

Trace element partitioning between mantle wedge peridotite and hydrous MgO-rich melt

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ABSTRACT

Magmas erupted at convergent margins consist of components from both mantle wedge and subducted slab. In an effort to quantify the relative contributions of these sources, we have determined 19 trace element partition coefficients (D values) for orthopyroxene and clinopyroxene, in equilibrium with spinel and hydrous high-MgO melt under conditions appropriate to melting in the mantle wedge, i.e., 1.3 GPa, 1245 °C, and f_{O_2} of NNO + 1. All trace elements are more incompatible in clinopyroxene during hydrous melting than during anhydrous melting of fertile and depleted peridotite. Orthopyroxene D values are relatively insensitive to pressure, temperature, and phase composition. The new D values are used to calculate the trace-element composition of the mantle wedge, which produced primitive South Sandwich Islands and St. Vincent (Lesser Antilles) arc basalts. Both sources correspond to previously depleted mantle that has been enriched in LILEs and LREEs by slab-derived fluids. In the case of the South Sandwich Islands, the calculated source is in very close agreement with dredged fore-arc lherzolites. Our partitioning data confirm that hydrous melting of wedge peridotite itself cannot produce the characteristic enrichments of LILEs over REEs and HFSEs. Our estimates of the slab component in South Sandwich Islands and St. Vincent are consistent with estimates from other arcs, derived by alternative methods.

INTRODUCTION

Volcanic rocks produced at convergent plate margins are chemical hybrids of melts and fluids derived from subducted-slab material and mantle-wedge peridotite. In terms of their trace elements, these rocks are characterized by enrichment in large-ion-lithophile elements (LILEs) relative to rare-earth elements (REEs) and, in particular, relative to the high-field-strength elements (HFSEs) (Davidson 1996). Depletion of HFSEs has been attributed to a variety of subduction-related processes, most of which infer retention of HFSEs in a titanate phase in the slab during dehydration (Saunders et al. 1980), and/or partial melting either of the metabasaltic portion of the slab (Marsh 1976) or its metasedimentary cover (Turner et al. 1997). However, the relative contribution of such accessory phases is unknown because the ability of the silicate mantle-wedge peridotite itself to fractionate HFSEs from other trace elements is currently unquantifiable.

Peridotite partial melting in the mantle wedge is a significantly different process from that responsible for melt generation beneath mid-ocean ridges, in that melting typically takes place in the presence of a slab-derived, H₂O-rich fluid (e.g., Tatsumi and Eggins 1995). Addition of H₂O and other components to peridotite both lowers the melting temperature and alters the melting reactions (Gaetani and Grove 1998). Trace-element partitioning between mineral and melt is primarily a function of phase composition, pressure (P), and temperature (T). Because P and T affect the partitioning of different

valence cations to differing extents (Blundy and Wood 2003), it is possible that low-temperature hydrous melting in the wedge is characterized by quite different HFSE/REE fractionations compared to the relatively high- T anhydrous melting responsible for MORB generation. Accurate determination of partition coefficients (where $D_i = [i]$ in crystal/[i] in melt) at P and T relevant to melt production is thus imperative for modeling processes involved in generating primary arc magmas from the wedge, and in particular establishing the baseline effect of peridotite in generating LILE/HFSE fractionations. Our data complement the recent experimental study of Gaetani et al. (2003) on clinopyroxene-melt and garnet-melt partitioning of trace elements during melting of the hydrous mantle wedge.

High-MgO arc basalts (>9 wt% MgO) are thought to represent near-primary liquids in equilibrium with mantle peridotite. Pichavant et al. (2002) applied the inverse experimental approach (Myers and Johnston 1996) to a hydrated high-MgO basalt from the Soufrière Volcano, St. Vincent, Lesser Antilles Arc, to determine the point of multiple-saturation with a mantle lherzolite assemblage. Multiple saturation (opx + cpx + sp) was achieved in basalt starting mixes containing 1.5 wt% H₂O at 1235 °C, 1.15 GPa. Olivine is not produced in these experiments due to the peritectic nature of low-pressure peridotite melting. We have obtained a similar result in our trace-element-doped experiment MW1-5, using a very similar starting composition, at 1245 °C, 1.3 GPa. This experiment produced melt pools and pyroxene crystals large enough for ion microprobe analysis from which we have determined partition coefficients applicable to hydrous melt generation in the mantle wedge including, for the first time, D values for orthopyroxene.

