comparable with MORB. Instead, the gabbroic eclogite data can be compared to the unaltered gabbro data which form well-defined positive trends on the same plots. (a) Barium appears depleted with respect to Nb in many of the basaltic eclogites and in at least half of the gabbroic eclogites. (b) Strontium behaviour is less clear and is dominated by the processes of plagioclase accumulation (gabbros) and fractionation (basalts). This may mask any loss of Sr, though all the metabasalts lie within or above the MORB field suggesting no significant loss of Sr, and possibly Sr gain. (c) U/Yb ratios for both gabbroic and basaltic lithologies suggest that there has been no significant loss of U.

against four international rock standards, for which the typical reproducibility was better than 4% (1σ).

The extraction and purification of Os and Re from samples closely follow techniques described previously [15]. Both Re and Os were analysed on Pt filaments as OsO_3^- and ReO_4^- by negative-thermal ionisation mass spectrometry (N-TIMS) using the electron multiplier mode on a ThermoFinnigan® Triton (see [16,17]). Repeated analyses ($n=44$) of 14 pg aliquots of the Johnson Matthey Os standard solution gave a $^{187}\text{Os}/^{188}\text{Os}$ mean value of 0.17402 ± 46 (2σ , RSD: 0.26%) over the time period of analysis, in good agreement with the accepted value of 0.17398 [15]. The accuracy of the isotope and elemental determinations is difficult to assess as Os is inevitably heterogeneously distributed even in rock standards. However, the reproducibility of duplicate sample dissolutions suggests that incomplete digestion and/or sample-spike equilibration are not significant. From December 2002 to October 2004 total procedural blanks for Os ranged between 0.04 and 0.30 pg with a mean of 0.11 pg. For Re they were between 2.4 and 15.3 pg with a mean of 5.1 pg.

The mean $^{187}\text{Os}/^{188}\text{Os}$ ratio of the blanks was 0.309 ± 0.115 . However, although the absolute values for the blank varied between each batch of reagent, the short-term reproducibility of the Os blank (relating to each reagent batch) was usually $\pm 10\%$ or better. Consequently, the blank corrections used relate to the appropriate reagent batch rather than the long-term mean.

4. Results

4.1. Major and trace element data

Major and trace element data for the gabbros and eclogites are given in Table 2 (supplementary material, available on-line). The majority of data for gabbroic lithologies display a negative co-variation between MgO and Al_2O_3 (not shown) consistent with the presence of variable proportions of cumulate plagioclase and olivine. Several samples which lie off this trend may reflect a higher than usual proportion of augite (up to 20% by mode). Basaltic samples display a negative co-variation between MgO and $\text{Fe}_2\text{O}_{3\text{TOT}}$ (also not shown)

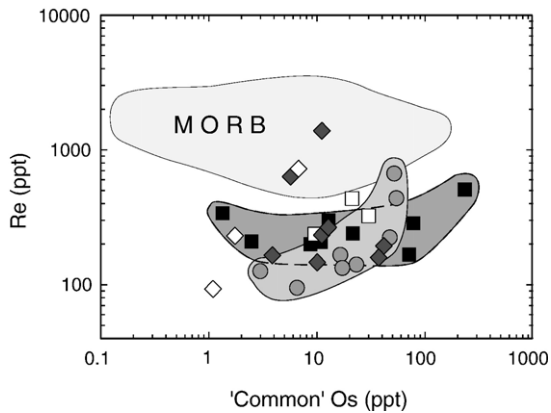


Fig. 4. Os vs. Re for all ZSO samples. For symbols see Fig. 3. Re concentrations of the gabbroic eclogites span a broader range than the gabbros while having a narrower Os range. The gabbros do not display co-variation between Os and Re, unlike the gabbroic eclogites. There is no systematic relation between Os and Re in the metabasalt samples. *Osmium concentrations are 'common' Os – in-grown ^{187}Os subtracted. MORB field drawn from Schiano et al. [7].

suggesting that fractional crystallisation has not progressed to the point where Fe–Ti oxide crystallisation results in a reduction of Fe concentrations in the residual melt.

Gabbroic lithologies show strong positive anomalies in Ba, Sr, and Eu on a N-MORB normalised spidergram (Fig. 2), which are thought to be related to the abundance of plagioclase (~50 to 70%). Basaltic eclogites show a similar pattern to MORB although with somewhat higher abundances of trace elements. Unlike the Lau basin data, ZSO metabasalts do not possess distinct negative Nb, Ta or Zr anomalies which is strong evidence in favour of a typical MORB source for these basalts rather than supra-subduction mantle wedge source enriched in fluid-mobile elements (Fig. 2).

In order to discern which elements have been depleted during metamorphism, Ba, Sr and U are plotted against a hypothetical 'immobile' element (in this case Nb), and their concentrations are normalised to Yb to account for differences in fractional crystallisation and primary melt fraction (Fig. 3) [18]. MORB data display a clear positive co-variation on all plots, against which the metabasalts have been compared. The gabbros are cumulates and are thus unlikely to be simply crystallised from a single discrete magma, therefore they cannot be directly compared to the MORB trends. Instead, the gabbroic eclogite data may be compared to the data for the unaltered gabbros which define clear co-variations on these plots.

The large-ion lithophile element (LILE) Ba appears to be depleted with respect to Nb in the majority of metabasaltic eclogites and in at least half of the gabbroic eclogites (Fig. 3a). The extent of Ba depletion can be

estimated assuming both the immobility of Nb and that the original sample composition fell either within the MORB field (for basalts) or within the field defined by the measured unaltered gabbros (for gabbroic lithologies). Thus, it can be estimated that the circled sample (Fig. 3a) may have lost approximately 80% of its initial Ba. Both Rb and K (not shown) also display depletion with respect to Nb in many samples, although not always in the same samples. All the Pfulwe metabasalts lie within the MORB field for Sr, suggesting no significant loss of this element (Fig. 3b). Most of the Allalin metabasalts have Sr/Yb ratios that are greater than those of MORB, for a given Nb content. The extent of depletion of Sr in the gabbroic eclogites is less than that for Ba, Rb or K, but there appears to have been loss of Sr from 4 to 5 samples, possibly 30% from the circled sample.

Two of the Allalin metabasalts plot below the MORB trend on the U/Yb diagram (Fig. 3c) suggesting a small degree of U loss, while 3 samples collected at Pfulwe pass contain slightly higher U than MORB, for their measured Nb contents. However, these differences are minor and in general the U/Yb ratios for the gabbroic and basaltic lithologies of the ZSO suggest that there has been no significant loss of U compared to Nb in either gabbroic or basaltic samples.

4.2. Re and Os elemental data

4.2.1. Gabbroic lithologies

The mean Os concentrations of the gabbros and gabbroic eclogites are 25 ppt ($n=9$) and 29 ppt ($n=8$) respectively (excluding one very Os-rich gabbro). Given the likelihood of heterogeneous distribution of Os in these samples, the abundance of Os in the gabbros and gabbroic eclogites is effectively indistinguishable, as are the Re concentrations of 266 ppt ($n=9$) and 264 ppt ($n=8$), respectively.

