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0016-7037(95)00405-X

The role of hydrothermal fluids in the production of subduction zone magmas: Evidence from siderophile and chalcophile trace elements and boron

P. D. NOLL JR.,[1,*] H. E. NEWSOM,[1] W. P. LEEMAN,[2] and J. G. RYAN[3]

[1]Department of Earth and Planetary Sciences and Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131, USA
[2]Department of Geology and Geophysics, Rice University, Houston, TX 77251, USA
[3]Department of Geology, University of South Florida, Tampa, FL 33620, USA

Abstract—In order to evaluate the processes responsible for the enrichments of certain siderophile/chalcophile trace elements during the production of subduction-related magmas, representative lavas from seven subduction zones have been analyzed for Pb, As, Sb, Sn, W, Mo, Tl, Cu, and Zn by inductively coupled plasma–mass spectrometry (ICP–MS), radiochemical epithermal neutron activation analysis (RENA), and atomic absorption (AA). The siderophile/chalcophile elements are compared to the highly fluid-mobile element B, the light rare earth elements (LREEs), U, and Th in order to place constraints on their behavior in subduction zones. Boron, As, Sb, and Pb are all enriched in arc lavas and continental crustal rocks more so than expected assuming normal magmatic processes (melting and crystallization). Tin, W, and Mo show little evidence of enrichment. Correlations of Pb/Ce, As/Ce, and Sb/Ce with B/La are statistically significant and have high correlation coefficients (and, more importantly, slopes approaching one) suggesting that Pb, As, and Sb behave similarly to B (i.e., that they are fluid-mobile). In addition, across-arc traverses show that B/La, As/Ce, Pb/Ce, and Sb/Ce ratios decrease dramatically with distance towards the back-arc basin. W/Th, Tl/La, Sn/Sm, and Mo/Ce ratios and Cu and Zn concentrations have much less systematic across-arc variations and correlations with B/La are not as strong (and in some cases, not statistically significant) and the regression lines have much lower slopes. Mixing models between upper mantle, slab-derived fluid, and sediment are consistent with a fluid-derived component in the arcs displaying extra enrichments of B, Pb, As, and Sb. These observations imply efficient mobilization of B, Pb, As, Sb, and possibly Tl into arc magma source regions by hydrothermal fluids derived from metamorphic dehydration reactions within the slab. Tin, W, and Mo show little, if any, evidence of hydrothermal mobilization. Copper appears to be slightly enriched in arc lavas relative to mid-ocean ridge basalts (MORBs) whereas Zn contents of arc lavas, MORB, ocean island basalts (OIBs), and continental crustal samples are similar suggesting that the bulk partition coefficient for Zn is approximately equal to one. However, Zn contents of the upper mantle are lower than these reservoirs implying an enrichment of the source region in Zn prior to melting.

These nonigneous enrichments have implications not only for arc magma genesis but also for continental crust formation and crust-mantle evolution. The mobility of Pb, As, Sb, and B in hot, reducing, acidic hydrothermal fluids may be greatly enhanced relative to the large-ion lithophile elements (LILEs; including U) as a result of HS^-, H_2S, OH^-, or other types of complexing. In the case of Pb, continued transport of Pb from subducted slabs into arc magma source regions throughout Earth history coupled with a U fluxing of the mantle a the end of the Archean may account for the depletion of Pb in the upper mantle, the low U/Pb of most arc volcanics and continental crustal rocks, and provide an explanation for the Pb- Paradox (Hofmann et al., 1986; McCulloch, 1993; Miller et al., 1994). Recycled slabs will then retain high U/Pb ratios upon entering the deep mantle and may eventually become incorporated into the source regions of many OIBs; some with HIMU (high $^{238}U/^{204}Pb$) signatures.

1. INTRODUCTION

Many siderophile/chalcophile elements behave as ordinary incompatible elements during magmatic processes (melting and crystallization) in the absence of metal, sulfide phases, and in some cases, fluid phases. However, several of these siderophile (elements that follow Fe, e.g., W, Mo, Sb, Cu, Sn, etc.) and chalcophile (elements that follow S, e.g., Cu, Pb, Zn, As, Sb, Mo, Tl, etc.) elements are also commonly mobilized by hydrothermal fluids such as black smokers and ore-forming fluids. These properties allow for the use of siderophile/chalcophile elements as powerful tracers of subduction zone processes. By using ratios of siderophile and/or chalcophile elements to purely lithophile elements (those that follow oxygen) with the same bulk partition coefficient, one can facilitate the evaluation of nonmagmatic processes (assuming a closed system) occurring within the subduction zone environment. Since melting and/or crystallization will not affect the ratio (even though the absolute abundances of the elements will vary), any change in the ratio must be due to some other process. Leeman et al. (1994) demonstrated that variations in B/La ratios due to normal fractional crystallization are rarely significant for Central American lavas implying $D_B \approx D_{La}$, where D is the bulk mineral/melt partition coefficient. Numerous other workers have shown that $D_{As, Sb, Pb, Mo} \approx D_{Ce}$, $D_{Sn} \approx D_{Sm}$, $D_W \approx D_{Ba,Th}$ (Hofmann et al., 1986; Newsom et

* *Present address:* Chemical Science and Technology Division, CST-8 Inorganic Elemental Analysis, MS G740, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

al., 1986; Sims et al., 1990; Jochum et al., 1993) . Thus, the ratios Pb/Ce, As/Ce, Sb/Ce, Mo/Ce, Sn/Sm, W/Th, and B/La are largely independent of the degree of magmatic evolution and are used to monitor enrichments (or depletions) of the siderophile/chalcophile elements relative to contents of other highly incompatible and relatively immobile trace elements (e.g., REEs, Th).

In a limited study of two volcanoes from the Aleutians, Miller et al. (1994) showed that Pb is enriched relative to Ce in the arc magmas, consistent with the nonmagmatic transfer of Pb into the continental crust. In this paper we present new data for a suite of siderophile/chalcophile elements (Cu, Pb, Zn, As, Sb, Sn, W, Mo, and Tl) and B contents in arc lavas from around the world and examine which of these elements are fluid-mobile and show anomalous enrichments in arc lavas and the continental crust. Across-arc traverses are employed in order to identify systematic changes in trace element concentrations of arc lavas with distance from the volcanic front and thus depth to the subducting slab. The role and nature of hydrothermal fluids within subduction zones will be addressed as well as the subduction connection to continental crust formation and the influence of hydrothermal enrichments on crust-mantle evolution.

2. GEOCHEMISTRY OF BORON AND THE SIDEROPHILE/CHALCOPHILE ELEMENTS

The fluid-mobile nature of B, its crystal chemistry, and behavior in magmatic and metamorphic systems has been discussed in detail by previous authors (Leeman, 1987; Morris et al., 1990; Bebout et al., 1992, 1993; Moran et al., 1992; Edwards et al., 1993; Domanik et al., 1993; Ryan and Langmuir, 1993; Leeman et al., 1994). The geochemical behavior of the siderophile/chalcophile elements is consistent with the relationship between ionic charge, ionic radius, and compatibility (e.g., Jochum et al., 1993). Bulk partitioning is dependent on ionic radius and ionic charge and, for a given radius, the partition coefficient decreases with increasing charge (Fig. 1). Copper and Zn are relatively compatible elements in magmatic systems whereas B, As, Sb, Pb, Tl, Sn, W, and Mo are incompatible (in the absence of a fluid or sulfide phase). In addition, most of these elements (except B, W, and Sn) can be extremely enriched in sulfide minerals (e.g., Wedepohl, 1978; Doe, 1992; Lambert et al., 1992). Of the minerals considered to be "common mantle phases," magnetite and ilmenite are generally the most enriched in siderophile/chalcophile elements. Most ferromagnesian silicates have little As, Sb, Tl, Pb, Sn, W, and B (generally < 1μg/g) but can be quite enriched in Cu and Zn (up to hundreds of μg/g). As observed in hydrothermal vents (black smokers) and sulfide ore deposits, the elements Cu, Pb, Zn, As, Sb, Tl, and sometimes Mo are considered fluid-mobile, especially in the presence of Cl and/or S. Tin and W generally form oxide and/or tungstate ore deposits (cassiterite, scheelite, wolframite) and are usually immobile in fluids until the late stages of crystallization of felsic magmas. Tin and W sulfides are extremely rare and these two elements are not generally found in ore deposits containing Cu, Pb, Zn, As, Sb, and Tl. For these reasons it may be expected that Sn and W will also behave differently within subduction zones. A more detailed discus-
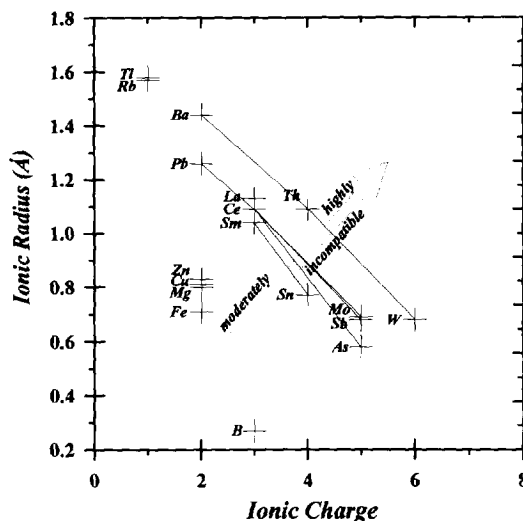

Fig. 1. Plot of ionic radius vs. ionic charge (after Jochum et al., 1993). Siderophile/chalcophile–lithophile element groups which have constant ratios form subparallel arrays. Incompatibility increases with increasing radius for a given charge and vice versa.

sion of the crystal chemistry of the siderophile/chalcophile trace elements and boron is given in Noll (1994).