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EXPERIMENTAL DESIGN

The high-MgO basalt starting composition MW1 (Table 1) was produced by mixing appropriate amounts of fired oxides, Fe metal powder and oven-dried carbonates. With the exception of Fe, all components were thoroughly ground together under acetone, decarbonated at 600 °C for 30 minutes, and then glassed at 1300 °C for 1 minute. Nineteen trace elements were added to this glass as micro-liter quantities of atomic absorption standard solutions (10–1000 ppm doping level) before the mix was ground and glassed for a second time. The resulting glass was hydrated at 1300 °C, 0.1 GPa in a 5 mm diameter platinum capsule using a TZM apparatus. FTIR analysis of polished wafers determined the water content in the glass to be 3.00 ± 0.35 wt%. This amount was reduced to the desired 1.5 wt% in the starting mix by combining the hydrous glass with the necessary quantity of anhydrous glass and Fe oxide. The latter was added as a mixture of Fe metal and Fe₂O₃, in weight proportions 1:4 appropriate to achieve an f_{O_2} equivalent to NNO + 1 (Kress and Carmichael 1991), consistent with the wedge environment (Wood et al. 1990), but somewhat more oxidizing than the experiments of Gaetani et al. (2003). The final mix was thoroughly ground and stored at >120 °C before use.

The experiment was carried out in an end-loaded, piston-cylinder apparatus using 12.7 mm diameter BaCO₃ cells with crushable alumina inner pieces and a W/Re (D-type) thermocouple. A pressure correction of –9% (McDade et al. 2002) was applied to the assembly. Experimental conditions were 1245 °C, 1.3 GPa, and 49 hour run duration. Throughout the experiment, f_{O_2} and H₂O content within the charge were maintained using the double-capsule buffer technique. The inner 2 mm diameter Au₈₀Pd₂₀ capsule contained MW1 mix and 5% natural olivine (Fo₉₁) to ensure saturation. The outer 3 mm diameter Pt capsule contained MW1 hydrous melt. This design, based on Hall (1999), optimizes Fe and H₂O retention during hydrous silicate melting experiments.

The major-element compositions of the experimental products were determined by electron microprobe analysis at the University of Edinburgh; trace elements in the pyroxenes and melt were determined by ion microprobe analysis, also at Edinburgh. Details of the analytical techniques are provided in Table 1.

RESULTS

Experimental products consisted of clinopyroxene, orthopyroxene, spinel, and melt. Olivine was not identified in the inner capsule but did crystallize in the outer buffer. The pyroxenes were generally euhedral, with orthopyroxene (≤ 50 μ m) typically larger than clinopyroxene (≤ 30 μ m) in longest dimension. Spinel was smaller, anhedral, and commonly enclosed within orthopyroxene. Melt pools were ≤ 100 μ m in longest dimension and largely free of quench modification. Both the crystals and melt pools were compositionally homogeneous, as evidenced by the small standard deviation of the means of the electron probe analyses of each phase. Phase compositions and proportions are compiled in Table 1. The calculated clinopyroxene and orthopyroxene partition coefficients are listed in Table 2 and plotted in Figure 1.

Clinopyroxene contained 7.5 wt% Al₂O₃, 7 mol% jadeite, 41% diopside, and 23% Ca-Tschermak's molecule. The Fe²⁺/Fe³⁺ (calculated using the algorithm of Droop 1987) was 0.96. Orthopyroxene contained 6.8 wt% Al₂O₃ and an mg no. of 92. The Cr/(Cr + Al) ratio of spinel was 0.12, with Fe²⁺/Fe³⁺ ratio of 0.79 and mg no. of 82. The melt contains 3.4% wt% Na₂O and is highly magnesian with 10.1 wt% MgO and mg no. of 72. The H₂O content of the melt (determined by ion microprobe analysis) was 1.64 ± 0.14 wt% (Table 1). These phase compositions are consistent with those in a relatively refractory peridotite, and very similar to those of Gaetani et al. (2003). As noted above, the absence of olivine in our run products is primarily a consequence of the peritectic nature of the olivine-orthopyroxene reaction in basaltic melts. Its presence in the outer capsule indicates that our melt was very close to olivine

TABLE 1. Major and trace element compositions of the starting material (MW1) and of the phases produced in experiment MW1-5