A comparison of Re and Os abundances in the gabbros (Fig. 4) reveals a range of Os values but little co-variation of Re. In contrast, the gabbroic eclogites appear to display a positive co-variation where samples with low Os also contain low abundances of Re. The range of osmium concentrations in the gabbroic eclogites (3.5–57 ppt) is comparable to that of the gabbros (2.5–250 ppt), whereas Re abundances in the gabbroic eclogite suite show a greater range from 90 to 670 ppt compared to 170 to 510 ppt for unaltered gabbros. This may reflect a greater degree of disturbance for the eclogites, but overall there is little evidence for a significant loss or gain of rhenium or osmium. The range of Re concentrations in gabbroic lithologies is smaller and the mean lower than the data previously published for gabbros (128–1102 ppt,

Table 1
Re and Os isotope data for gabbroic and basaltic lithologies

Sample reference	Mass (g)	[Re] ppt	[Os] ppt	$^{187}\text{Os}/^{188}\text{Os}^a$	$^{187}\text{Re}/^{188}\text{Os}$	[Os] ^b ppt	Blank (%)		Model age ^c (Myr)
							(Os)	(Re)	
<i>Gabbros</i>									
S01/5G	0.4055	300	13.22	0.3662±0.0025	106	12.82	5.8	11.3	130
dupl. ^d	2.0241	254	11.25	0.3893±0.0020	103	10.84	2.8	17.1	148
dupl.(CT) ^e	2.9711	307	11.20	0.3927±0.0099	135	10.81	7.5	1.0	115
S01/36ix	0.4164	227	23.29	0.2782±0.0088	46	22.83	0.6	5.0	184
dupl. ^d	0.4193	240	21.99	0.2841±0.0014	52	21.53	1.0	4.5	171
S01/39iiiix	0.4601	145	11.18	0.3336±0.0042	63	10.88	6.9	21.0	189
dupl. ^d	0.4066	208	19.93	0.3005±0.0028	50	19.48	0.7	5.4	199
S02/6ix	0.4016	507	253.4	0.1575±0.0008	9.4	252.3	0.1	2.3	142
dupl. ^d	2.0303	422	217.4	0.1616±0.0003	9.3	216.3	0.1	1.1	172
S02/10iiiixG	2.0854	170	57.57	0.1824±0.0010	12.6	57.12	0.4	23.6	225
S02/83vix	0.4110	292	81.44	0.1926±0.0008	16.4	80.69	0.9	11.6	210
dupl. ^d	2.0929	315	78.76	0.1941±0.0001	19.1	77.99	0.1	1.4	185
dupl. ^d	0.3054	279	79.13	0.1935±0.0006	16.2	78.39	0.2	8.2	216
S02/83viix	2.0493	209	2.81	1.204±0.015	392	2.47	1.5	1.9	163
S02/83viiiixG	2.1229	200	8.97	0.3091±0.0017	99	8.72	1.1	21.0	105
dupl.(CT) ^e	2.9643	234	6.86	0.434±0.018	168	6.59	12.2	1.4	107
S02/83viiiix	0.4044	338	2.56	2.742±0.135	978	1.34	10.9	0.4	160
<i>Transitional gabbroic eclogites</i>									
S01/5E	0.4007	452	22.77	0.3924±0.0034	95	22.00	3.4	7.8	163
dupl. ^d	0.4068	438	21.93	0.4025±0.0045	97	21.16	0.6	2.6	166
dupl. ^d	0.2950	435	21.18	0.4123±0.0018	99	20.41	0.7	5.4	167
S02/10iiiixE	0.4006	324	30.50	0.2452±0.0007	40.4	30.01	2.6	18.5	164
S02/83viiiixE	0.4056	237	9.87	0.3921±0.0022	115	9.54	1.3	6.8	134
<i>Gabbroic eclogites</i>									
S01/3iix	0.4199	224	47.72	0.1944±0.0013	22.2	47.27	0.3	4.5	161
dupl. ^d	0.3982	366	57.01	0.1890±0.0005	20.6	56.51	0.6	15.4	157
S01/35iix	0.4361	437	55.22	0.2279±0.0005	37.7	54.46	0.2	3.8	148
S01/35iiiix	0.4211	667	52.98	0.2720±0.0007	60.6	51.96	0.2	2.5	136
S01/40iiiix	0.4027	166	16.81	0.2738±0.0034	46.7	16.49	0.8	6.7	178
S01/40vix	0.4042	141	23.50	0.2281±0.0056	28.0	23.18	0.6	7.8	199
S01/40viix	2.0885	92	6.71	0.3266±0.0021	66.3	6.56	0.6	4.2	173
S02/33i	0.4219	133	17.42	0.2170±0.0007	35.1	17.21	0.7	11.6	140
S02/85ixE	0.4206	150	3.52	0.7523±0.052	221.6	3.25	3.6	12.1	172
<i>ZSO metabasaltic eclogites</i>									
<i>Pfulwe</i>									
S02/41ii	0.4236	1385	26.43	10.845±0.085	598	11.10	1.2	0.5	1065
S02/41v	0.3965	165	4.21	0.7947±0.0090	200	3.87	7.5	3.9	197
S02/74ii	0.4176	233	12.30	0.9728±0.0025	97.9	11.08	1.0	6.9	512
S02/75iC	0.4292	632	6.04	0.5905±0.0023	524	5.69	2.1	2.7	52
S02/75iiR	0.4260	147	10.32	0.3373±0.0010	66.8	10.03	1.2	10.6	182
S02/75iiiC	0.4082	194	43.08	0.4004±0.0009	21.9	41.57	0.7	3.3	722
S02/75iiiR	0.4125	267	13.60	0.6435±0.0027	98.9	12.74	2.3	2.4	308
S02/75ivC	0.3986	159	37.82	0.2638±0.0013	20.1	37.14	0.8	4.0	384
<i>Allalin</i>									
S02/4i	0.4057	230	2.41	3.06±0.30	443	1.74	18.7	44.9	395
S02/4iiiix	0.4165	725	7.58	1.043±0.003	508	6.77	1.8	1.4	107
<i>Allalin</i>									
S02/7i	0.4595	93	1.93	6.06±0.23	392	1.09	7.2	10.3	900

excluding 2 very Re-rich samples, [8]), but this may be due to the cumulate nature of the Allalin Gabbro. The data obtained here and those published previously [8,19] indicate that the mean concentrations of Re and Os in gabbroic lithologies are, respectively, lower and slightly higher than in MORB.

4.2.2. Metabasaltic eclogites

There is no clear co-variation between Re and Os in the metabasaltic suite. The mean Os abundance for the ZSO metabasalts is 15 ppt, and the mean Re abundance is 385 ppt. The average Os content falls within the range observed for MORB (<1–50 ppt, [7,20], Gannoun, personal communication) although is slightly higher than the MORB mean of ~8 ppt. However, the average Re concentration is considerably lower than that of typical MORB which has a mean of ~1.1 ppt ([7,21], Gannoun, personal communication).

4.3. Re–Os isotope data

4.3.1. Gabbroic lithologies

Gabbroic rocks possess high Re/Os ratios which lead to radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios at the present-day, compared to their parental mantle source. The least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ value measured is 0.158 for an Os-rich gabbro, while an Os-poor gabbro has evolved to a composition of 2.74 (Table 1). Surprisingly, regression of the isotope data (Fig. 5) for unaltered gabbros and completely recrystallised gabbroic eclogites yields best-fit lines with indistinguishable slopes (and initial isotope compositions) which therefore indicate very similar ages. The combined dataset (gabbro and eclogite) yields an errorchron age of 160 ± 6 Ma (MSWD = 114), with an initial isotopic composition of 0.137. While the scatter of data about the best-fit line is too great for this to be considered as an isochron, this age estimate is indistinguishable from the 164 Ma U–Pb zircon age for the Allalin unit [9], considered to represent the time of magmatic crystallisation.