3. SAMPLES AND METHODS

Samples studied include nineteen basalt to basaltic andesite lavas from the Central American Quaternary volcanic front (Morris et al., 1990; Leeman et al., 1994), a cross-arc transect of four volcanoes (basaltic andesite to andesite) from northeastern Japan (Morris and Tera, 1989; Morris et al., 1990), six basaltic andesite to andesite lavas from the southern Volcanic Zone of Chile (Morris et al., 1990), a cross-arc transect of six basaltic lavas from the southern Washington Cascades (Leeman et al., 1990), thirteen basaltic to dacitic lavas comprising three cross-arc transects from the Kurile Islands, and four representative basaltic lavas from Kamchatka, four basaltic lavas from the Mariana Islands, and seven basaltic to dacitic samples from the Aleutians (Morris et al., 1990). All samples have been previously analyzed for major elements and most for INAA trace elements (W. P. Leeman, unpubl. data; Carr et al., 1990; Leeman et al., 1994), B, and [10]Be (Morris and Tera, 1989; Morris et al., 1990; Leeman et al., 1994; Ryan et al., 1995; and unpubl. data of J. Morris, F. Tera, and J. Ryan).

Most samples were prepared for this study using a high purity alumina ball mill to grind the samples to minus 200 mesh. Prior to grinding the samples, the ball mill was cleaned with deionized water in an ultrasonic cleaner for fifteen minutes. Upon removal from the ultrasonic cleaner, the ball mill was rinsed with deionized water and then acetone and allowed to dry. After the ball mill was dry, a small amount of sample (≈1 gram) was ground and discarded. Next, approximately 10 g of sample was ground to minus 200 mesh in several stages and then stored in new polypropylene sample bottles. This procedure was repeated for all the samples.

In this study, Cu and Zn were determined by established atomic absorption (AA) techniques. Lead, Sn, and Tl (and some As and Sb) were determined by inductively coupled plasma–mass spectrometry (ICP–MS). Arsenic, Sb, W, and Mo were determined using a radiochemical epithermal neutron activation (RENA) procedure (Sims and Gladney, 1991). Brief descriptions of the RENA and ICP–MS procedures are given below. Further details of the sample preparation, RENA, ICP–MS, and AA procedures can be found in Noll (1994).

3.1. Radiochemical Epithermal Neutron Activation (RENA)

Nominally 400 mg of rock powder is irradiated with epithermal neutrons. The activated samples are then fused using a mixed salt

fusion (NaOH + Na_2O_2) and the fusion cake is dissolved with deionized H_2O and concentrated HCl. The dissolved solution is then passed through an inorganic ion exchange column containing Al_2O_3. Arsenic, Sb, W, and Mo are retained (>95%) on the Al_2O_3 which is then counted on a γ-ray detector. The procedure used was slightly modified from Gladney (1978) and Sims and Gladney (1991) in that separate synthetic standards for As + Sb (dissolved in HNO_3) and W + Mo (dissolved in H_2O) are used to enhance the stability of these solutions. Mixing of all four elemental solutions together results in the formation of Mo and W oxides (WO_3^{-6} and MoO_3^{-6}) which precipitate rapidly, thus altering the concentration of these elements in the standard solutions.

3.2. Inductively Coupled Plasma–Mass Spectrometry (ICP–MS)

For analyses by ICP–MS, two multi-acid digestion procedures were used and are described below. Approximately 200 mg of powdered rock is placed in a 17 mL Teflon™ screw-top vial (Savillex™ brand) along with 5 mL of concentrated reagent grade HNO_3 and 5 mL of concentrated SUPRAPURE® HF (Jenner et al., 1990). After the samples had digested in the tightly sealed vials on a hot plate at 90°C for 8–12 h, the caps were removed and the samples were evaporated to near dryness. At this point 12 mL of 50% HNO_3 was added and the samples were heated for 30 min at 90°C. After cooling, the samples were then transferred to 100 mL volumetric flasks containing the appropriate internal standards and brought to 100 mL volume with deionized H_2O. By evaporating to near dryness most of the HF and Si is removed (as SiF_4) and the resulting solutions have very low total dissolved solids (TDS). Unfortunately, As and Sb also suffered slight losses during evaporation possibly due to the formation of As and Sb fluorides (Cotton and Wilkinson, 1980). Copper and Zn did not appear to be affected by evaporation and Sn, Tl, and Pb were not affected by evaporation (see Appendix).

Samples were analyzed by standard addition (Weberling and Cosgrove, 1965; Caulcutt and Boddy, 1983) with a single addition and by use of a three standard calibration curve similar to that used in atomic absorption (AA) analyses. For standard addition, 50 mL of the sample, as prepared above, is transferred into another 100 mL flask containing the appropriate additions for the elements of interest. Both the sample (unknown) and the sample with the additions (standard) are brought to 100 mL volume with 3% HNO_3. This results in an unknown and a standard with identical matrices, 100 ng/mL (ppb) Ga, In, and Bi or Th internal standards, and a dilution factor of 1000 times. The amount of standard added was estimated for Tl, Sn, and Pb from literature data and compilations of rock standards (e.g., United States Geological Survey (USGS) rock standards). For As and Sb, the RENA data were used as a guide. The amount of standard added was calculated to result in approximately 2–3 times the amount in the unknown. It is assumed that the working curve is linear over the concentration range employed which is a valid assumption for ICP–MS, which commonly exhibits linearity of over five to seven orders of concentration magnitude. Standard addition was employed to compensate for matrix suppression of As, Sb, and Pb. However, in the early phases of the developmental work, dilution factors were on the order of only 200 times. With an increase of the dilution factor to 1000 times most of these matrix effects were actually eliminated with no significant loss of signal (Noll, 1994).

Because of the possible loss of As and Sb as fluorides, a variation on the method described above (which avoids evaporation) was also evaluated . After the samples had been digested on the hot plate they were then cooled to room temperature and transferred to 100 mL polypropylene volumetric flasks containing 5 mL of a saturated boric acid (reagent grade) solution (48 g/L) and the appropriate internal standards and brought to 100 mL volume with 3% HNO_3. From this point, the samples were prepared as above. This method resulted in the ability to determine As and Sb along with Pb, Tl, and Sn (and also numerous other trace elements including the REE). However, since this variation on sample preparation was developed late in the course of this study, most samples were evaporated to near dryness. As a result, all As and Sb data reported here were determined by RENA except where otherwise noted.

Sample analyses were carried out on a VG™ Instruments PQ2 PlasmaQuad ICP–MS. Operating parameters are listed in Table 1.

Table 1. Operating parameters for ICP-MS.	
Instrument	VG® Elemental PQ2
Plasma gases	all argon
Plasma power	1400W
Reflected power	<3W
Generator	27.12 MHz
Coolant gas flow	13 L min.$^{-1}$
Nebulizer gas flow	0.679 L min.$^{-1}$
Auxiliary gas flow	0.72 L min.$^{-1}$
Nebulizer	Meinhard
Sample uptake rate	1.5 mL min.$^{-1}$
Spray chamber	water cooled at 9°C
Ion lenses	optimized on ^{69}Ga and ^{115}In

Samples were introduced via a peristaltic pump and a Meinhard nebulizer. The ion lenses were optimized using ^{69}Ga and ^{115}In so that the analytical response was relatively uniform across the entire mass range. The elements of interest were analyzed in "peak jumping" mode (i.e., only the isotopes of interest were analyzed and other masses were skipped). Typical analytical response for this instrument is 2.0 × 10^5 to 4.0 × 10^5 counts per second on a 100 ng/mL (ppb) indium standard.

Isotopes analyzed include ^{75}As, ^{121}Sb, ^{123}Sb, ^{117}Sn, ^{118}Sn, ^{119}Sn, ^{120}Sn, ^{203}Tl, ^{205}Tl, ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The concentration data reported here represent the average of values calculated for various isotopes (generally those without major interferences) and adjusted for isotopic abundance, except for As (which is monoisotopic). It was assumed that the lead isotopic composition of the standard used is that of "common" lead. A more accurate approach would have been to use a certified isotopic standard for Pb. However, considering the good agreement between ICP–MS results for USGS rock standards BHVO-1 and AGV-1 (see Appendix) and the consensus values, it would seem that the isotopic composition of the Pb standard used in this study is indeed close to that of "common" Pb.

The avoidance of Cl during sample preparation (HCl, $HClO_4$) reduces the possibility of formation of $^{40}Ar^{35}Cl$ which has a mass of 75, coincident with ^{75}As. No $^{40}Ar^{35}Cl$ was detected during sample or blank analysis and most As values were within error for USGS rock standards (see Appendix). Cobalt oxide ($^{59}Co^{16}O$) can also potentially interfere with ^{75}As but oxide levels for Co are generally on the order of CoO/Co <0.0017% (Jarvis et al., 1992). The samples analyzed in this study average 29 ± 12 μg/g (1 s) Co. This amounts to a 0.05% contribution to the As peak from CoO. These levels of CoO require no corrections on the ^{75}As data as this is less than the analytical error. Antimony, Sn, Tl, and Pb all have isotopes with no major interferences and the good agreement between consensus values and those obtained by ICP–MS for USGS rock standards testifies to this (see Appendix).

4. RESULTS

The dataset used throughout this work is given in Tables 2 and 3 (Noll, 1994). The data in Table 2 were determined in the course of this study whereas the data in Table 3 are from other workers (Carr et al., 1990; Morris et al., 1990; M. J. Carr, pers. commun., 1993; W. P. Leeman, pers. commun., 1993; J. G. Ryan, pers. commun., 1993; Ryan et al., 1995). All of the samples are transitional between the tholeiitic and calc-alkaline series and almost all are sub-alkaline (Noll, 1994). The samples selected for this study represent typical tholeiitic to calc-alkaline arc volcanics which allows for direct comparison from one geographic region to another.