	MW1	cpx	melt	opx	sp1
\bar{r}	11	17	7	4	
SiO ₂ (wt%)†	48.13	49.67(45)	46.80(88)	52.53(77)	1.79(63)
TiO ₂	1.07	0.42(2)	1.42(2)	0.20(2)	0.37(1)
Al ₂ O ₃	15.40	7.50(22)	15.58(42)	6.88(71)	45.55(90)
Cr ₂ O ₃	0.15	0.56(8)	0.05(2)	0.42(4)	9.37(43)
MgO	11.46	17.96(28)	10.65(71)	31.20(63)	21.16(58)
CaO	10.42	16.86(28)	9.57(29)	1.94(8)	0.46(19)
FeO(total)	8.89	5.08(11)	7.46(20)	6.24(35)	18.54(30)
MnO	0.17	0.14(2)	0.17(3)	0.15(5)	0.16(3)
Na ₂ O	2.45	0.95(3)	3.50(23)	0.15(5)	0.08(3)
K ₂ O	0.34	0.00	0.51(4)	0.01(0)	0.02(1)
H ₂ O	1.5		1.64(14)**		
Total‡	99.98	99.4(7)	98.3(13)	99.8(13)	97.5(14)
mg no.§	69.7	86.3	71.8	89.9	
Mode II		18.6(21)	70.8(16)	7.6(19)	3.0(6)
\bar{r}		4	3	4	
Li (ppm)#		6.6(30)	62.9(63)	11.7(11)	
Sc		48.5(25)	45.6(12)	45.8(54)	
V		30.6(18)	91.5(40)	39.2(65)	
Sr		4.18(31)	54.1(78)	0.24(6)	
Y		58.4(5)	104.1(3)	10.5(13)	
Zr		28.2(11)	274(5)	7.40(22)	
Nb		2.01(0)	260(13)	0.74(39)	
La		6.19(67)	143.1(81)	0.43(20)	
Ce		12.2(11)	138.0(64)	0.69(24)	
Nd		231(11)	1093(32)	10.3(12)	
Sm		394(11)	1085(11)	22.6(28)	
Eu		863(33)	1924(2)	59.1(45)	
Er		260.2(87)	450(11)	54.2(62)	
Yb		125.9(22)	231.9(7)	38.0(40)	
Lu		117.0(69)	225.3(88)	41.8(40)	
Hf		8.95(40)	43.5(22)	2.70(80)	
Ta		1.01(67)	46.0(26)	0.19(10)	
Th			597		
U			797		

Note: Numbers in brackets are 1 s.d. of the mean composition in terms of least significant digits.

* Number of analyses averaged.

† Major elements determined by Cameca Camebax electron microprobe using an accelerating voltage of 15 kV, a beam current of 25 nA and the PAP correction procedure.

‡ Totals for run products include all trace elements analysed (as oxides).

§ mg no. is 100 Mg/(Mg + Fe).

|| Wt% phase proportions determined by weighted least-squares mass balance.

Trace element concentrations determined by Cameca ims-4f ion microprobe at the University of Edinburgh using a ~7 nA primary O⁻ beam accelerated at a nominal 10 kV, and a 75 ± 20 eV offset to reduce molecular interferences. Beam size was minimised using a small aperture. Any crystal analyses containing >0.1 ppm Ba were considered to result from beam overlap on adjacent glass, and were rejected. Relative ion yields were determined from NIST 610 glass. Analysis of secondary standards (DDI garnet and KH1 clinopyroxene) indicate accuracy of $\pm 10\%$ for concentrations >1 ppm, and $\pm 30\%$ for concentrations <1 ppm. Further details of the ion microprobe analytical technique are provided in Blundy et al. (1998). Analysis of secondary standards used for both electron and ion microprobe analysis can be obtained from the authors on request.

** Water in glass determined by ion microprobe as ¹H/³⁰Si using the same analytical conditions as trace elements. Empirical calibration was carried out using two hydrous basalt glasses (MW1 and a synthetic hydrous Cascade basalt), whose H₂O was previously determined by FTIR analysis at 3.0 and 4.0, respectively, and an anhydrous glass. To reduce magnet hysteresis, only masses 1 to 30 were analyzed during H₂O determinations.

saturation, as also manifested by its high mg no.

With the exception of Cr, all trace elements measured in clinopyroxene are incompatible ($D < 1$; Table 2, Fig. 1a). HFSEs and LILEs are less compatible than REEs ($D_{Zr}/D_{Sm} = 0.28$; $D_{Sr}/$

TABLE 2. Mineral-melt partition coefficients

	D_{cpx}	D_{opx}
Li	0.104(49)	0.187(25)
Na	0.271(20)	0.044(5)
Sc	0.206(61)	1.00(12)
V	0.334(25)	0.429(74)
Cr	11.2(48)	8.4(34)
Sr	0.077(13)	0.0044(13)
La	0.043(5)	0.003(1)
Ce	0.089(9)	0.005(2)
Nd	0.211(12)	0.009(1)
Sm	0.363(11)	0.021(3)
Eu	0.449(17)	0.031(2)
Er	0.578(24)	0.121(14)
Y	0.561(5)	0.101(12)
Yb	0.543(10)	0.164(17)
Lu	0.520(37)	0.186(19)
Ti	0.296(14)	0.141(14)
Zr	0.103(5)	0.027(1)
Hf	0.206(14)	0.062(19)
Nb	0.008(4)	0.0028(15)
Ta	0.022(15)	0.0041(22)

Note: Uncertainties (1 s.d.) expressed in terms of least significant digits.