Several hand specimens can be divided into a gabbroic portion (which has not experienced any fluid infiltration) and a transitional portion (variably recrystallised during sea-floor and subduction-related fluid

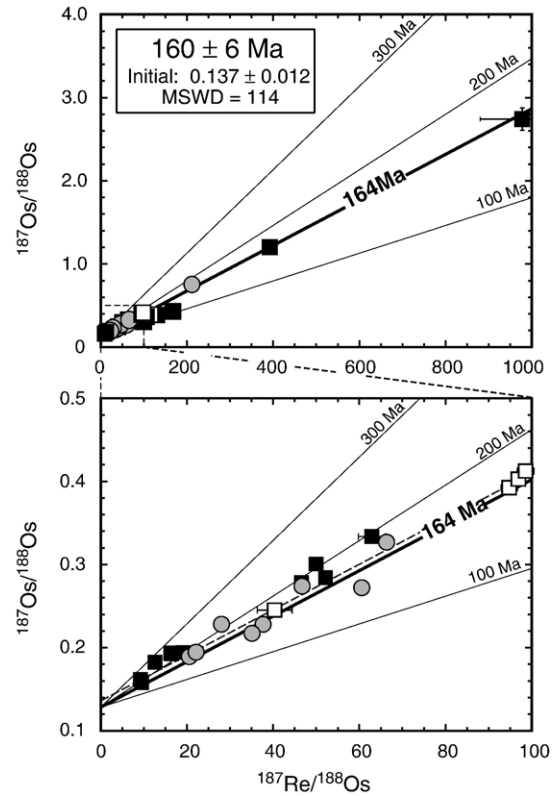


Fig. 5. ^{187}Re – ^{187}Os isochron diagram for gabbroic lithologies from the Allalin Gabbro (ZSO). (Symbols — see Fig. 3). The gabbro and gabbroic eclogite data define indistinguishable age-trends which are in good agreement with the 164 Ma reference line. Regression of the data, using *Isoplot*, gives an ‘errorchron’ age within error of the 164 Ma U–Pb age of magmatic zircon [9], and a reasonable initial composition.

infiltration). These samples provide a window on the effects of seafloor alteration, as their proximity to the 164 Ma reference line on the isochron plot precludes major changes to the Re–Os system at any time significantly after igneous crystallisation. Two of the transitional portions are characterised by increased Re/Os ratios compared to their respective protoliths, while the other remains the same within error. Osmium concentrations differ noticeably; one is higher, one lower and the third is comparable to the gabbroic portion of the same sample, though this variation could be

Notes to Table 1:

^a Errors shown are $2\sigma_{\text{mean}}$; $^{187}\text{Os}/^{188}\text{Os}$ ratios normalised using $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ and corrected using measured $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ of 0.002047 and 0.00037 respectively; given isotope ratios are blank corrected.

^b Denotes ‘common’ Os: total Os after subtraction of in-grown ^{187}Os .

^c Model age was calculated using $\text{TMA} = 1/\lambda * \text{Ln}[(^{187}\text{Os}/^{188}\text{Os})_{\text{sample}} - (^{187}\text{Os}/^{188}\text{Os})_{\text{chond}}] / [(^{187}\text{Re}/^{188}\text{Os})_{\text{sample}} - (^{187}\text{Re}/^{188}\text{Os})_{\text{chond}}]$.

^d Replicates of the same powder through repeated chemistry and mass spectrometry.

^e Samples duplicated (~2 g of powder) using inverse aqua regia (3 ml HCl:9 ml HNO₃) in sealed Carius tubes at 230 °C for 7 days. Os was extracted and purified using CCl₄ and concentrated HBr, respectively. Re was extracted from the inverse aqua regia using iso-amylol [58,59].

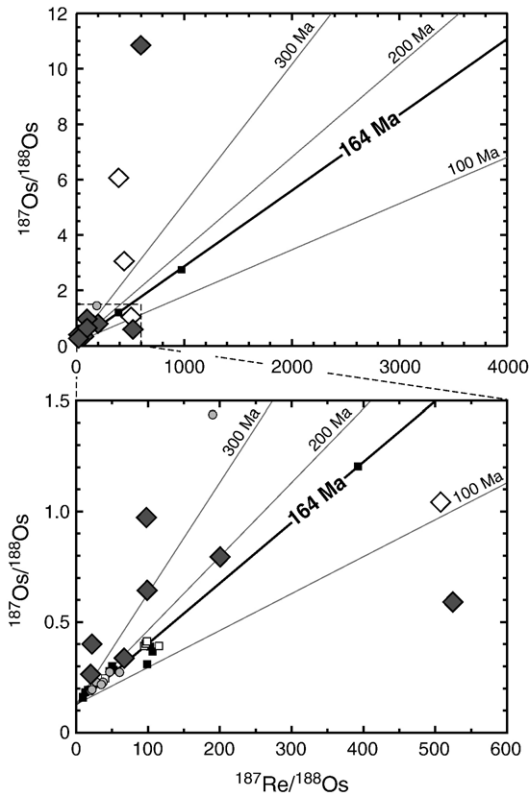


Fig. 6. ^{187}Re – ^{187}Os isochron diagram for basaltic eclogites from the ZSO. All but two of the basaltic data lie to the upper-left of the 164 Ma reference line and possess Re/Os ratios that are too low to account for their $^{187}\text{Os}/^{188}\text{Os}$ ratios. This indicates a potential episode of Re loss, a significant time after crystallisation.

explained by variable sampling of Os-rich microphases, the so called ‘nugget effect’. Rhenium abundances increase in all the samples and in two cases Re addition has been greater than 40% of the initial composition, or over 100 ppt in absolute terms. Therefore, Re enrichment appears to have taken place in these gabbros with no subsequent loss during subduction dehydration.

4.3.2. Basaltic eclogites

Due to the compatible nature of Os (and incompatible behaviour of Re) basalts tend to possess higher $^{187}\text{Re}/^{188}\text{Os}$ ratios than gabbros (this study [7,8,22]). This explains why the metabasalt samples analysed here display a greater range of $^{187}\text{Os}/^{188}\text{Os}$ values than in the gabbro suite (Table 1 and Fig. 6). In contrast to the data for gabbroic lithologies, the metabasalts do not reveal an age-indicative co-variation of $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ (Fig. 6). Rather, the majority of the basaltic eclogites lie to the upper-left of the 164 Ma reference line and thus have Re concentrations which are too low to explain their radiogenic Os isotopic composition.

5. Discussion

5.1. Major and trace element behaviour during eclogite-facies metamorphism

Large ion lithophile element (LILE) abundances are typically elevated in arc melts which are considered to result from the mobility of these elements in fluids during dehydration in the slab. The data for Ba (Fig. 3a) and for Rb and K (not shown) obtained here are consistent with depletion during dehydration. The behaviour of Sr is less clear (Fig. 3b) and is likely to be dominated by the processes of plagioclase accumulation (in the gabbros) and fractional crystallisation (in the basalts). For the basalts this may mask any loss of Sr. Most of the Allalin metabasalts contain greater Sr/Yb ratios than MORB, which may result from limited fractional crystallisation or else an enrichment in Sr during metamorphism.

The absence of any evidence for U depletion is in accord with a number of other high-pressure terrain studies [23–25], and has consequences for any hypothesis that explains U enrichment in arc melts through its mobility during dehydration of mafic crust. It has been suggested that U loss from basaltic material does not occur at temperatures ≤ 600 °C [24] — consistent with the absence of U depletion in metabasites in the ZSO (this study, max $T = \leq 600$ °C), the Raspas complex, Ecuador (< 600 °C [23]) and New Caledonia (~ 600 °C [25]). Subduction zones which consume old oceanic crust may remain at temperatures below 600 °C beyond pressures of 3.0 GPa (even with slow subducting slabs) [26,27], and thus may not undergo substantial U loss at the depth required for a significant flux into the mantle source of arc magmas. In this case, alternative hypotheses may be required, one possibility being that the main U flux is derived from subducted sediments, although high $^{238}\text{U}/^{230}\text{Th}$ ratios in many arc rocks may not be consistent with marine sediment input [28]. Another explanation to explain the lack of a complementary isotopic signature to match a large flux of elements from the slab, involves the ‘stripping’ of mantle by slab-derived fluids, thus a large part of the elemental input into arc magma sources need not be derived from the slab itself [29]. Significantly, experimental data [30] indicates that fluid–mineral partitioning of U is dependent on fluid composition and increases dramatically ($D_{\text{fluid}}/D_{\text{cpx}} < 0.3$ –36) as the Cl content of the fluid increases. The absence of U depletion in the Allalin eclogites and the presence of very low Cl concentrations within the vein mineralogy (below detection limits, < 150 ppm) is consistent with

this experimental finding. If U mobility is highly variable, it is possible that some recycled material may possess higher $^{238}\text{U}/^{204}\text{Pb}$ (μ) ratios than predicted, which, in turn, may have implications for the modelling of HIMU sources.