4.1. Siderophile/Chalcophile Element Abundances and Bimodal Compatibility

From Fig. 2 it can be seen that B, Pb, As, and Sb display "bimodal compatibility" (Hofmann, 1988). In other words,

Table 2. Siderophile/chalcophile trace element data for arc volcanics. All values in µg/g.

Sample	Volcano	Dist.[##]	Cu[†]	Pb[#]	Zn[†]	As[‡]	Sb[‡]	Sn[*]	W[‡]	Mo[‡]	Tl[#]
CENTRAL AMERICA											
Guatemala											
P701	Pacaya	----	85	4.8	108	0.75	0.10	0.8	0.2	0.6	0.070
E-1	Pacaya	----	78	4.0	101	0.73	0.09	1.0	0.1	0.5	0.070
Gut-102	Tecuamburro	----	60	2.6	94	3.17	0.34	0.8	0.3	0.7	0.030
El Salvador											
IZ-108	Izalco	----	107	3.5	79	0.96[#]	0.15[#]	0.6	<0.1	0.1	0.083
SM-7	San Miguel	----	186	2.9	82	2.41	0.32	0.8	0.2	0.8	0.035
SA-204	Santa Ana	----	135	4.1	110	1.79	0.22	0.8	0.3	1.1	0.060
AR-82	Arenal	----	112	4.1	80	1.12[#]	0.14[#]	1.4	----	----	0.035
AP-3	St. Vicente	----	115	1.7	74	0.60[#]	0.03[#]	0.5	----	----	0.010
Nicaragua											
NE-203	Nejapa	----	116	1.2	87	0.05	0.01	0.4	<0.1	0.2	0.001
NE-202	Nejapa	----	143	0.7	86	0.48[#]	0.03[#]	0.5	0.3	0.8	0.010
CN-1	Cerro Negro	----	160	1.9	84	1.20	0.16	0.4	0.1	0.4	0.040
MT-101	Momotombo	----	117	2.8	80	1.85	0.24	0.6	0.2	0.6	0.085
MS-4	Masaya	----	241	14.3	150	1.52	0.26	1.0	0.5	1.2	0.040
TE-1	Telica	----	160	5.3	81	3.86	0.69	1.6	0.3	1	0.140
Costa Rica											
PP7	Poas	----	90	5.1	85	0.45	0.05	0.6	0.3	0.8	0.020
D-2	Irazu	----	103	2.1	76	0.69	0.10	0.7	0.6	1.7	0.090
IZ-63-G	Irazu	----	118	4.8	72	1.51	0.21	0.9	0.7	2.2	0.089
T-24-2	Turrialba	----	----	4.1*	----	1.41*	----	0.9*	----	----	----
T-85	Turrialba	----	----	2.9*	----	2.60*	----	0.5*	----	----	----
JAPAN											
E-21	Esan	0 km	58	8.28*	83	7.00[§]	1.50[§]	----	----	----	0.011*
Komaga-taki		40 km	9	8.4	59	2.43	0.20	0.6	0.4	1.2	0.076
KAT-2	Rausa-dake	40 km	18	6.2	63	1.19	0.09	0.8	0.5	1.5	0.149
Oshima-oshima		140 km	37	6.9	81	0.56	0.07	0.6	0.7	1	0.295
CHILE											
Osorno (1835)		----	85	4.6	79	4.66	0.33	0.7	0.4	0.5	0.060
Mirador (1979)		----	65	4.3	87	4.91	0.29	0.8	0.2	0.5	0.051
San Jose (1800's)		----	26	13.5	75	5.07	0.36	1.3	0.9	2	0.181
Villarica (1984-85)		----	126	9.8	94	6.00	0.91	0.9	0.4	0.9	0.062
Mocho Chosuenco (1863)		----	63	12.6	91	7.87	0.68	1.0	0.5	0.9	0.306
Antuco (1853)		----	68	5.5	85	2.81	0.18	0.6	0.2	0.6	0.062
CASCADES											
DS-6	Mt. St. Helens	0 km	56	2.12*	88	0.60	0.07	----	0.3	1.5	0.028*
DS-72b	Mt. St. Helens	0 km	61	4.18*	83	0.53	0.09	----	0.2	0.9	0.063*
DS-23b	Indian Heaven	30 km	36	8.20*	102	0.30	0.12	----	0.1	0.5	0.045*
DS-61-80	Indian Heaven	30 km	69	1.03*	92	0.17	0.02	----	0.1	0.5	<0.001*
L83-97	Simcoe	80 km	28	2.80*	112	0.38	0.19	----	0.4	0.8	0.007*
L83-94	Simcoe	100 km	35	0.90*	126	0.25	0.24	----	0.4	1.1	----
KURILES											
Iturup Traverse											
B15-394	Medvhizya	0 km	76	5.5	70	1.23	0.11	0.4	0.1	0.4	0.013
B15-392	Medvhizya	0 km	51	8.2	91	4.71	0.44	0.6	0.6	2.1	0.127
B15-81/1	Iturup Seamounts	40 km	60	6.4	65	0.78	0.10	0.9	0.3	1.1	0.215
B150-80/5	Iturup Seamounts	60 km	47	4.4	73	0.48[#]	0.07	0.6	0.7	0.9	0.113
B15-73/1	Iturup Seamounts	110 km	8	5.3	54	0.88	0.10	0.8	0.8	3.1	0.699
Chirpoy Traverse											
B15-325	Chernogo	25 km	44	8.8	66	5.09	0.40	0.8	0.3	1.8	0.182
B17-684	Brat	25 km	68	3.8	80	0.92	0.08	0.4	0.1	0.5	0.052
B17-603	Brouton Island	50 km	34	3.1	62	0.44	0.05	0.6	0.3	1	0.053

Table 2. Continued.

Sample	Volcano	Dist.	Cu	Pb	Zn	As	Sb	Sn	W	Mo	Tl
Onekotan Traverse											
H-3	Nemo Caldera	0 km	68	6.3	147	5.70	0.54	0.7	0.5	1.6	0.082
8322/3	Krenitsina	0 km	25	12.8	87	9.19	0.70	0.9	0.7	2.4	0.228
B11-75/4	Onekotan Seamounts	60 km	68	4.7	73	0.87	0.09	0.6	0.3	1	0.057
B11-72/3	Onekotan Seamounts	75 km	136	4.1	83	0.57	0.04	0.5	0.2	0.9	0.124
KAMCHATKA											
K-8	Alaid (1981)	----	138	4.4	99	0.91	0.05	0.8	0.3	1.2	0.075
B11-575	Alaid (1972)	----	110	4.5	100	0.85	0.06	0.4	0.2	1.1	0.025
K-1	Klychevskoi (1932)	----	----	2.94*	----	0.88	0.17	----	0.1	0.5	0.197*
K-3	Tolbachik (1975)	----	113	1.76*	79	0.89	0.07	----	0.2	0.5	0.057*
OTHER KURILES											
8342/2	Tiyatiya (1973)	----	88	5.72*	113	3.91	0.25	----	0.3	1.4	0.053*
MARIANAS											
AG1A	Agrigan	----	----	1.74*	----	----	----	----	----	----	0.012*
AN8	Anatahan	----	----	2.51*	----	----	----	----	----	----	0.046*
SA2	Sarigan	----	----	3.09*	----	----	----	----	----	----	0.099*
PAF3B	Pagan	----	----	1.63*	----	----	----	----	----	----	0.106*
ALEUTIANS											
UM-21	Umnak	----	----	5.08*	----	----	----	----	----	----	0.069*
BOG-1927	Bogoslof	----	----	3.52*	----	----	----	----	----	----	0.106*
BOG-1796	Bogoslof	----	----	8.30*	----	----	----	----	----	----	0.278*
KAN-5-8	Kanaga	----	----	8.45*	----	----	----	----	----	----	0.473*
ADAG-81-DR	Adak	----	----	0.21*	----	----	----	----	----	----	0.003*
K81-7A	Kasatouchi	----	----	6.65*	----	----	----	----	----	----	0.139*
MM77-102		----	----	1.74*	----	----	----	----	----	----	0.026*

†Atomic Absorption (AA), *Inductively coupled plasma-mass spectrometry (ICP-MS) employing standard addition, ‡Radiochemical epithermal neutron activation (RENA), *ICP-MS employing a 3 point calibration curve, §Instrumental neutron activation analysis (INAA), ⁑Distance from the volcanic front (towards back-arc basin) in kilometers.

the siderophile or chalcophile element to lithophile element ratios are rather uniform in mid-ocean ridge basalts (MORB) + ocean island basalts (OIB) but are higher in the bulk continental crust. Arc volcanics are enriched as well. Lanthanum and Ce concentration ranges for arcs and oceanic rocks are similar; however, B, As, Sb, and Pb concentrations range from comparable to MORB-OIB to much greater than bulk continental crust. Since all of these elements have similar bulk partition coefficients the ratios should be similar in all reservoirs. Apparently, B, As, Sb, and Pb partition one way in mantle-derived magmatic systems and differently in arc and continental crust generation systems. Hofmann et al. (1986) and Newsom et al.(1986) were the first to point out this apparent change in the bulk partition coefficient for the element Pb. The uniform Pb/Ce ratio in MORB + OIB indicates that $D_{Pb} \approx D_{Ce}$ during the production of oceanic rocks. However, for arc lavas and the continental crust to have a Pb/Ce ratio higher than MORB + OIB implies that during continental crustal formation and arc magma genesis $D_{Pb} \ll D_{Ce}$. Boron, As, and Sb data (Fig. 2a,c,d) show trends similar to the Pb data. Ratios of B/La, As/Ce, and Sb/Ce are relatively uniform in MORB and OIB, are higher in continental crust and arc volcanics, and display negative correlations when plotted against the appropriate normalizing element (La or Ce), analogous to those for Pb/Ce.