$D_{\text{yb}} = 0.14$). With the exception of Sc, V, and Li, all trace elements are less compatible in orthopyroxene (Fig. 1b) than in clinopyroxene. In both pyroxenes $D_{\text{Ti}} > D_{\text{Hf}} > D_{\text{Zr}}$ and, as commonly observed, $D_{\text{Zr}}/D_{\text{Hf}} \approx 0.5$. In Figure 1, the new D values are compared with those for clino- and orthopyroxenes determined under anhydrous conditions at 1.5 GPa in both fertile MORB-pyrolite at 1255–69 °C (cpx = Blundy et al. 1998; opx = Wood unpublished) and depleted Tunaquillo lherzolite at 1315 °C (McDade et al. 2003). We also show the recently published clinopyroxene-melt partition coefficients of Gaetani et al. (2003), generated under very similar conditions to our own (e.g., their run B287, 1.2 GPa, 1315 °C, 1 wt% dissolved H_2O). The overall agreement in the shape of the patterns for all four clinopyroxene-melt and three orthopyroxene-melt determinations shows clearly that the geochemical signature of primitive arc basalts cannot be a consequence of an unanticipated effect of H_2O on partition coefficients.

The hydrous melting D values tend to be lower than the 1.5 GPa anhydrous values for most elements despite the lower-temperature at which hydrous melting occurs, which in general would be expected to yield higher partition coefficients. Gaetani et al. (2003) arrived at a similar conclusion based on clinopyroxene-melt partitioning experiments at 1.2 to 1.6 GPa with 1–6 wt% H_2O dissolved in the melt. For the case of the REE, these findings are entirely consistent with the predictions of Wood and Blundy (2002) who showed that, for clinopyroxene, the effect of H_2O on REE component activities in melts tends to counteract the effect of lower-temperature and result in an overall decrease in partition coefficient. The most striking difference between hydrous and anhydrous partition coefficients, and one that was not anticipated, is the change in relative sense of fractionation between the heavy REE, Sc, and V. In all anhydrous partitioning experiments pertaining to mantle melting [including two experiments of Hauri et al. (1994) and one of Hart and Dunn (1993), omitted from Fig. 1a for clarity], D_{Sc} is greater than D_{Lu} by a factor of 1.3 to 5.1. In our new hydrous partitioning experiment, $D_{\text{Sc}}/D_{\text{Lu}}$ is 0.4. D_{V} is similarly reduced in the anhydrous experiment, although the ratio $D_{\text{V}}/D_{\text{Sc}}$ is similar in both anhydrous and hydrous systems. These

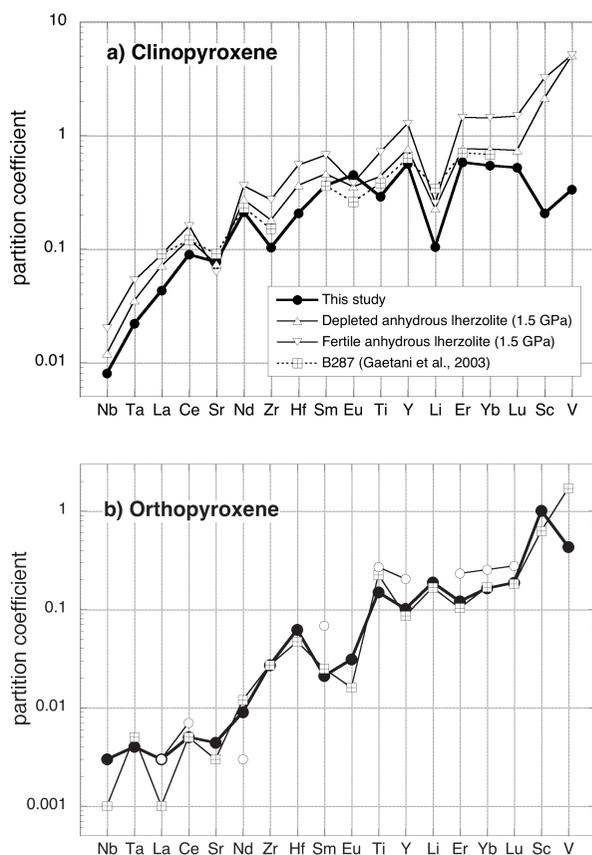


FIGURE 1. (a) Experimentally determined clinopyroxene D values for hydrous (MW1-5), fertile (Blundy et al. 1998), and depleted (McDade et al. 2003) peridotites. Also plotted are the recently published hydrous peridotite data of Gaetani et al. (2003) from their run B287 at 1.2 GPa, 1315 °C, with 0.98 ± 0.24 wt% H_2O dissolved in the melt. Note the close correspondence between MW1-5 and B287 for all elements except D_{Eu} , which is lower in B287. This feature probably reflects slightly more reducing conditions in the Gaetani et al. (2003) experiments, which used a graphite-lined Pt capsule. This is also true of the two anhydrous experiments shown, which also show low D_{Eu} . (b) Experimentally determined orthopyroxene D values for hydrous (MW1-5), fertile (Wood unpublished), and depleted (McDade et al. 2003) peridotites. Again, the elevated D_{Eu} in the hydrous experiment is a consequence of elevated f_{O_2} .

observations are in contrast to orthopyroxene-melt partitioning (Fig. 1b) where the sense of Lu-Sc fractionation is unaffected by H_2O , but V-Sc fractionation is reversed. We note also that in both clino- and orthopyroxene the ratio $D_{\text{Sr}}/D_{\text{Ce}}$ is increased (closer to 1) in hydrous relative to anhydrous melting (Fig. 1), resulting in smaller positive Sr anomalies (relative to adjacent REEs) in hydrous melts than those produced from a dry source.