5.2. Re and Os behaviour during subduction metamorphism

5.2.1. Gabbroic lithologies

The distribution of Os and Re in the gabbros is highly variable and may be influenced by the ‘nugget effect’ or some other sampling bias. Therefore, a more robust means of assessing the behaviour of Re and Os in these rocks is through the analysis of ^{187}Re – ^{187}Os isotope variations. The isotope data for the gabbros define an errorchron with an age that is indistinguishable from the igneous age of this body. This is a key observation because it indicates that the Re–Os system has remained largely ‘closed’ during high-pressure metamorphism and that significant Re loss cannot have occurred in any of the gabbroic eclogites, at least not any substantial time after crystallisation.

5.2.2. Basaltic lithologies

In contrast, the absence of any ^{187}Re – ^{187}Os age information in the ZSO metabasalt suite suggests that the system has been perturbed by a process subsequent to igneous crystallisation, most likely during high-pressure metamorphism. While there has been no direct dating of igneous crystallisation of the ZSO basalts, there is a minimum age constraint of 153–154 Ma from the dating of ophiolitic sediments at Sparrenflue [9]. Furthermore, the age of the basalts is likely to be very similar to that of the gabbro since there is no field evidence for km scale transport between the Allalin Gabbro and the metabasalts of the ZSO.

If the basalt age is indeed similar to that of the gabbro, then most basalts possess $^{187}\text{Re}/^{188}\text{Os}$ ratios that are lower than required to generate the measured $^{187}\text{Os}/^{188}\text{Os}$ ratios over the last 164 Ma (Fig. 6). This could either result from a reduction in Re, or else an addition of Os. The behaviour of Os in these samples is difficult to constrain because there is no co-variation with any other element, although the Os abundance in the basalts is comparable to that of MORB, suggesting that Os loss has not occurred. In contrast, Re behaves as a moderately incompatible element and consequently Yb (or Y) and Re data are usually positively correlated. Published data for MORB [7] define a well-constrained Re vs. Yb trend and thus Re concentrations can be compared to those expected for their given Yb concentration (Fig. 7). Measured Re

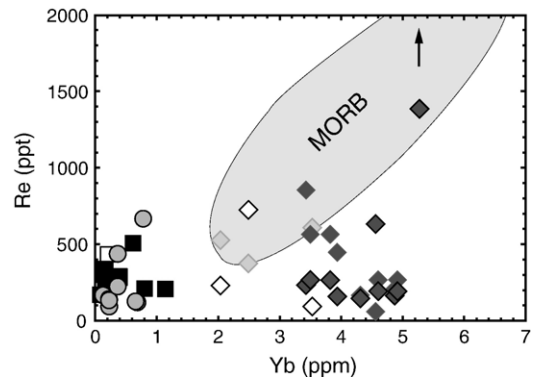


Fig. 7. Yb concentration plotted against Re. (Symbols — see Fig. 3). MORB data define a broad field with positive co-variation [7], in which few of the basaltic eclogites lie. Yb contents of the basaltic eclogites are comparable to those of MORB but Re concentrations are markedly lower, further evidence for the proposed Re loss. Estimates of initial Re content from the isochron diagram (dark grey diamonds, no border — Pfulwe basalts, light grey diamonds — Allalin) are also significantly lower than MORB for several samples. This can be explained by Re loss during eruptive degassing in a shallow basin.

concentrations for ZSO metabasalts are almost all lower than typical MORB for a given Yb abundance indicating significant Re loss of 40 to 90% (with a mean of 63%).

If Os is assumed to be immobile, and therefore present in the same concentration as before metamorphism, then the degree of Re loss can also be estimated using the isochron. The position of a data point on a 120 Ma age reference line (the time of metamorphism with respect to the igneous crystallisation age — ~ 45 Ma before present), can be back-calculated using the measured $^{187}\text{Re}/^{188}\text{Os}$ ratio and therefore the initial Re/Os ratio and Re abundance can be estimated. Using this method, the average Re loss for the metabasaltic eclogites is 53%, comparable to the previously published estimate of approximately 60% Re loss from basaltic samples subjected to HP metamorphism [6]. It is of interest to note that the initial Re concentrations estimated in this way are considerably lower than those expected given the measured Yb content. One possible explanation is that Os is also mobile during metamorphism and was also depleted in the samples, leading to an underestimate of the initial Re concentration. Alternatively, substantial Re loss may have occurred during volcanic degassing at the time of emplacement of the basalts [31]. Thirdly, sulphide fractionation could fractionate Re from Yb [32], but there is little to suggest that the fractionation history of the ZSO basalts differs significantly from published MORB samples. The available data do not provide a means of discriminating between these possibilities, although the small, young basin into which these basalts were extruded was likely to have been shallow, consistent with volatile loss of Re [31].

5.3. Recycling of oceanic crust in the mantle

A number of authors have suggested that metasomatised lithospheric mantle in the source of OIB can explain the observed isotopic signatures and trace element chemistry [33–35]. While the argument in favour of such material for many OIB is attractive, whether or not it is a viable source for HIMU-type OIB is less clear. Some evidence suggests that significant Re addition and/or Os loss does not occur during metasomatism [36]. However, other work indicates that the Re–Os system can be perturbed by melt percolation [e.g. [37–39]], although it is unclear whether the scale of Re addition would be great enough to account for the observed $^{187}\text{Os}/^{188}\text{Os}$ in time-scales over which very radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ values would be generated [35]. It may also be possible to generate radiogenic Os signatures through entrainment of outer core material into lower mantle plumes, given the likelihood of a high Re/Os ratio for the outer core [40]. However, the lithophile nature of U compared to Pb precludes a high U/Pb ratio in the outer core and therefore core–mantle interaction is unlikely to impart elevated $^{206}\text{Pb}/^{204}\text{Pb}$ to mantle material, which, in turn, would imply decoupling of the U–Pb and Re–Os sources.

Major element compositions have been used to infer that many OIB cannot be produced by the melting of pyroxenite layers thought to represent recycled oceanic crust (e.g. [6] and references therein). The high silica content of pyroxenites is thought to preclude the derivation of silica-deficient melts of the type seen in some OIB. However, recent experimental work [41] suggests that it may be possible to produce silica-poor magmas from the melting of garnet pyroxenite. This is because most MORB-eclogites are too silica-rich, but olivine-bearing gabbros or MORB/lower oceanic crust mixtures have low silica and high MgO contents that makes them appropriate compositions for garnet pyroxenites that would melt to produce alkaline OIB at high pressures [41]. On this basis, it may not be necessary to place a low upper limit on the proportion of oceanic crust in the mantle source of OIB.

In any event, the elevated $^{187}\text{Os}/^{188}\text{Os}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ signatures in many OIB have been, at least in part, attributed to the presence of ancient recycled oceanic crust (possessing high Re/Os and U/Pb ratios) in the mantle source [2,3,5,42,43,44]. The data obtained in this study, combined with Os and Pb data previously published, can be used to assess whether ancient recycled oceanic crust is a viable source component for many OIB when present in geologically reasonable amounts, and in particular, whether the observed isotopic compositions could be generated from mantle containing a complete section of oceanic crust (that is, gabbro and basalt).

Previous work suggests that significant Re loss occurs during subduction, resulting in lower $^{187}\text{Re}/^{188}\text{Os}$ ratios in recycled mafic crust [6]. Consequently, over time subducted MORB will evolve to less radiogenic Os isotope compositions than would be anticipated from unaltered MORB. This requires that the mantle sources of some OIB contain very high proportions of recycled material, some 70 to 90%, perhaps inconsistent with the major element chemistry of alkaline OIB. Alternatively, it may be possible to generate the observed ratios with lower proportions of recycled crust in the source if bulk mixing is not appropriate or, if as is likely, preferential melting of mafic lithologies occurs.