Molybdenum, Sn, and W (Fig. 3a,c,d) do not appear to be enriched in the continental crust (Jochum et al., 1993; Sims et al., 1990) or arc lavas (this study) relative to the REE and Th. In fact, Sn/Sm and Mo/Ce ratios are relatively constant in nearly all types of terrestrial rocks of all ages (Newsom et al., 1992; Jochum et al., 1993) implying that these ratios may be indicative of the primitive mantle. Data for arc volcanics (this study), however, show that arc magmas may actually be slightly depleted in Sn relative to MORB and OIB (Fig. 3c). Earlier studies on the W content of the continental crust indicated a small enrichment relative to Ba (Sims et al., 1990). However, data from Noll (1994) indicate that W/Ba ratios for arc lavas overlap those for MORB-OIB and that some arc lavas may actually be depleted in W (or enriched in Ba). Because Ba contents can vary due to its fluid-mobile nature, W is here normalized to Th (Fig. 3d). It is interesting to note, and perhaps this is not unexpected, the very different behavior of Sn, W, and Mo relative to B, Pb, As, and Sb. Possible explanations for this follow in the discussion.

Little is known about the geochemical behavior of Tl. Its similarity in size and charge to Rb indicate that it may behave like Rb in geochemical systems. Based on the relationships in Fig. 1, La may have a bulk D similar to Tl and is relatively immobile in fluids. Because of this, La is used as a normalizing lithophile element to Tl (chalcophile). Assuming that Tl

Table 3. Additional elemental concentrations[§] in arc volcanics. Trace elements in μg/g, major element oxides in wt.%.

Sample	B	La	Ce	Sm	Th	SiO_2	K_2O	Na_2O	MgO	FeO*
CENTRAL AMERICA										
Guatemala										
P701	8.2	11.1	23.9	4.1	1.5	51.70	----	----	----	----
E-1	8.0	10.2	24.8	3.6	----	51.70	0.84	3.59	3.52	8.95
Gut-102	----	4.4	12.9	----	----	54.00	----	----	----	----
El Salvador										
IZ-108	18.8	6.6	12.3	2.6	1.6	52.70	0.94	3.55	4.32	8.20
SM-7	20.0	8.6	23.5	3.8	0.9	51.90	0.88	2.98	3.43	8.90
SA-204	15.0	12.0	30.6	4.4	----	52.30	1.41	3.43	4.29	9.55
AR-82	11.5	13.2	26.6	----	1.1	54.61	0.64	3.08	4.76	7.91
AP-3	5.7	5.3	12.7	2.7	----	49.61	0.35	2.41	6.01	10.63
Nicaragua										
NE-203	3.2	3.2	8.0	2.3	----	47.70	0.14	2.20	11.09	11.60
NE-202	2.9	3.3	9.8	2.4	0.2	48.16	0.24	2.54	9.64	11.43
CN-1	13.3	3.5	7.1	2.0	0.2	50.80	0.46	2.20	4.73	9.71
MT-101	25.0	6.0	13.5	2.9	0.7	55.00	0.92	2.92	4.52	9.20
MS-4	24.5	10.2	22.3	4.0	1.8	51.70	1.18	2.87	5.35	12.10
TE-1	36.0	6.8	16.2	5.1	1.3	52.70	1.34	2.78	4.48	9.83
Costa Rica										
PP7	3.6	60.3	104.5	7.1	5.5	46.10	1.21	1.09	14.47	9.02
D-2	6.0	41.4	83.2	7.1	----	51.30	1.59	2.78	9.16	8.11
IZ-63-G	14.5	38.1	74.2	6.5	10.1	55.20	1.98	3.46	5.69	6.83
T-24-2	10.0	33.0	67.0	----	5.0	53.00	1.48	3.50	6.29	7.57
T-85	3.3	42.0	82.0	----	5.4	52.20	1.10	3.63	6.54	8.81
JAPAN										
E-21	29.1	3.8	7.5	1.6	1.6	61.53	0.56	2.67	3.40	8.51
Komaga-taki	15.8	7.0	15.6	3.1	2.1	59.70	----	----	----	----
KAT-2	17.0	12.5	29.0	4.4	5.4	62.10	----	----	----	----
Oshima-oshima	4.8	22.5	45.0	4.8	6.9	56.40	----	----	----	----
CHILE										
Osorno (1835)	15.0	6.2	15.3	2.7	1.2	53.70	0.52	2.98	4.51	7.33
Mirador (1979)	15.0	6.9	15.2	3.1	0.6	53.70	0.54	3.79	4.58	10.07
San Jose (1800's)	20.0	30.1	57.6	5.4	12	63.00	2.71	4.19	2.53	4.87
Villarica (1984-85)	27.0	9.1	16.2	5.1	3.0	53.00	0.70	3.22	6.57	9.17
Mocho Chosuenco (1863)	23.0	14.0	34.3	4.8	2.9	59.10	1.32	4.40	3.33	7.46
Antuco (1853)	12.0	9.0	20.4	3.1	1.4	50.40	0.68	3.10	10.01	9.47
CASCADES										
DS-6	4.0	21.2	45.3	5.5	2.5	50.00	1.31	3.89	6.62	10.14
DS-72b	5.7	11.3	26.8	3.4	1.4	53.00	0.99	4.27	5.46	8.22
DS-23b	2.9	65.9	141.0	10.9	0.8	52.20	2.19	4.18	6.02	7.65
DS-61-80	2.2	4.8	11.5	----	----	49.70	----	----	----	----
L83-97	1.5	40.5	78.4	8.0	4.2	50.00	2.17	4.28	5.80	10.97
L83-94	2.2	17.1	37.5	----	1.7	49.10	0.76	3.22	6.88	11.99
KURILES										
Iturup Traverse										
B15-394	8.6	2.4	6.8	1.8	0.3	52.00	0.27	2.28	5.62	10.08
B15-392	29.0	4.5	10.8	2.9	0.9	61.30	0.78	3.04	3.55	7.76
B15-81/1	12.9	14.9	32.9	3.9	4.6	57.60	1.71	3.35	3.60	6.77
B150-80/5	8.5	11.8	24.6	3.7	3.0	55.20	1.23	2.95	4.53	8.05
B15-73/1	12.2	24.3	51.6	4.5	6.6	64.70	3.56	4.39	1.37	3.75
Chirpoy Traverse										
B15-325	28.0	9.2	20.7	3.9	2.6	61.20	1.43	3.57	3.13	6.84
B17-684	8.2	4.9	11.8	2.4	1.0	51.80	0.61	2.38	5.12	9.90
B17-603	4.5	14.0	32.1	4.1	2.7	52.80	1.41	3.15	7.77	7.13

Table 3. Continued.

Sample	B	La	Ce	Sm	Th	SiO₂	K₂O	Na₂O	MgO	FeO*
Onekotan Traverse										
H-3	34.1	3.8	8.8	2.7	0.8	62.00	0.88	3.74	2.10	8.62
8322/3	49.6	7.7	21.5	4.5	2.0	65.00	1.30	4.12	1.86	5.65
B1Γ-75/4	8.9	12.7	28.1	3.7	3.0	52.90	1.60	3.24	4.53	7.32
B11-72/3	4.6	10.8	22.3	4.1	2.1	48.80	1.39	2.92	4.97	10.03
KAMCHATKA										
K-8	13.0	13.4	29.0	4.4	2.5	51.30	1.84	3.25	4.03	9.37
B11-575	9.7	12.3	24.9	4.2	2.2	53.30	1.82	3.17	4.49	9.73
K-1	12.5	6.1	13.2	3.1	0.7	51.10	0.94	2.93	7.61	8.26
K-3	31.0	6.0	13.3	2.8	0.6	51.30	0.89	2.48	9.69	9.00
OTHER KURILES										
8342/2	37.2	5.7	15.2	3.7	0.8	53.50	1.51	2.83	4.18	10.98
MARIANAS										
AG1A	7.3	8.1	15.7	3.0	0.9	51.35	0.74	2.65	4.98	11.63
AN8	4.6	5.7	11.8	2.4	0.6	49.80	0.46	2.24	4.56	9.71
SA2	7.2	7.7	15.3	2.9	1.0	53.53	0.73	2.52	6.09	9.07
PAF3B	13.0	3.7	7.8	1.9	0.3	49.75	0.49	1.98	7.34	10.36
ALEUTAINS										
UM-21	17.0	----	----	----	----	----	----	----	----	----
BOG-1927	3.7	8.0	18.9	3.9	3	46.74	1.63	2.64	5.49	10.66
BOG-1796	14.0	20.6	49.9	4.5	10.3	61.32	2.41	4.22	1.11	4.73
KAN-5-8	32.0	10.2	24.4	3.7	3.7	54.05	1.30	3.20	3.90	8.77
ADAG-81-DR	----	----	----	----	1.9	----	----	----	----	----
K81-7A	11.0	5.4	13.6	2.3	1.6	49.63	0.77	2.27	8.87	8.92
MM-77-102	----	----	----	----	----	----	----	----	----	----

*All Fe as FeO. §Data sources: M. Carr (pers. commun., 1989); LEEMAN et al. (1990); MORRIS et al. (1990); W.P. Leeman (pers. commun., 1993); J. Ryan (pers. commun., 1993); LEEMAN et al. (1994); RYAN et al. (1995).

has the same relative incompatibility as La, it appears that Tl may be enriched in arc lavas and the continental crust though there is considerable overlap with the estimated range of MORB-OIB (Fig. 3b). Thallium is also highly mobile in ore-forming hydrothermal solutions and enrichment of Tl in sulfides is generally accompanied by enrichments of Pb, As, Sb, and Ag (Wedepohl, 1978). However, without more data for oceanic rocks it is difficult to evaluate the Tl contents of arc lavas in terms of enrichments/depletions.