DISCUSSION

The new partition coefficients can be used to calculate the source compositions of primitive arc basalts. Such calculations can in turn be used to constrain the composition of the “slab

component” that must be added to the mantle wedge at subduction zones. This exercise, although not new, previously has been compromised by uncertainty as to whether the partition coefficients appropriate to hydrous melting of peridotite are the same as those for anhydrous melting, for which there are now a large number of reliable determinations. Without comparably reliable data for hydrous melting of the wedge, it was hitherto not possible to establish with any certainty to what extent geochemical anomalies in arc basalts are a result of changes in partitioning and to what extent they are the result of the slab component. Our new data, together with those of Gaetani et al. (2003), show clearly that there is remarkably little difference in partitioning behavior for mantle melting under hydrous and anhydrous conditions. In the current study, we present some simple illustrative calculations for two volcanic arcs: the South Sandwich Islands in the southern Atlantic, and the Lesser Antilles arc in the Caribbean.

To a first approximation, melting of the mantle wedge beneath a volcanic arc can be considered in terms of two components: a “pre-subduction” peridotite, widely held to be depleted relative to the primitive mantle; and a “slab-component,” variously derived from fluids released through dehydration of the slab, and/or partial melts of its sedimentary cover. In combination, these components give rise to an enriched (or “modified”) wedge peridotite that is melted to form primitive arc basalts. The trace-element composition of the modified wedge can be estimated from that of a primary magma using the hydrous melting partition coefficients presented here. In turn, this composition can be used to estimate the extent of prior depletion of the peridotite by using the anhydrous melting partition coefficients of McDade et al. (2003). This exercise simply involves using the heavy REE to estimate how much melt must have been extracted from the primitive mantle in order to produce the modified wedge composition. Implicit in this methodology is an assumption that negligible amounts of the heavy REE are added during subduction. For this reason, we confine our calculations to the more incompatible elements, light REE (La-Eu), HFSE (Nb, Zr, Hf, Ti), and LILE (Sr). Many key characteristics of the arc environment are currently under-constrained and, although some of our assumptions may be revised in the future, we believe that the following model does not significantly depart from the current consensus among sub-arc melting models.

The hydrous melting partition coefficients presented here may be combined with the trace-element composition of a primitive arc basalt to estimate the composition of the source peridotite, provided that some estimate can be made of the melt fraction (F) and the proportions of olivine, orthopyroxene, and clinopyroxene in the source. In most arcs, values of F in the range 0.15 to 0.2 are derived from a variety of geochemical evidence (e.g., Tatsumi and Eggins 1995). Although the values we use here fall within this range, the calculated composition of the slab component is, in fact, rather insensitive to the exact value of F . The source mineralogy at the point of extraction is determined both by F and the extent of any prior (pre-subduction) depletion. Where this has been significant, all clinopyroxene may be exhausted to leave a harzburgitic residue (Tatsumi and Eggins 1995; Grove et al. 2002). In our cal-

culations, we assume non-modal batch melting of hydrous lherzolite at 1.2 GPa according to the reaction (Gaetani and Grove 1998): $0.62 \text{ cpx} + 0.51 \text{ opx} + 0.12 \text{ sp} = 0.25 \text{ ol} + 1.0 \text{ melt}$. For hydrous harzburgite, we assume modal batch melting of a source with 71% olivine, 23% orthopyroxene, and 3% spinel, approximately equivalent to the mineralogy at the point of clinopyroxene exhaustion. Hydrous melting partition coefficients for orthopyroxene are taken from Table 2; those for olivine are taken from McDade et al. (2003), assuming that H_2O has a negligible effect on olivine-melt partition coefficients; those for spinel are assumed negligible for all elements except Ti, for which a value of 0.176 is used (Table 1). As our starting compositions, we have taken two primitive arc basalts with 10–13 wt% MgO: SV031 from St. Vincent (Heath et al. 1998) and SSM1-3 from the South Sandwich Islands (Pearce et al. 1995). For St. Vincent, we set $F = 0.18$ and for the South Sandwich Islands, we set $F = 0.20$ as adopted by the above authors. The calculated modified-peridotite source compositions using these parameters are given in Table 3 and plotted in Figure 2.