There are several ways in which the modelling presented here differs from that undertaken previously [6]. Firstly, the gabbroic portion of the crust has been included, and is elementally distinct from basaltic crust (this study, [8,19,45]), resulting in a different isotopic evolution. Secondly, the basalt data obtained here are not considered representative of the Re–Os composition of subducted basaltic material, due to their higher Os and lower MgO content than typical MORB. It is also possible that the ZSO basalts experienced Re loss during degassing (which does not appear to be significant in deeper oceanic basins [7,31]) thus, the Yb–Re method for estimating initial Re may overestimate Re loss during metamorphism. Consequently, 50% Re loss from the metabasalts is referenced to published data for MORB glass ([7,21], A. Gannoun, pers. comm.). Whether the Os isotope composition of MORB glass is truly representative of the mantle source is a subject of debate [e.g. [46,47]], but it is unlikely that the measured Re and Os concentrations are significantly in error. It has also been assumed that subducting oceanic crust has evolved, on average, for 50 Ma prior to subduction modification. This is a younger age than that of subducting crust at the present-day (~120 Ma [48]) but evidence suggests that plate movement was more rapid in the early Proterozoic and thus the average age of subducted crust could have been as low as 25–40 Ma [48].

The abundances and ratios used in these calculations are presented in Table 4 (supplementary material). In this model, it has been assumed that the U–Pb budget of half the basaltic crust has been modified by hydrothermal alteration while the other half consists of unaltered N-MORB (values from [49,50]). The U–Pb data used for gabbroic crust includes some samples which have experienced hydrothermal alteration (this study, [19,51]). Subsequently, the entire volume of basaltic crust has been modified (in terms of U–Pb) during subduction, on the basis of evidence from natural samples [24] (One mixing line has been calculated based on crust that has undergone U and Pb loss indicated by experimental data

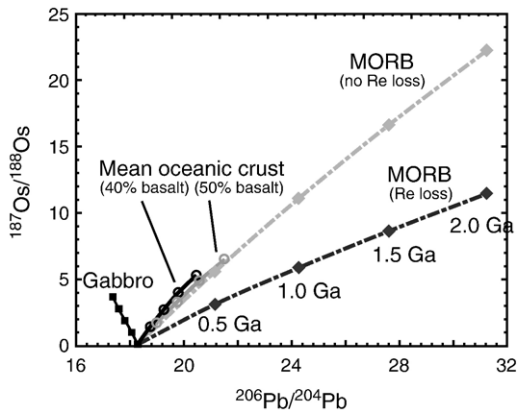


Fig. 8. Evolution of basalt, gabbro and complete oceanic crust in ^{187}Os – ^{206}Pb space. All curves are calculated assuming modification of U and Pb through hydrothermal alteration (values from [50]) and subduction (using evidence from natural samples, (this study, [24])). However, it is assumed that subduction affects the entire basaltic section of crust, but due to the differing rheology/hydration of gabbro, the model only includes subduction modification of half the gabbroic section: therefore loss of U and Pb has not occurred in 50% of the gabbro. Re–Os evolution is calculated assuming all basalt has lost 50% of its original Re (this study, [6]), while gabbro has not undergone any Re loss (this study). MORB possesses much higher $^{187}\text{Re}/^{188}\text{Os}$ ratios than MOR-gabbro, thus over time MORB evolves to a much more radiogenic Os isotopic composition. However, average MORB contains less Os than average MOR-gabbro and therefore has a lesser impact when mixed with the mantle.

[52]. Due to the more competent and less hydrated nature of gabbroic bodies, only half of the gabbroic crust has been modified for U and Pb. Previous studies indicate that significant net fluxes of Re and Os do not occur during hydrothermal alteration [22,53], although it is possible that redistribution is a significant process promoting Re loss from basalts during subduction. MORB has been modelled both with no Re loss and with 50% Re loss during subduction (this study, [6]). For complete crust, it has been assumed that the basaltic volume loses 50% Re but the gabbroic volume does not lose any Re (this study). Combined crust is assumed to comprise 60% gabbro, and altered and unaltered MORB in equal quantities (20% of each). The gabbro section comprises some cumulate gabbros (this study, [45]) and isotropic gabbros (50% of each) [8].

Unmodified MORB will develop $^{187}\text{Os}/^{188}\text{Os}$ of ~ 22 over 2 Ga (Fig. 8), whereas 50% Re loss from basaltic material during subduction will yield $^{187}\text{Os}/^{188}\text{Os}$ ratios of only ~ 11.0 over the same period of time. Gabbros will also develop very radiogenic Os isotope signatures, but not as high as those of MORB due to their lower Re/Os ratios. The incorporation of gabbro in the evolution of the entire oceanic crust leads to considerably less radiogenic Os isotope compositions than those generated

in MORB alone. However, the higher abundance of Os in gabbros means that they have a greater impact on the Os composition of the mantle compared to MORB. Fig. 9 illustrates the isotope compositions produced when 2 Ga gabbro, MORB and complete oceanic crust are mixed with mantle of enriched plume (EP) composition (see [54]). If gabbros retain their magmatic Re/Os ratios, they can generate Os isotope signatures that are comparable to those of subducted whole crust or MORB (when the basaltic portion is assumed to have lost $\sim 50\%$ Re). The evolution of unaltered MORB would lead to considerably more radiogenic compositions, which would yield a $^{187}\text{Os}/^{188}\text{Os} = 0.150$ in 1.5 Ga with 30% recycled material in the source. Table 3 (supplementary material) contains data for 1 and 2 Ga crust and illustrates that relatively old ages (≥ 2.0 Ga) of recycled material are required to attain the radiogenic Os signatures of HIMU-type OIB, given the estimated isotope composition of subducted oceanic crust. A

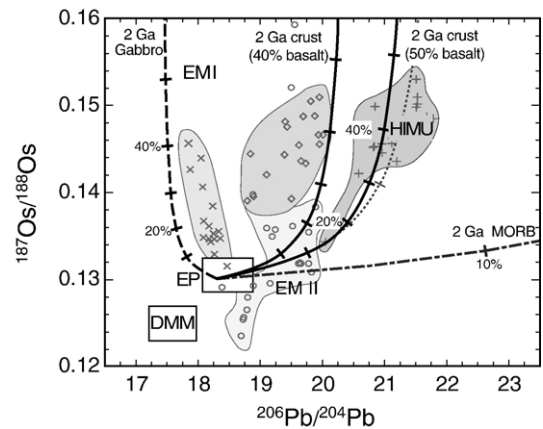


Fig. 9. Mixing of oceanic crust components with enriched-plume (EP) mantle in ^{187}Os – ^{206}Pb isotope space. Key to symbols — see Fig. 8. Mixing of EP mantle with subducted MORB, of which 50% has been modified by hydrothermal alteration [50], results in extremely high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios over 2 Ga. In contrast, subducted gabbro produces mantle with a lower Pb isotope signature than the ambient mantle. Complete sections of oceanic crust, 40:60 basalt–gabbro (black) and 50:50 basalt–gabbro (grey), produce mixing arrays which require ~ 40 – 50% recycled material to produce the extreme OIB compositions found in the Canary Islands and HIMU-type OIB respectively. The fine, grey dashed line denotes mixing with complete crust (40:60 basalt–gabbro) that has undergone Pb and U loss according to experimental values [52]. See Table 4 (supplementary material) and text for details of the parameters used. Crosses (+) denote ‘HIMU type’ OIB [2,44], open diamonds are data from the Canary Islands [3,42], crosses (x) are data from Hawaii [62,63] which plot between the EP and EMI components, open circles are data from EMII islands [2,43,44]. With the exception of much of the EMII data all OIB have elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios compared to primitive or depleted MORB mantle values. HIMU islands and Canary Island data are therefore differentiated by Pb isotopes, but both require a source of radiogenic Os.

similar timescale has been inferred from Pb isotopes by a number of authors on the basis that the correlation between ^{206}Pb and ^{207}Pb has age significance [e.g. [1]].