Unlike the other siderophile/chalcophile elements above, Cu and Zn behave as compatible elements in these systems. Purely lithophile elements with bulk Ds similar to Cu and Zn are not available. Therefore, Cu and Zn are here interpreted in terms of absolute abundances. The mean concentration of Zn in mafic arc lavas and MORB + OIB are indistinguishable within one standard deviation (arcs = 87 ± 20 µg/g, 1s; MORB + OIB = 104 ± 21 µg/g, 1s). Gurney and Ahrens (1973) indicate that the uniform Zn contents imply a bulk partition coefficient for Zn of approximately unity. However, mantle derived basalts have more than 2–3 times the Zn content of the mantle (≈48 µg/g; Wänke et al., 1984). Therefore, either $D_{Zn} \neq 1$ or the source areas for basalts must be enriched in Zn, prior to melting, by some process. Copper concentrations are more variable and average 84 ± 50 µg/g (1s) in arc lavas and 41 ± 34 µg/g (1s) in MORB + OIB. Although there is considerable overlap, the Cu contents of arc lavas may be up to twice that of MORB-OIB. The estimated primitive mantle abundance of Cu is 28.2 µg/g (Wänke et al., 1984). Copper

correlates with Ni in certain MORB suites suggesting $D_{Cu} > 1$ (J. G. Ryan, pers. commun. 1994) in magmatic systems. The enrichment of Cu in arc lavas implies possible enrichment of the arc magma source region in Cu by non-magmatic processes.

4.2. Siderophile/Chalcophile Elements and Boron

The fluid-mobile nature of B is employed here to evaluate the behavior of the siderophile/chalcophile elements within subduction zones. The B/La ratio is used in like fashion to the ratios in Figs. 2 and 3. Since $D_B \approx D_{La}$ in magmatic systems (Leeman et al., 1994) the ratio should not change in response to melting or crystallization. Thus, changes in the B/La ratio are attributed mainly to the fluid-mobility of B. In Figs. 4 and 5, B/La is plotted against the siderophile/chalcophile elements normalized to the appropriate lithophile element (except for Cu and Zn). Linear regression analysis of the datasets in Figs. 4 and 5 indicate that all correlations of siderophile/chalcophile element ratios with the B/La ratio are statistically significant. This is based on a two-tailed t-test of the correlation coefficient, r, at the 95% confidence level (Miller and Miller, 1984). Copper and Zn concentrations are not statistically correlated with B/La (Noll, 1994).

The linear regression correlation coefficient (r) measures how well the data fit a straight line. A high r value (r^2 is the coefficient of determination) indicates a high degree of correlation, and vice versa. However, the slope of the regression
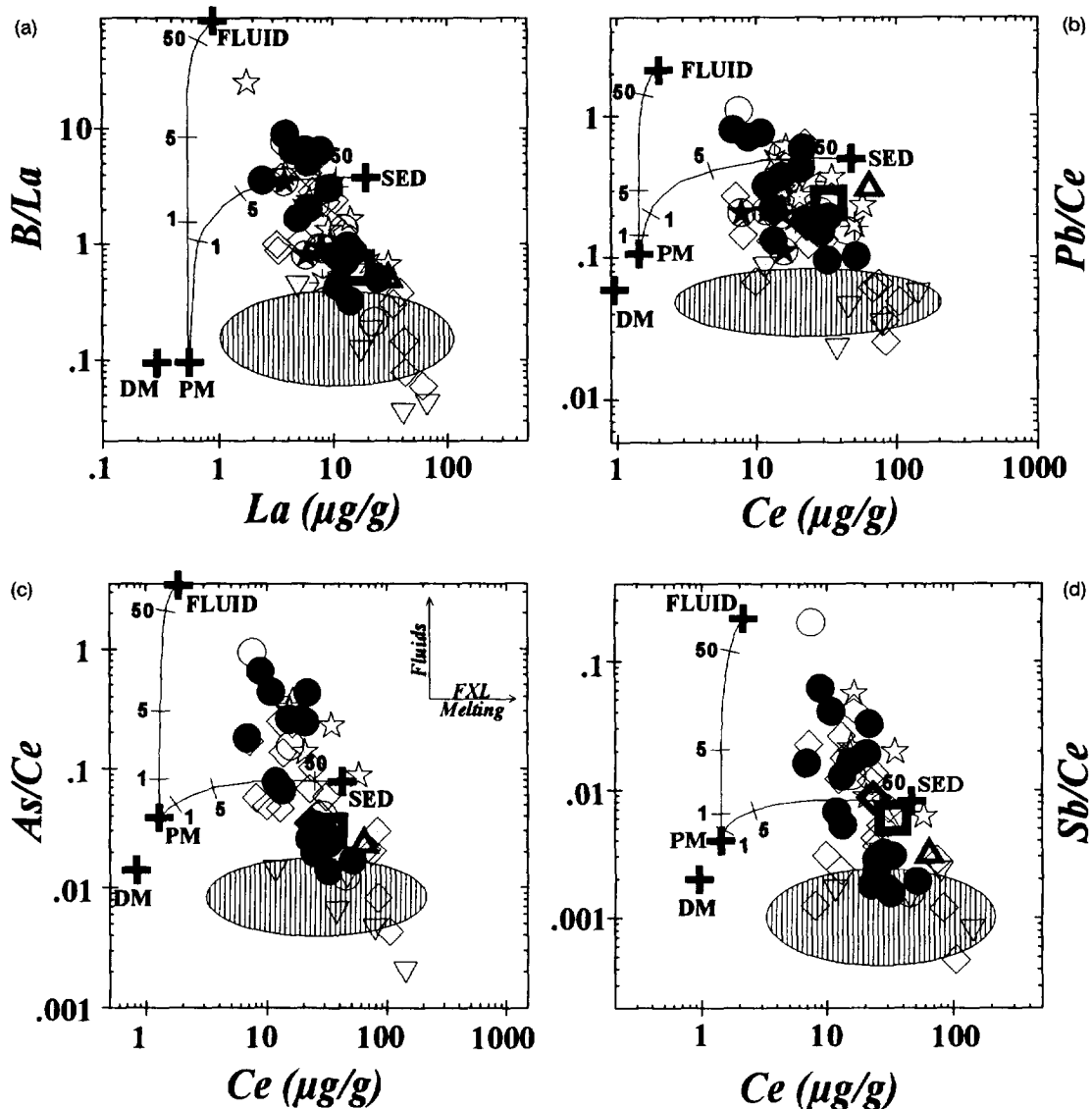
Fig. 2. Data from this study plotted on (a) B/La vs. La, (b) Pb/Ce vs. Ce, (c) As/Ce vs. Ce, and (d) Sb/Ce vs. Ce diagrams. Filled circles = Kurile/Kamchatka, open diamonds = Central America, open circles = Japan, open stars = Chile, open traingles = Cascades, four-point star with cross = Aleutians, star in circle = Marianas, open heavy diamond = lower crust, open heavy square = bulk crust, and open heavy triangle = upper crust (Taylor and McLennan, 1985). Ruled region represents limits of literature MORB + OIB data. Note that magmatic processes such as melting and crystallization (FXL) will not affect the ratios but minor fluid additions result in dramatic increases in the ratios. Pb/Ce, As/Ce, and Sb/Ce display similar trends to B/La suggesting fluid-mobility of Pb, As, and Sb. The negative sloping trend of the data reflects decreasing B, As, Sb, and Pb concentrations within the mantle wedge with distance from the volcanic front. Volcanic front magmas have high ratios and LREE contents similar to MORB whereas back-arc-basin magmas (or magmas from hot, "dry" arcs) have low ratios and overlap the field for OIB (see text for discussion). Tic marks on mixing lines indicate percentage of fluid (FLUID) or sediment (SED) mixed with primitive mantle (PM). Depleted mantle (DM) is also shown, however, for clarity, mixing lines are not drawn to DM (see text for discussion of mixing models).

line relates to the dependence or independence of one variable relative to the other. For example, a dataset with $r = 1$ but a slope of zero indicates a perfect correlation but that y is independent of x. A dataset with $r = 0.7$ and $m = 1$ indicates a fairly good correlation and that y and x are behaving similarly. For the current discussion it is important to realize that B is being used to evaluate the siderophile/chalcophile elements. Of course, the higher the r value, the better the correlation,