Both of our modified-peridotite wedge compositions have heavy REE that are below the levels found in primitive mantle, a sure indication of prior melt extraction. Although the extent of heavy REE depletion is quite modest, to extract sufficient basaltic melt to achieve such depletion has the effect of very efficiently stripping out the more incompatible elements on the left-hand side of Figure 2. We have calculated the extent of prior depletion by removing just enough melt to match the Y, Er, Yb, and Lu contents of the modified wedge as calculated above. Thus, our estimates of the amount of prior melt depletion are minima. We used the mineral-melt partition coefficients from McDade et al. (2003) and the anhydrous peridotite 1.5 GPa melting reaction of Robinson et al. (1998): $0.82 \text{ cpx} + 0.40 \text{ opx} + 0.08 \text{ sp} = 0.30 \text{ ol} + 1.0 \text{ melt}$. The initial, undepleted, peridotite composition is the PUM estimate of Sun and McDonough (1989). Using the near-solidus phase compositions of Robinson et al. (1998), we estimated a starting mode of 61.4% olivine, 20.1% orthopyroxene, 17.4% clinopyroxene, and 1.1% spinel. The melting model is non-modal, dynamic melting with a critical (or residual) porosity of 1%. Note that because the results of this calculation impact on the initial mode used for calculating the modified-wedge composition (as described above), we have performed the two sets of calculations iteratively.

We have only considered prior melt extraction in the spinel lherzolite stability field. Although we cannot rule out some prior garnet lherzolite melting, the fit of the spinel lherzolite models to Y, Er, Yb, and Lu for both arcs (Figs. 2a and 2b) suggests that the involvement of garnet was minimal, as this phase would introduce greater fractionation between these elements than is observed. We also considered prior depletion to be a single-stage event from an initial PUM reservoir. Isotopic evidence, e.g., $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, clearly require two or more stages of depletion. However, from a trace-element perspective, it does not make much difference if a single stage of prior depletion is assumed. Grove et al. (2002), for example, used a two-stage depletion in their calculations. We did not feel that this extra layer of complexity was warranted. It would have a negligible effect on the results.

Our calculations show that the original pre-subduction peri-

TABLE 3A. Estimates of the composition of the mantle wedge and slab components at South Sandwich Islands

	SSM1-3*	Modified wedge	Slab component	Pre-subduction wedge	PUM†
Nb	0.21	0.042	10.5	0.00004	0.713
La	0.78	0.156	38.7	0.00153	0.687
Ce	2.13	0.428	102	0.0207	1.775
Sr	106	21.3	5298	0.0614	21.1
Nd	2.39	0.482	92.2	0.113	1.354
Zr	16.9	3.43	729	0.511	11.2
Hf	0.56	0.117	15.8	0.0539	0.309
Sm	0.86	0.174	20.3	0.0927	0.444
Eu	0.36	0.0731	12.6	0.0228	0.168
Ti	2578	599	35483	457	1300
Y	10.1	2.13	61.8	1.88	4.55
Er	0.97	0.206		0.205	0.48
Yb	1.01	0.221		0.236	0.493
Lu	0.16	0.0354	0.00618	0.0353	0.074
‡		0.20			0.117
Cpx§		0		0.088	0.174
Opx§		0.12		0.175	0.201
Oliv§		0.87		0.735	0.614
Sp§		0.01		0.002	0.011

Notes: For details of method see text. Blank spaces indicate data irrelevant or unavailable. All trace element concentrations in parts per million.

* Primitive South Sandwich Islands basalt from Pearce et al. (1995).

† Primitive Upper Mantle from Sun and McDonough (1989).

‡ Melt fraction at end of each stage.

§ Modal mineralogy (wt%) at onset of each stage.

TABLE 3B. Estimates of the composition of the mantle wedge and slab components at St. Vincent

	SV031*	Modified wedge	Slab component	Pre-subduction wedge	PUM†
Nb	4.7	0.85	115	0.020	0.713
La	5.7	1.04	132	0.089	0.687
Ce	12.7	2.33	267	0.422	1.775
Sr	202	37.0	4736	3.01	21.1
Nd	8.9	1.68	147	0.630	1.354
Zr	61	11.4	1007	4.20	11.2
Hf	1.68	0.329	20.9	0.181	0.309
Sm	2.47	0.479	28.4	0.278	0.444
Eu	0.92	0.182	12.7	0.092	0.168
Ti	6415	1403	66700	929	1300
Y	18	3.77	38.5	3.50	4.55
Er				0.373	0.48
Yb	1.74	0.378		0.395	0.493
Lu	0.27	0.059		0.059	0.074
‡		0.18			0.044
Cpx§		0.034		0.144	0.174
Opx§		0.105		0.192	0.201
Oliv§		0.733		0.656	0.614
Sp§		0		0.008	0.011

Notes: For details of method see text. Blank spaces indicate data irrelevant or unavailable. All trace element concentrations in parts per million.

* Primitive St. Vincent basalt from Heath et al. (1998).

† Primitive Upper Mantle from Sun and McDonough (1989).

‡ Melt fraction at end of each stage.