Without alteration MORB evolves to $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of approximately 21 over 2 Ga, however, with increased U/Pb ratios resulting from alteration and subduction, $^{206}\text{Pb}/^{204}\text{Pb}$ of >21 can be generated in 500 Ma. It has been suggested that if HIMU mantle contains recycled oceanic crust then it must be relatively young (≤ 0.5 Ga), otherwise melts from such mantle would possess more radiogenic Pb than is observed even in extreme HIMU [6]. At first sight, this conclusion is at odds with the requirement of 2 Ga ages given by Os isotopes. However, crucially, gabbroic oceanic crust contains low concentrations of U relative to Pb (this study, [19,45]) and thus does not generate radiogenic signatures, and in fact develops lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than the ambient mantle. Furthermore, Pb concentrations in gabbro are somewhat higher than those of MORB [19,45], and as a consequence this has a strong influence on the evolution of the crust as a whole, and significantly limits the development of high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios, and thus permits older ages for the recycled component. In any event, Pb isotope data suggests that young recycled crust would impart a negative $\Delta^{207}\text{Pb}/^{204}\text{Pb}$ to the source of OIB (compared to the Northern Hemisphere reference line), and this is not observed in extreme HIMU-OIB (e.g. Mangaia) [55].

Thus, a complete section of oceanic crust may generate considerably lower $^{206}\text{Pb}/^{204}\text{Pb}$ ratios than MORB that has in part undergone seafloor and subduction alteration. As only half of the gabbroic volume has been modified by subduction, complete crust evolves to Pb compositions which are too low to account for HIMU-type OIB. Therefore, to attain the necessary Pb composition a greater proportion of basalt ($\geq 50\%$) is required in the crust as a whole (or $\sim 40\%$ using the experimental values). Due to the high Pb concentrations in sediments, the addition of $\sim 2\%$ sediment also drastically decreases the evolved Pb isotope ratios [56], though much of this Pb may be lost during subduction. Sediment, like gabbro, only has a small effect on the Os isotope evolution [5], thus the addition of sediment and gabbro cannot easily be differentiated in terms of Pb or Os isotopes, but will produce different signatures for other tracers such as Sr. In addition, lower oceanic crust may impart a positive Eu and/or Sr anomaly to OIB. However, the absence of a Eu anomaly does not preclude the presence of gabbro in the source as it may be balanced by a complementary negative anomaly in recycled basalt and secondly, plagioclase fractionation in an OIB melt may overprint any positive Eu anomaly from the source. The addition of

pelagic sediments, with relatively low Re/Os and only moderate Os concentrations [57] may not be sufficient to explain the radiogenic Os signatures observed, particularly if sediments, like basalts, lose a large proportion of their Re during subduction.

The result of these calculations is that a $\geq 40\%$ recycled component is required in the mantle source of some OIB, higher than estimates using lithophile isotope systems [2,4,5,44]. However, as Re and Os abundances in oceanic crust are heterogeneous and poorly constrained, particularly for the gabbroic portion, it is possible that estimates of Re/Os ratios in oceanic crust are conservative. If so, HIMU signatures may be generated with lower proportions of crust. Furthermore, it has been established that eclogite and/or pyroxenite have lower solidus temperatures, and greater melt productivity, than peridotites. Thus for a source with 5% pyroxenite, 15–20% of the melt may be derived from pyroxenite [58], and such differential melt production will be more significant for low degree melts such as those seen in some OIB. Consequently, radiogenic Os from the oceanic crustal portion of the mantle source may be preferentially incorporated into the melt (e.g. [6]), and this remains a plausible process which would considerably reduce the required quantities of recycled crust in OIB sources.

5.4. Implications

The nature of U–Pb and Re–Os distribution in the crust and the fluid-mobile nature of Pb, and possibly U, results in markedly different evolution of the two isotope systems. By varying the proportions of basalt and gabbro within the recycled crust, significantly different Pb isotope values can be generated while at the same time having little effect on Os isotopes. It is possible that OIB which possess high Os isotope ratios, but relatively low $^{206}\text{Pb}/^{204}\text{Pb}$ values [3,42], are the result of a greater input of gabbroic material into the source, thus lowering the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio, but not significantly affecting the Os signature. Previously, the favoured explanations for OIB with this signature were either the recycling of oceanic crust with lower U/Pb ratios, or a relatively young age (1.2 Ga) for the recycled component [3,42].

The suggestion that individual components of recycled lithosphere may give rise to the isotopic variations observed within a single plume has been proposed by several authors. For example, it has been suggested that the range of OIB compositions in the French Polynesian islands are the result of sampling of various parts of recycled lithosphere (HIMU: altered mafic crust, EMI and II: the addition of entrained sedimentary material) [56]. It has also been suggested that Os, O and Pb data from

Hawaii are consistent with some islands having a source which has a significant component of recycled oceanic crust (plus sediment), whereas other islands display unradiogenic Os isotope signatures and light oxygen isotopes which suggest a lithospheric component [59]. It is interesting to note that unradiogenic Pb isotope ratios in the Hawaiian plume (EMI mantle component) can be generated by ancient recycled gabbro, while the presence of gabbro in the source has been independently inferred due to the occurrence of positive Eu anomalies [60]. Finally, the presence of gabbroic recycled crust in the source of Icelandic picritic lavas has been proposed on the basis of strong positive Sr and Pb anomalies [61].

6. Conclusions

Basaltic material is likely to lose a significant proportion of its original Re during subduction-related metamorphism (~50–60%, this study, [6]). In contrast, the gabbroic samples analysed in this study do not display any significant depletion of Re and the Re–Os system appears to have remained ‘closed’ during eclogite-facies metamorphism. Although gabbros have lower Re/Os ratios than basaltic crust, their higher Os abundance results in a greater contribution to the mantle Os budget than basalts. In addition, gabbros usually constitute a larger proportion of oceanic crust and therefore have the potential to play a significant role in determining the signature imparted to the mantle by recycled oceanic crust.

Modelling of Os and Pb isotopes over 2 Ga timescales indicates that recycled basalt alone will evolve to very radiogenic Os and Pb isotope signatures. By mixing such basalt with ‘enriched plume’ mantle the resulting Pb isotopic value is considerably higher than any known OIB, while $^{187}\text{Os}/^{188}\text{Os}$ is comparable to HIMU-type OIB. However, the effect of combining gabbro (60%) with basalt (40%) (i.e. complete crust) is that the resulting source has a less radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ composition but retains a similar $^{187}\text{Os}/^{188}\text{Os}$ composition. Gabbro, therefore, potentially plays a key role in limiting the development of high $^{206}\text{Pb}/^{204}\text{Pb}$ ratios while having little impact on the Os isotope evolution. It is possible that HIMU-type OIB could result from melting of a mantle source which contains a significant proportion ($\geq 40\%$) of complete oceanic crust consisting of MORB and complementary gabbros, and that other OIB may result from a larger proportion of gabbro in their source.

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Appendix A

The isotopic composition of oceanic crust was modelled assuming isolated evolution within the mantle, with subsequent mixing. The following mixing equation was used:

$$\begin{aligned} &^{187}\text{Os}/^{188}\text{Os}_{(\text{total})} \\ &= \frac{(f * [\text{Os}]_{\text{C1}} * ^{187}\text{Os}/^{188}\text{Os}_{\text{C1}}) + ((1-f) * [\text{Os}]_{\text{C2}} * ^{187}\text{Os}/^{188}\text{Os}_{\text{C2}})}{(f * [\text{Os}]_{\text{C1}}) + ((1-f) * [\text{Os}]_{\text{C2}})} \end{aligned}$$

A note on average Re–Os concentrations. Despite the ever-growing Re–Os dataset, there remains a relatively small dataset for low Os mafic samples. Furthermore, the extremely heterogeneous distribution of Re and Os makes establishing an ‘average’ whole-rock composition problematic. Median abundance values for Os and Re in gabbros and MORB are lower than mean values. However, Os is relatively lower than Re and therefore the median gives a higher $^{187}\text{Re}/^{188}\text{Os}$ ratio, and over time a higher $^{187}\text{Os}/^{188}\text{Os}$, but its impact in the mantle is less. Mean values are used herein because it is considered important to include the full range of abundances which would otherwise be omitted with a median value.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.epsl.2006.10.029](https://doi.org/10.1016/j.epsl.2006.10.029).