but more importantly (for those correlations that are statistically significant); the higher the slope, the more the element of interest is behaving like B. Figure 6 plots the slopes of the regression lines for the statistically significant correlations in Figs. 4 and 5. It can be seen that As/Ce and Sb/Ce have slopes that approach one. Pb/Ce, Tl/La, and Mo/Ce have intermediate slopes, whereas Sn/Sm and W/Th have slopes approaching zero. These data indicate that As/Ce and Sb/Ce ratios, and
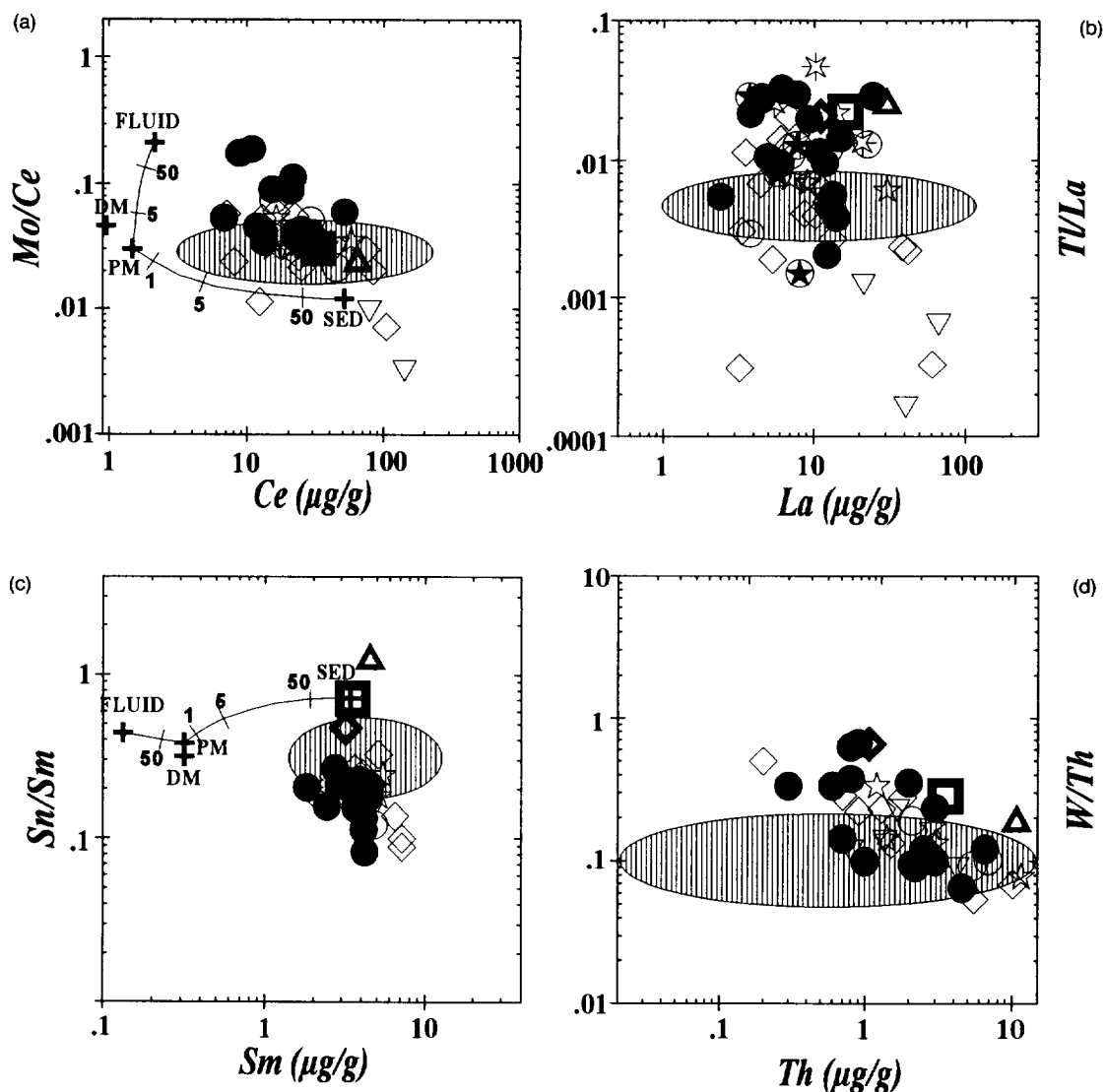
FIG. 3. Data from this study plotted on (a) Mo/Ce vs. Ce, (b) Tl/La vs. La, (c) Sn/Sm vs. Sm, and (d) W/Th vs. Th diagrams. Mo/Ce and Sn/Sm ratios are fairly uniform in most rocks implying little deviation from primitive mantle values. Field for MORB + OIB for Tl/La vs. La is approximate. Sn/Sm ratios in arc lavas are generally lower than in oceanic rocks whereas W/Th ratios overlap MORB + OIB. These trends suggest little, if any, mobilization of Mo, Sn, and W by hydrothermal fluids. Tl/La ratios are slightly elevated relative to MORB + OIB indicating possible mobility of Tl. Mixing lines and symbols as in Fig. 2.

to a lesser extent, Tl/La, Pb/Ce, and Mo/Ce ratios increase with increasing B/La whereas Sn/Sm and W/Th ratios are independent of the B/La ratio.

4.3. Across-Arc Traverses

Samples taken along traverses perpendicular to the volcanic front at increasing distances towards the back-arc region provide constraints on the mechanisms of arc magma generation under differing conditions (temperature, pressure, water content, etc.). Presented here are data for samples from Japan, the Cascades, and from three traverses across the Kurile arc (Fig. 7). It should be pointed out that the suites of samples for each traverse are not necessarily comagmatic. The traverses represent the interaction of a variably depleted subducted slab

with the mantle wedge. Even though the samples range from basalt to dacite, effects related to melting/crystallization (assuming a closed system) are minimized by the use of ratios of the siderophile/chalcophile elements to normalizing lithophile elements with the same bulk partition coefficient.

The most striking feature for the Japan traverse (Fig. 7a) is the dramatic decrease in the B/La, As/Ce, Sb/Ce, and Pb/Ce ratios with distance from the volcanic front. As/Ce and Sb/Ce decrease the most (nearly two orders of magnitude) followed by B/La and then Pb/Ce. The Mo/Ce ratio also decreases noticeably whereas the Sn/Sm and W/Th ratios decrease only slightly. The Tl/La ratio increases with distance which may indicate that Tl concentrations are increasing faster than La in melts generated at further distances from the volcanic front (i.e., Tl immobile in fluids and $D_{Tl} < D_{La}$). Copper concen-
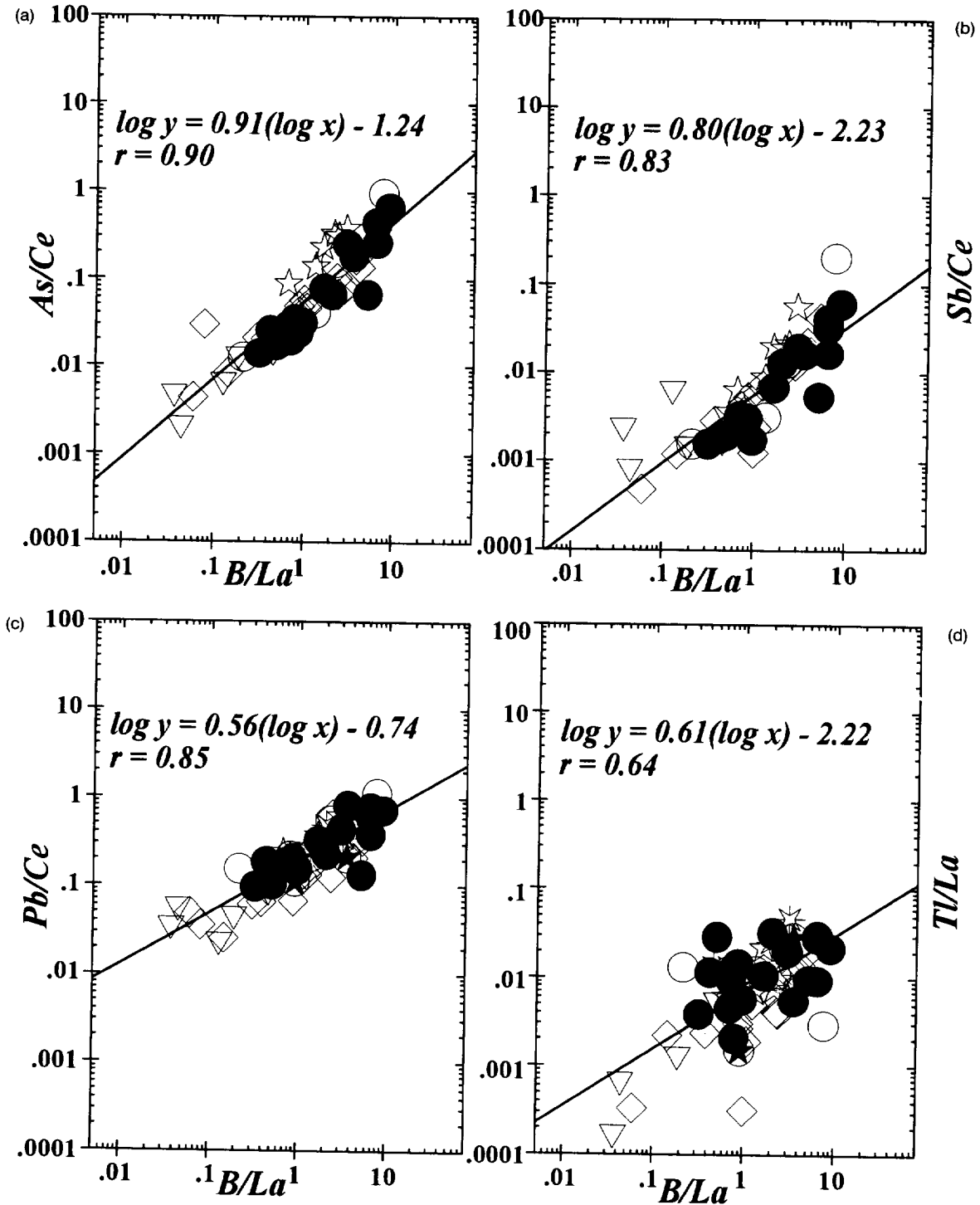
Fig. 4. Siderophile/chalcophile trace element ratios for arc lavas plotted against B/La. (a) As/Ce, (b) Sb/Ce, (c) Pb/Ce, and (d) Tl/La. All correlations are statistically significant. Symbols as in Fig. 2.

trations decrease slightly and then increase. Zinc appears to be fairly constant from front arc to back arc.