§ Modal mineralogy (wt%) at onset of each stage.

dotite source for South Sandwich Islands is equivalent to PUM after 11.7% melt extraction, whereas the St. Vincent source is equivalent to PUM after 4.4% partial melting (Table 3). These estimates concur with the generally greater level of depletion in the South Sandwich Islands arc (Fig. 2a) relative to the Lesser Antilles (Fig. 2b). In both cases, the pre-subduction peridotite, prior to addition of the slab component, is a lherzolite with 9–14 wt% clinopyroxene (Table 3). At the point of arc basalt extraction, i.e., after addition of the slab component and

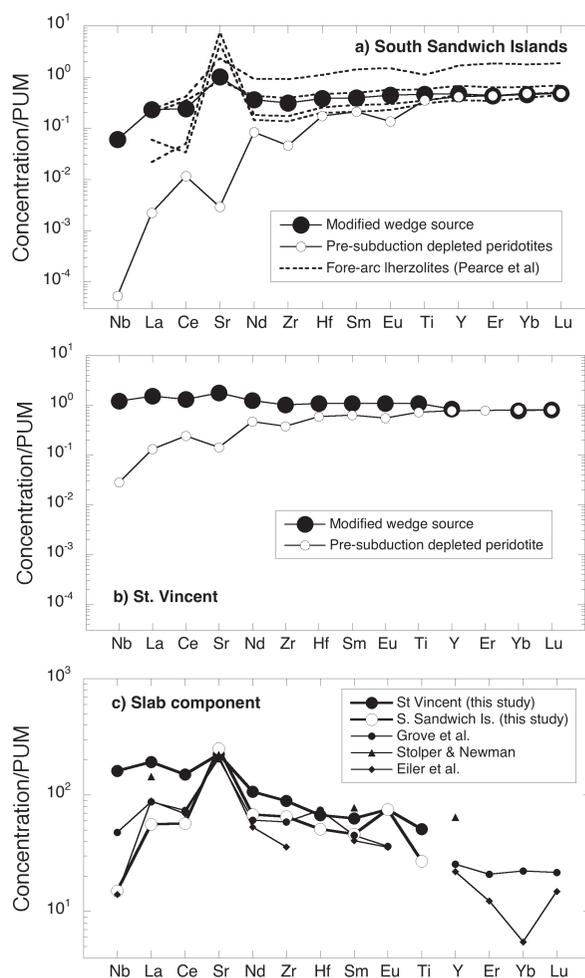


FIGURE 2. Calculated compositions of peridotite source and slab component for two island arcs: South Sandwich Islands and St. Vincent (Lesser Antilles). Data are taken from Table 3. (a) South Sandwich Islands. Modified-wedge source (filled circles) is calculated from the composition of MgO-rich basalt SSM1-3 (Pearce et al. 1995), assuming a harzburgitic residue and $F = 0.20$. The calculated pre-subduction peridotite (open circles) was derived by matching the heavy REE contents to a peridotite produced by 11.7% non-modal dynamic melting of a PUM source. The broken lines denote four lherzolites from the trench-fracture zone intersection at the south end of the arc (Pearce et al. 2000). Their compositions closely match that of our calculated modified wedge. (b) St. Vincent (Lesser Antilles). Modified-wedge source (filled circles) is calculated from the composition of MgO-rich basalt SV031 (Heath et al. 1998), assuming a lherzolitic residue and $F = 0.18$. The calculated pre-subduction peridotite (open circles) was derived by matching the heavy REE contents to a peridotite produced by 4.5% non-modal dynamic melting of a PUM source. (c) Composition of slab component at both arcs calculated using Equation 1 from the data provided in Table 3. Only elements more incompatible than Y are plotted, because heavy REE were used to obtain the pre-subduction peridotite composition, as shown in a and b. Also shown are estimates of the slab component from Stolper and Newman (1994), Eiler et al. (2000), and Grove et al. (2002). Our estimates bracket these but suggest two distinctive varieties of slab component, one (St. Vincent) rich in Nb, Ti, and light REE, the other (South Sandwich Islands) depleted in these elements, but sharing a common Zr/Hf.

subsequent partial melting, the residue at South Sandwich Islands is clinopyroxene-free harzburgite, whereas that at St. Vincent is a depleted lherzolite with ~3 wt% clinopyroxene. This result accords with the experimental evidence that clinopyroxene was present in the source of St. Vincent primitive basalts (Pichavant et al. 2002). In the case of the South Sandwich Islands, our calculated modified-wedge source is in excellent agreement with the composition of four dredged lherzolites (2–13 % clinopyroxene) from the trench-fracture zone intersection at the southern end of the arc (Pearce et al. 2000) (Fig. 2a). Pearce et al. (2000) estimated that these lherzolites represent residues after <10% partial melting of fertile mantle, followed by “melt impregnation” by subduction-related magma to modify their bulk compositions. We consider that the agreement between our calculated South Sandwich Islands source and the dredged peridotites from this area lends strong support to our methodology.