References

- [1] A.W. Hofmann, W.M. White, Mantle plumes from ancient oceanic-crust, *Earth Planet. Sci. Lett.* 57 (2) (1982) 421–436.
- [2] L. Reisberg, A. Zindler, F. Marcantonio, W. White, D. Wyman, B. Weaver, Os isotope systematics in ocean island basalts, *Earth Planet. Sci. Lett.* 120 (3–4) (1993) 149–167.
- [3] F. Marcantonio, A. Zindler, T. Elliott, H. Staudigel, Os isotope systematics of La Palma, Canary-Islands — evidence for recycled crust in the mantle source of HIMU ocean islands, *Earth Planet. Sci. Lett.* 133 (3–4) (1995) 397–410.
- [4] E. Widom, Sources of ocean island basalts: a review of the osmium isotope evidence, *Physica A* 244 (1–4) (1997) 484–496.
- [5] M. Roy-Barman, C.J. Allegre, $^{187}\text{Os}/^{186}\text{Os}$ in Oceanic Island Basalts — tracing oceanic-crust recycling in the mantle, *Earth Planet. Sci. Lett.* 129 (1–4) (1995) 145–161.

- [6] H. Becker, Re–Os fractionation in eclogites and blueschists and the implications for recycling of oceanic crust into the mantle, *Earth Planet. Sci. Lett.* 177 (3–4) (2000) 287–300.
- [7] P. Schiano, J.L. Birck, C.J. Allegre, Osmium–strontium–neodymium–lead isotopic covariations in mid-ocean ridge basalt glasses and the heterogeneity of the upper mantle, *Earth Planet. Sci. Lett.* 150 (3–4) (1997) 363–379.
- [8] J. Blusztajn, S.R. Hart, G. Ravizza, H.J.B. Dick, Platinum-group elements and Os isotopic characteristics of the lower oceanic crust, *Chem. Geol.* 168 (1–2) (2000) 113–122.
- [9] D. Rubatto, D. Gebauer, M. Fanning, Jurassic formation and Eocene subduction of the Zermatt-Saas-Fee ophiolites: implications for the geodynamic evolution of the Central and Western Alps, *Contrib. Mineral. Petrol.* 132 (3) (1998) 269–287.
- [10] T. Reinecke, Very-high-pressure metamorphism and uplift of coesite-bearing metasediments from the Zermatt-Saas zone, Western Alps, *Eur. J. Mineral.* 3 (1) (1991) 7–17.
- [11] J. Meyer, Mineralogie und Petrologie des Allalingsabbros. Unpublished PhD thesis., PhD thesis, 1983b.
- [12] A.C. Barnicoat, N. Fry, High-pressure metamorphism of the Zermatt-Saas ophiolite zone, Switzerland, *J. Geol. Soc.* 143 (1986) 607–618.
- [13] A.C. Barnicoat, V71C-07: dolomite breakdown under ultra-high pressure conditions in the Allalin Gabbro of SW Switzerland, *American Geophysical Union* 77 (46) (1996) 762.
- [14] J.M. Amato, C.M. Johnson, L.P. Baumgartner, B.L. Beard, Rapid exhumation of the Zermatt-Saas ophiolite deduced from high-precision Sm–Nd and Rb–Sr geochronology, *Earth Planet. Sci. Lett.* 171 (3) (1999) 425–438.
- [15] J.L. Birck, M.R. Barman, F. Capmas, Re–Os isotopic measurements at the femtomole level in natural samples, *Geostand. Newsl.* 21 (1) (1997) 19–27.
- [16] R.A. Creaser, D.A. Papanastassiou, G.J. Wasserburg, Negative thermal ion mass-spectrometry of osmium, rhenium, and iridium, *Geochim. Cosmochim. Acta* 55 (1) (1991) 397–401.
- [17] J. Volkening, T. Walczyk, K.G. Heumann, Osmium isotope ratio determinations by negative thermal ionization mass-spectrometry, *Int. J. Mass Spectrom. Ion Process.* 105 (2) (1991) 147–159.
- [18] J.A. Pearce, Role of the sub-continental lithosphere in magma genesis at active continental margins, in: *Continental Basalts and Mantle Xenoliths*, C.J. Hawkesworth, M.J. Norry (Eds.), Shiva, Nantwich, UK, 1983, pp. 230–249.
- [19] S.R. Hart, J. Blusztajn, H.J.B. Dick, P.S. Meyer, K. Muehlenbachs, The fingerprint of seawater circulation in a 500-meter section of ocean crust gabbros, *Geochim. Cosmochim. Acta* 63 (23–24) (1999) 4059–4080.
- [20] M. Roy-Barman, C.J. Allegre, ^{187}Os – ^{186}Os Ratios of mid-ocean ridge basalts and abyssal peridotites, *Geochim. Cosmochim. Acta* 58 (22) (1994) 5043–5054.
- [21] W. Sun, V.C. Bennett, S.M. Eggins, R.J. Arculus, M.R. Perfit, Rhenium systematics in submarine MORB and back-arc basin glasses: laser ablation ICP-MS results, *Chem. Geol.* 196 (1–4) (2003) 259–281.
- [22] B. Peucker-Ehrenbrink, W. Bach, S.R. Hart, J. Blusztajn, T. Abbruzzese, Rhenium–osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP sites 504 and 417/418, *Geochem. Geophys. Geosyst.* 4 (7) (2003), doi:10.1029/2002GC000414.
- [23] R.J. Arculus, H. Lapierre, E. Jaillard, Geochemical window into subduction and accretion processes: Raspas metamorphic complex, Ecuador, *Geology* 27 (6) (1999) 547–550.
- [24] H. Becker, K.P. Jochum, R.W. Carlson, Trace element fractionation during dehydration of eclogites from high-pressure terranes and the implications for element fluxes in subduction zones, *Chem. Geol.* 163 (1–4) (2000) 65–99.
- [25] C. Spandler, J. Hermann, R. Arculus, J. Mavrogenes, Geochemical heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia, *Chem. Geol.* 206 (1–2) (2004) 21–42.
- [26] S. Poli, M.W. Schmidt, Petrology of subducted slabs, *Annu. Rev. Earth Planet. Sci.* 30 (2002) 207–235.
- [27] S.M. Peacock, The importance of blueschist-eclogite dehydration reactions in subducting oceanic-crust, *Geol. Soc. Amer. Bull.* 105 (5) (1993) 684–694.
- [28] C.J. Hawkesworth, K. Gallagher, J.M. Hergt, F. McDermott, Mantle and slab contributions in arc magmas, *Annu. Rev. Earth Planet. Sci.* 21 (1993) 175–204.
- [29] R.J. Arculus, R. Powell, Source component mixing in the regions of arc magma generation, *J. Geophys. Res., Solid Earth Planets* 91 (B6) (1986) 5913–5926.
- [30] H. Keppler, Constraints from partitioning experiments on the composition of subduction-zone fluids, *Nature* 380 (6571) (1996) 237–240.
- [31] J.C. Lassiter, Rhenium volatility in sub-aerial lavas: constraints from subaerial and submarine portions of the HSDP-2 Mauna Kea drillcore, *Earth Planet. Sci. Lett.* 6766 (2003) 1–15.
- [32] M. Roy-Barman, G.J. Wasserburg, D.A. Papanastassiou, M. Chaussidon, Osmium isotopic compositions and Re–Os concentrations in sulfide globules from basaltic glasses, *Earth Planet. Sci. Lett.* 154 (1–4) (1998) 331–347.
- [33] Y.L. Niu, M.J. O’Hara, Origin of ocean island basalts: a new perspective from petrology, geochemistry, and mineral physics considerations, *J. Geophys. Res., Solid Earth Planets* 108 (B4) (2003).
- [34] Y.L. Niu, M.J. O’Hara, Mantle plumes are NOT from ancient oceanic crust, in: H.R.P. Stoffers, J.-L. Cheminee (Eds.), *Oceanic Hotspots: Intraplate Submarine Magmatism and Tectonism*, Springer-Verlag, Berlin, 2004, pp. 239–252.
- [35] A.N. Halliday, D.-C. Lee, S. Tommasini, G.R. Davies, C.R. Paslick, J.G. Fitton, D.E. James, Incompatible trace elements in OIB and MORB and source enrichment in the sub-oceanic mantle, *Earth Planet. Sci. Lett.* 133 (3–4) (1995) 379–395.
- [36] M.R. Handler, V.C. Bennett, T.M. Esat, The persistence of off-cratonic lithospheric mantle: Os isotopic systematics of variably metasomatised southeast Australian xenoliths, *Earth Planet. Sci. Lett.* 151 (1–2) (1997) 61–75.
- [37] L. Reisberg, X.C. Zhi, J.P. Lorand, C. Wagner, Z.C. Peng, C. Zimmermann, Re–Os and S systematics of spinel peridotite xenoliths from east central China: evidence for contrasting effects of melt percolation, *Earth Planet. Sci. Lett.* 239 (3–4) (2005) 286–308.
- [38] J.P. Lorand, O. Alard, Platinum-group element abundances in the upper mantle: new constraints from in situ and whole-rock analyses of Massif Central xenoliths (France), *Geochim. Cosmochim. Acta* 65 (16) (2001) 2789–2806.
- [39] A. Buchl, G.E. Brugmann, V.G. Batanova, A.W. Hofmann, Os mobilization during melt percolation: the evolution of Os isotope heterogeneities in the mantle sequence of the Troodos ophiolite, Cyprus, *Geochim. Cosmochim. Acta* 68 (16) (2004) 3397–3408.
- [40] R.J. Walker, J.W. Morgan, M.F. Horan, Os-187 enrichment in some plumes — evidence for core–mantle interaction, *Science* 269 (5225) (1995) 819–822.
- [41] T. Kogiso, M.M. Hirschmann, D.J. Frost, High-pressure partial melting of garnet pyroxenite: possible mafic lithologies in the