The Iturup traverse across the Kurile arc (Fig. 7b) displays the same general features as the Japan traverse. The B/La, As/Ce, Sb/Ce, and Pb/Ce ratios all decrease substantially towards the back arc region. In this traverse, the Mo/Ce ratio initially decreases and then increases resulting in a nearly con-

stant ratio across the arc. The Sn/Sm and W/Th ratios display similar trends. Again, the Tl/La ratio increases with distance. Copper concentrations decrease while Zn contents remain uniform with distance. In Fig. 7c it can be seen that, for the Onekotan traverse across the Kurile arc, B/La, As/Ce, Sb/Ce, Pb/Ce, Mo/Ce, and W/Th all decrease noticeably from front arc to back arc. The Mo/Ce and Pb/Ce ratios vary almost

(a)

$$\log y = 0.31(\log x) - 0.79$$
$$r = 0.68$$

W/Th vs *B/La*

(b)

$$\log y = 0.20(\log x) - 0.76$$
$$r = 0.72$$

Sn/Sm vs *B/La*

(c)

$$\log y = 0.39(\log x) - 1.44$$
$$r = 0.75$$

Mo/Ce vs *B/La*
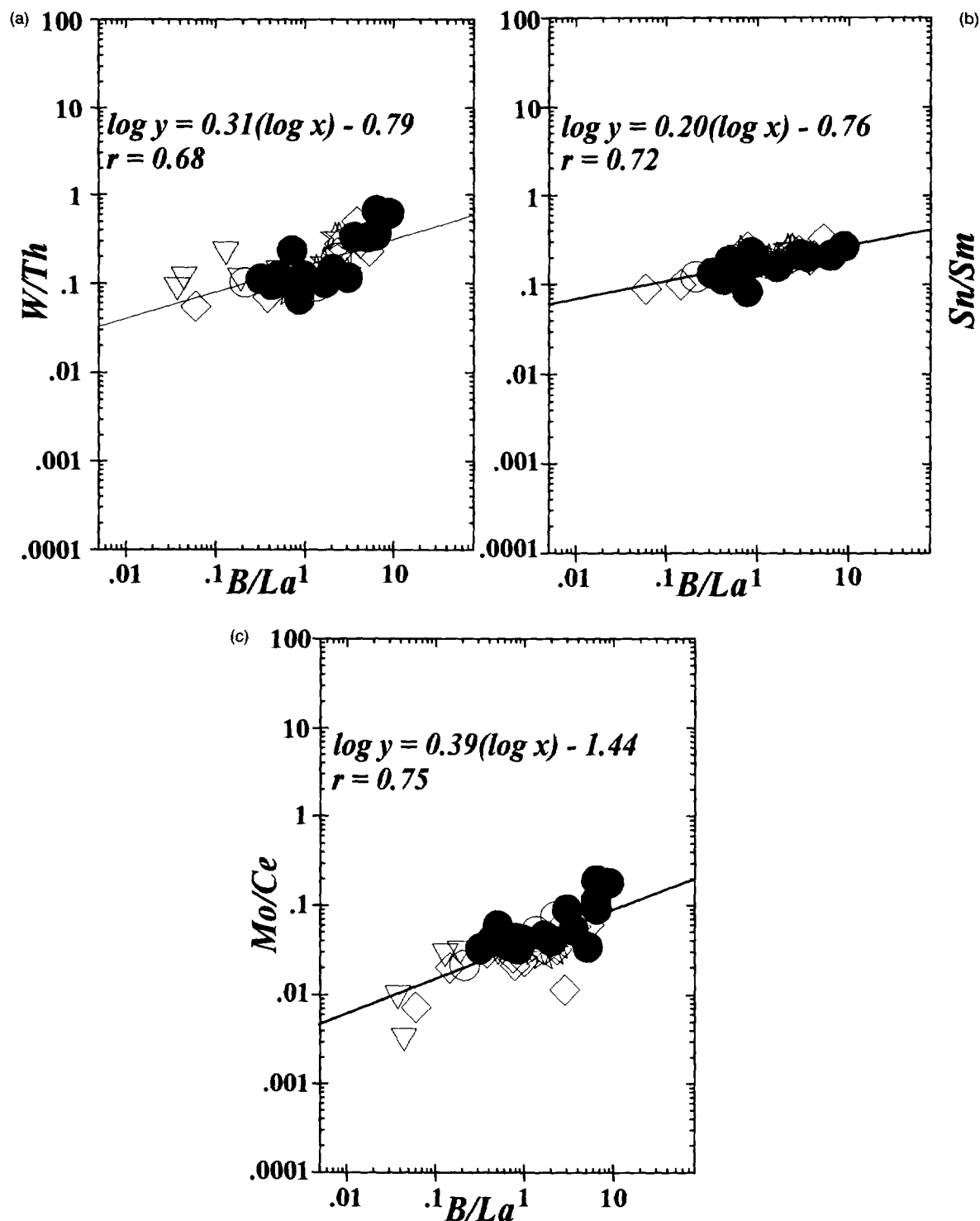
FIG. 5. Siderophile/chalcophile trace element ratios for arc lavas plotted against B/La. (a) W/Th, (b) Sn/Sm, and (c) Mo/Ce. All correlations are statistically significant. Symbols as in Fig. 2.

identically indicating that, in this case, Mo and Pb may be behaving similarly. The Sn/Sm ratio is again fairly constant with distance as are Cu and Zn concentrations. The Tl/La ratio decreases initially but increases towards the back-arc. The partial Chirpoy traverse (Table 2) across the Kurile arc (not shown, see Noll, 1994) exhibits the same general fea-

tures of the previous figures. B/La, As/Ce, Sb/Ce, and Pb/Ce all decrease dramatically towards the back arc region. The Mo/Ce ratio also decreases but only slightly. The Sn/Sm ratio is again nearly constant with distance whereas the W/Th ratio increases slightly. For this traverse, the Tl/La ratio decreases noticeably. Copper concentrations decrease
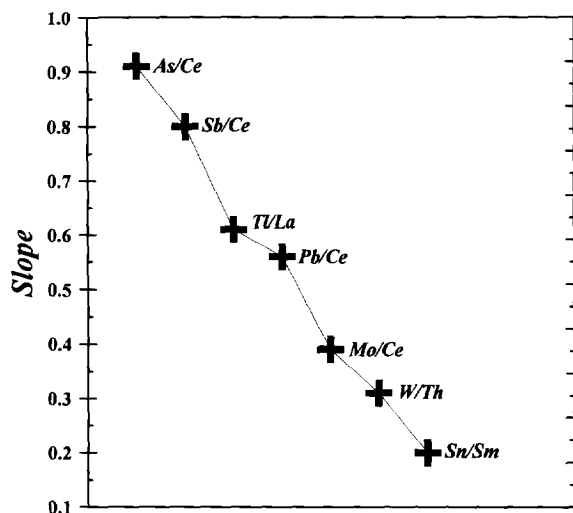
Fig. 6. Slopes of the regression lines calculated in Figs. 4 and 5. Arsenic and Sb have slopes approaching one; Tl, Pb, and Mo have intermdeiate slopes; and Sn and W have slopes approaching zero. This suggests that As and Sb (and to a lesser extent Tl, Pb, and Mo) are mobilized along with B. Tin and W concentrations are independent of B contents.

slightly while Zn contents remain uniform from front arc to back arc.

Across arc variations in siderophile/chalcophile element ratios and the B/La ratio for the Cascades are presented in Fig. 7d. The Cascades represents a very different situation from the previous arcs presumably related to the very different physical parameters of this arc as discussed below. In this case, Pb/Ce and Tl/La are the only ratios that systematically decrease with distance and the Pb/Ce ratio decreases only slightly. The B/La, As/Ce, Sb/Ce, Mo/Ce, and W/Th ratios all decrease initially and then increase in the back arc region. Zinc contents increase slightly and Cu decreases with distance.

5. DISCUSSION

Boron, As, Sb, and Pb display "bimodal compatibility" (Fig. 2) and are therefore enriched in the continental crust and arc lavas more than expected for magmatic processes alone. In contrast, Sn, W, and Mo(?) are not enriched in the continental crust or arc lavas (Fig. 3). Copper, Zn, and Tl (and Mo?) may show some enrichment in the crust and arc lavas (Fig. 3); however, much more data is needed to properly address the possibility of enrichments or depletions of these elements. Because of the lack of data for Tl and normalizing elements for Cu and Zn, and the earlier prediction that Sn, W, and Mo should behave differently from B, As, Sb, and Pb due to their respective solubilities in ore-forming and black smoker hydrothermal fluids, the bulk of the following discussion will focus on B, As, Sb, Pb, Mo, Sn, and W. The enrichments of B, As, Sb, and Pb (and the lack of enrichment of Sn, W, and Mo) in arc volcanics and the continental crust have important implications for the generation of subduction-related magmas and the production of new continental crust at convergent margins. These processes are also tied to the evolution of the mantle-continental crust system. We will ex-

amine several lines of evidence that support the role of hydrothermal fluids in the enrichment process. This is followed by a discussion on the possible nature of the fluids and the implications of fluid-derived enrichments on crust-mantle evolution.

5.1. Geochemical Behavior of Siderophile/Chalcophile Elements and Boron in Subduction Zones

Studies on the B-^{10}Be content of arc lavas (Morris et al., 1990; Ryan and Langmuir, 1993; Leeman et al., 1994) and the B contents of metamorphic rocks analogous to subducted oceanic crust and sediments (Moran et al., 1992; Bebout et al., 1993) have demonstrated that B is highly fluid-mobile within subduction zones. By using ratios of siderophile/chalcophile elements to lithophile elements with the same bulk partition coefficient, it has been shown that changes in these ratios must be due to nonmagmatic processes. The high As/Ce, Sb/Ce, and Pb/Ce ratios in arc lavas and continental crustal materials relative to MORB-OIB displayed in Fig. 2 imply that As, Sb, and Pb are enriched in these materials by non-magmatic processes. Strong correlations, combined with slopes of the regression lines approaching one, of As/Ce, Sb/Ce, and Pb/Ce with the B/La ratio (Fig. 4) indicate that As, Sb, and Pb vary systematically with B, implying that these elements are fluid-mobile.