The estimates of pre-subduction wedge peridotite and modified-wedge (post-subduction) peridotite enable us to calculate by difference the added slab component for both arcs. To do this, we need additionally to know the H₂O content of the added fluid and the amount of this fluid that was added to the wedge. We will assume that the fluid is 50% H₂O, a value intermediate between the estimates of Grove et al. (2002) and Stolper and Newman (1994). If the true value is higher or lower, then the calculated fluid concentrations will scale accordingly. To determine the amount of fluid added, we require some estimate of the H₂O in the primitive basalt (W_{bas}). From this estimate, we can calculate the source H₂O content (W_0) assuming complete incompatibility, i.e., $W_0 = F \times W_{\text{bas}}$, where F is the melt fraction required to produce the primitive basalt from the modified wedge (Table 3). Pichavant et al. (2002) estimated a primary magmatic H₂O content of 2 wt% for SV031, giving $W_0 = 0.36$ wt%. At South Sandwich Islands, we estimate a magmatic H₂O content of 1wt%, which corresponds to $W_0 = 0.20$ wt%. The total trace-element budget of the slab component is found by subtracting the pre-subduction wedge composition (C_{pre}) from the modified-wedge composition (C_{mod}) as calculated above. This trace-element inventory was added via a fluid with 50% H₂O, thus the concentration of each trace element (C_f) in the fluid is given by:

$$C_f = \frac{50(C_{\text{mod}} - C_{\text{pre}})}{W_0} \quad (1)$$

Using Equation 1, we have calculated the slab component concentration for each arc for the following elements: Nb, La, Ce, Sr, Nd, Zr, Hf, Sm, Eu, and Ti (Table 3). These values are plotted in Figure 2c, where they are compared with other estimates of the slab component from Stolper and Newman (1994), Eiler et al. (2000), and Grove et al. (2002). There is a remarkable general agreement among all of these estimates, despite the very different methods used to derive them. For the two arcs investigated here, we see quite distinct trace element patterns that bracket those found by the other authors. The slab components at both St. Vincent and the South Sandwich Islands, show elevated Sr/Nd ratios, although in the case of the South Sandwich Islands the calculated component has distinctly lower Nb/La and Ti/Eu, and La/Sm ~ 1. At St. Vincent, the slab compo-

nent is constrained to transport significant amounts of Nb and Ti, whereas at South Sandwich Islands, these elements are much less abundant in the slab component. It is tempting to suggest that these two contrasting components reflect the different proportions of slab-derived fluid and sediment-derived melt, with the latter more prevalent at St. Vincent and the former at the South Sandwich Islands. Of course, further application of this technique to other arcs is required before such a proposal can be made with any confidence. Nonetheless, we feel that the simple method we adopt here offers a reasonable and reliable means of estimating the chemical composition of the slab component. The absence of reliable partitioning data, especially for orthopyroxene, previously made this approach very inaccurate. New experimental determinations of trace-element partitioning during slab dehydration and sediment melting would be a valuable adjunct to the present approach, enabling the calculated slab signature to be related to a particular source mineralogy and conditions.

CONCLUDING REMARKS

The new partitioning data demonstrate that trace elements are generally more incompatible during melting of the mantle wedge than during melting beneath ridges. Water has little effect, however, on the overall *pattern* of partition coefficients, which remains similar to that observed during anhydrous melting of peridotite. Possible exceptions to this generalization are Lu-Sc-V fractionation in clinopyroxene and orthopyroxene, which do appear to be affected by H₂O. It is clear from our data that the pronounced enrichments in LILEs relative to both REEs and, in particular, HFSEs, which are characteristic of arc basalts, cannot be attributed to melting of the wedge peridotite itself. Instead, these characteristics are clearly imposed on arc basalts by the metasomatic effects of slab-derived fluids and/or melts. Our new partition coefficient data have been used to make estimates of the composition of the slab component added to the mantle wedge beneath volcanic arcs. Sample calculations for St. Vincent (Lesser Antilles) and the South Sandwich Islands produce quite contrasted slab component compositions that bracket previous estimates using quite different methods. Our approach should have general applicability to other arcs.

ACKNOWLEDGMENTS

We thank the workshop staff at the Department of Earth Sciences, University of Bristol for their technical expertise, and Richard Brooker for help with TZM and FTIR work. Stuart Kearns at Bristol and Richard Hinton, Pete Hill, and John Craven at the University of Edinburgh provided help with probe analysis. We gratefully acknowledge the award of research grant GR3/12643 from NERC and a Royal Society URF grant to J.D.B. Dana Johnston, Adam Kent, Chris Hawkesworth, Simon Turner, and Tim Elliott all provided some very useful input, for which we are very grateful.

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MANUSCRIPT RECEIVED OCTOBER 10, 2002

MANUSCRIPT ACCEPTED JULY 18, 2003

MANUSCRIPT HANDLED BY MARC HIRSCHMANN