- source of ocean island basalts, *Earth Planet. Sci. Lett.* 216 (4) (2003) 603–617.
- [42] E. Widom, K.A. Hoernle, S.B. Shirey, H.U. Schmincke, Os isotope systematics in the Canary Islands and Madeira: lithospheric contamination and mantle plume signatures, *J. Petrol.* 40 (2) (1999) 279–296.
- [43] E. Widom, S.B. Shirey, Os isotope systematics in the Azores: implications for mantle plume sources, *Earth Planet. Sci. Lett.* 142 (3–4) (1996) 451–465.
- [44] E.H. Hauri, S.R. Hart, Re–Os isotope systematics of HIMU and EM-II oceanic island basalts from the South-Pacific Ocean, *Earth Planet. Sci. Lett.* 114 (2–3) (1993) 353–371.
- [45] M. Zimmer, A. Kroner, K.P. Jochum, T. Reischmann, W. Todt, The Gabal-Gerf Complex — a Precambrian N-MORB ophiolite in the Nubian Shield, NE Africa, *Chem. Geol.* 123 (1–4) (1995) 29–51.
- [46] A. Gannoun, K.W. Burton, L.E. Thomas, I.J. Parkinson, P. van Calsteren, P. Schiano, Osmium isotope heterogeneity in the constituent phases of mid-ocean ridge basalts, *Science* 303 (5654) (2004) 70–72.
- [47] O. Alard, A. Luguët, N.J. Pearson, W.L. Griffin, J.P. Lorand, A. Gannoun, K.W. Burton, S.Y. O'Reilly, In situ Os isotopes in abyssal peridotites bridge the isotopic gap between MORBs and their source mantle, *Nature* 436 (7053) (2005) 1005–1008.
- [48] G.F. Davies, On the emergence of plate-tectonics, *Geology* 20 (11) (1992) 963–966.
- [49] S.-S. Sun, W.F. McDonough, Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes, in: A.D. Saunders, M.J. Norry (Eds.), *Magmatism in the Ocean Basins*, vol. 42, Geological Society Special Publication, London, 1989, pp. 313–345.
- [50] H. Staudigel, T. Plank, B. White, H.-U. Schmincke, Geochemical fluxes during seafloor alteration of the basaltic upper oceanic crust; DSDP sites 417 and 418, in: G.E. Bebout, D.W. Scholl, S.H. Kirby, J.P. Platt (Eds.), *Subduction, Top to Bottom*, vol. 96, American Geophysical Union, Washington, DC, 1996, pp. 19–38, pp. 384.
- [51] W. Bach, J.C. Alt, Y.L. Niu, S.E. Humphris, J. Erzinger, H.J.B. Dick, The geochemical consequences of late-stage low-grade alteration of lower ocean crust at the SW Indian ridge: results from ODP Hole 735B (Leg 176), *Geochim. Cosmochim. Acta* 65 (19) (2001) 3267–3287.
- [52] T. Kogiso, Y. Tatsumi, S. Nakano, Trace element transport during dehydration processes in the subducted oceanic crust: 1. Experiments and implications for the origin of ocean island basalts, *Earth Planet. Sci. Lett.* 148 (1–2) (1997) 193–205.
- [53] M. Sharma, G.J. Wasserburg, A.W. Hofmann, D.A. Butterfield, Osmium isotopes in hydrothermal fluids from the Juan de Fuca Ridge, *Earth Planet. Sci. Lett.* 179 (1) (2000) 139–152.
- [54] S.B. Shirey, R.J. Walker, The Re–Os isotope system in cosmochemistry and high-temperature geochemistry, *Annu. Rev. Earth Planet. Sci.* 26 (1998) 423–500.
- [55] M.F. Thirlwall, Pb isotopic and elemental evidence for OIB derivation from young HIMU mantle, *Chem. Geol.* 139 (1–4) (1997) 51–74.
- [56] C. Chauvel, A.W. Hofmann, P. Vidal, HIMU-EM: the French–Polynesian connection, *Earth Planet. Sci. Lett.* 110 (1–4) (1992) 99–119.
- [57] B. Peucker-Ehrenbrink, G. Ravizza, A.W. Hofmann, The marine $^{187}\text{Os}/^{186}\text{Os}$ record of the past 80-million years, *Earth Planet. Sci. Lett.* 130 (1–4) (1995) 155–167.
- [58] M.M. Hirschmann, E.M. Stolper, A possible role for garnet pyroxenite in the origin of the “garnet signature” in MORB, *Contrib. Mineral. Petrol.* 124 (2) (1996) 185–208.
- [59] J.C. Lassiter, E.H. Hauri, Osmium-isotope variations in Hawaiian lavas: evidence for recycled oceanic lithosphere in the Hawaiian plume, *Earth Planet. Sci. Lett.* 164 (3–4) (1998) 483–496.
- [60] A.V. Sobolev, A.W. Hofmann, I.K. Nikogosian, Recycled oceanic crust observed in ‘ghost plagioclase’ within the source of Mauna Loa lavas, *Nature* 404 (6781) (2000) 986–990.
- [61] C. Chauvel, C. Hemond, Melting of a complete section of recycled oceanic crust: trace element and Pb isotopic evidence from Iceland, *Geochem. Geophys. Geosyst.* 1 (2000) (1999GC000002).
- [62] V.C. Bennett, T.M. Esat, M.D. Norman, Two mantle-plume components in Hawaiian picrites inferred from correlated Os–Pb isotopes, *Nature* 381 (6579) (1996) 221–224.
- [63] E.H. Hauri, J.C. Lassiter, D.J. DePaolo, Osmium isotope systematics of drilled lavas from Mauna Loa, Hawaii, *J. Geophys. Res., Solid Earth Planets* 101 (B5) (1996) 11793–11806.