The behavior of As, Sb, Pb, and B in the across arc traverses for Japan and the Kuriles (systematics for the Cascades arc will be discussed shortly) exhibited in Fig. 7 provide further evidence in support of fluid-mobility. B/La, Pb/Ce, As/Ce, and Sb/Ce ratios display dramatic decreases with distance from the volcanic front (VF) towards the back-arc-basin (BAB). If the siderophile/chalcophile elements and B were behaving as typical incompatible elements (and immobile in fluids), their concentrations should change at the same proportion as the normalizing lithophile element and the ratios would remain constant. From Table 2 it can be determined that As and Sb decrease in absolute concentration in arc lavas on the order of 85% from the VF to the BAB (in some cases as much as 95%). Boron concentrations decrease an average of 70% (but can be as high as 89%) and Pb concentrations decrease approximately 40% (up to 65%). The LREEs (La and Ce), on the other hand, increase in concentration in the lavas from the VF to the BAB an average of 65% (ranges from 45–83%). It is difficult to envision a magmatic process that will increase the concentration of the LREEs and at the same time decrease the concentration of equally incompatible elements such as B, As, Sb, or Pb across an arc. However, mobilization of B, As, Sb, and Pb in hydrothermal fluids provides an explanation for this apparent dichotomy.

The decrease in B, As, Sb, and Pb across the arc can be explained by large fluid fluxes beneath the VF with decreasing amounts of liberated fluids towards the BAB as the slab is converted into eclogite. This serves to create a "chemical gradient" within the wedge. Boron, As, Sb, and Pb contents are high in the wedge beneath the VF but decline in concentration towards the BAB. The relatively immobile LREEs, however, remain somewhat constant in the wedge (and at similar levels to oceanic rocks; Ryan et al., 1995) over the same distance. Thus, the ratios in the wedge are altered before melting takes
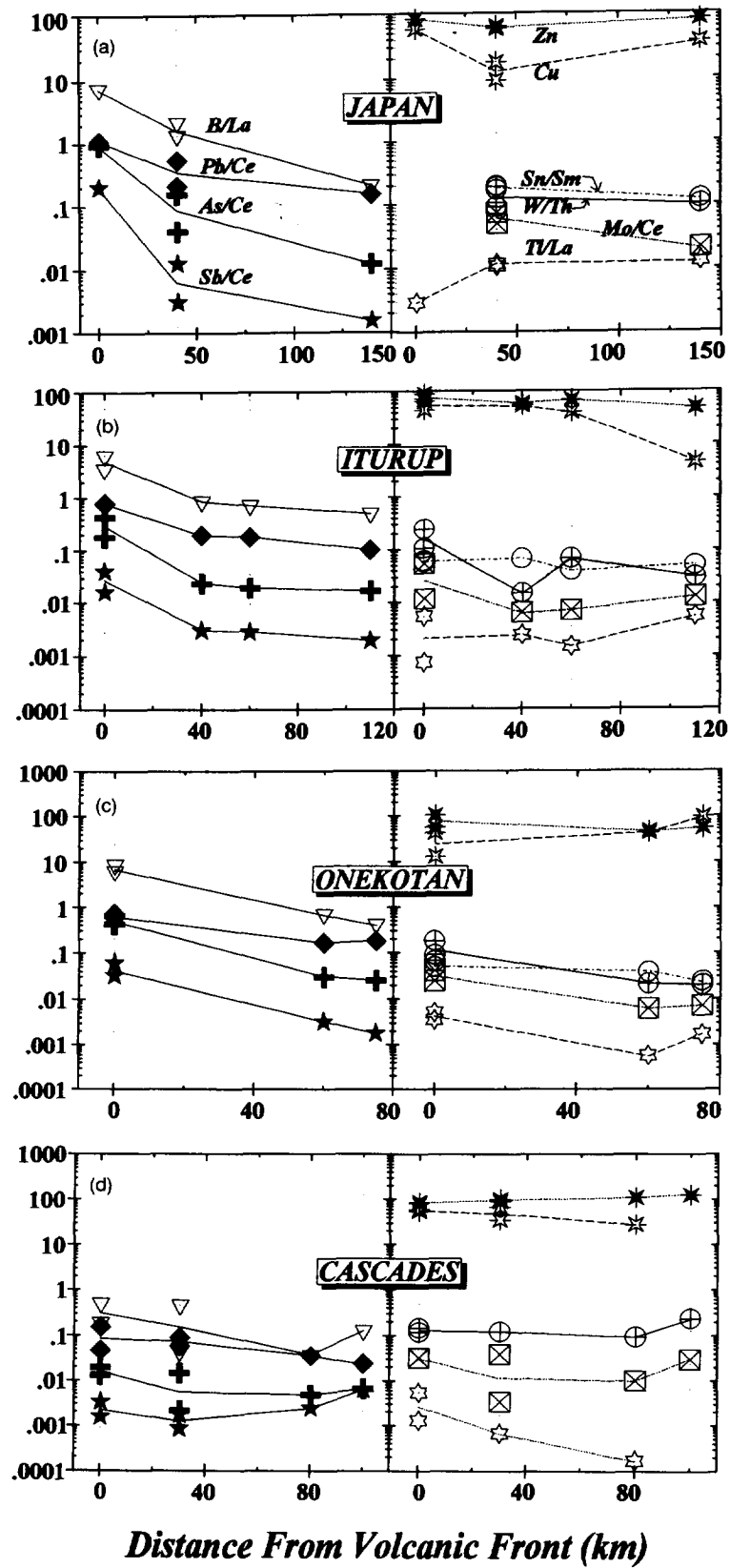
FIG. 7. Variation of element ratios across the Japan arc, two traverses across the Kurile arc (Iturup and Onekotan traverses), and across the Cascades arc (see text for discussion). Note: In several instances there is more than one sample at the same distance. In these cases, both samples are plotted and the trend line taken through the average.

place. This, in effect, establishes a VF "reservoir" which grades into a BAB "reservoir" with different ratios. This can be observed in Fig. 2 where VF lavas and continental crustal materials generally have higher B/La, As/Ce, Sb/Ce, and Pb/Ce ratios than MORB and OIB but BAB lavas and lavas from hot "dry" arcs (e.g., the Cascades) have ratios similar to OIB. The negative trend in the arc data on these plots represents the gradation from a VF "reservoir" to a BAB "reservoir".

Another important point is that after the initial modification of the mantle wedge: B, As, Sb, and Pb will behave as typical incompatible elements during future melting and crystallization events. Thus, during melting of the wedge (whether it is beneath the VF or the BAB), B, As, Sb, and Pb will indeed behave similarly to La and Ce. The reason the ratios are high in VF magmas and low in BAB magmas (Fig. 7) is because fluids changed the ratios in the wedge prior to melting. The increase in the absolute concentrations of the LREEs in arc magmas towards the BAB is most likely a result of the degree of melting. The wedge can have relatively constant concentrations of the LREEs from the VF to the BAB. Large degrees of melting beneath the VF will produce magmas with low LREE concentrations compared to magmas derived from low degrees of melting beneath the BAB. In contrast, the fluid-derived VF enrichments of B, As, Sb, and Pb are so large that they mask any enrichment of these elements in BAB magmas due to their incompatibility. Thus, B, As, Sb, and Pb decrease and La and Ce increase in concentration in arc magmas across the arc.

Elements that are not fluid-mobile will be controlled by magmatic processes within subduction zones. Immobile siderophile/chalcophile elements will behave similarly to the lithophile normalizing element and the ratios will remain constant from the volcanic front to the back-arc-basin. This appears to be the general case for Sn, W, and Mo (Fig. 7). The Sn/Sm, W/Th, and Mo/Ce ratios do not decrease significantly nor systematically from the VF to the BAB and in several cases remain nearly constant. This implies that Sn, W, and Mo do indeed have bulk Ds similar to Sm, Th, and Ce, respectively, and that these elements are not significantly mobilized by hydrothermal fluids within subduction zones. The absolute abundance data for these elements in arc lavas (Table 2) indicate that, on average, Sn decreases only 2%, Mo decreases 4.5%, and W increases 16% from the VF to the BAB. Here we see W behaving like a typical high field strength element (HFSE) similar to Nb, Ta, or Ti. Tin and Mo decrease somewhat across the arcs indicating that there may be a small degree of mobility for these two elements beneath the VF. Additionally, Sn, W, and Mo do not display "bimodal compatibility" which is evidently characteristic of fluid-mobile elements (Fig. 3). None of the arc lavas studied here have Sn/Sm ratios higher than MORB-OIB and many are actually depleted in Sn. W/Th and Mo/Ce ratios show considerable overlap with MORB-OIB though some arc lavas are slightly enriched in W and Mo.

It is interesting to note that Cu and Zn concentrations also generally decrease about 20—25% from the VF to the BAB whereas Tl increases ≈8%. Considering that most massive sulfide ore deposits contain considerable Cu-Pb-Zn it is reasonable to expect Cu and Zn to be mobilized along with Pb.

The Tl data is perplexing in that Tl tends to concentrate in sulfides that also contain As, Sb, Pb, and Ag as noted earlier. This would imply that Tl should be mobilized along with the As, Sb, and Pb; yet the data presented here suggests otherwise. More (and higher quality) data for Tl may shed some light on this discrepancy.

Assuming, for the moment, that hydrothermal fluids are indeed responsible for the enrichments of B, As, Sb, and Pb (and lack of enrichments of Sn, W, and Mo) in arc magmas, the elemental abundances and the ratios to lithophile elements should respond to differing physical parameters (subduction zone geometry, convergence rate, slab dip, etc.) in a predictable way. For example, for arcs with slow convergence rates and/or shallow slab dips (e.g., the Cascades) the temperature of the slab will equilibrate with that of the mantle at shallower depths. This may result in early (shallow) dehydration of the slab and loss of fluid-mobile elements in the forearc region (Leeman et al., 1994). This could limit the enrichment of fluid-mobile elements beneath the volcanic front and at deeper depths. With no hydrothermal enrichment these elements will behave as ordinary incompatible elements and as a result, there will be little or no variation of the element ratios with distance across the arc. Subduction of young, and thus, relatively warm lithosphere (S. Chile, Cascades) may result in similar geochemical trends.

For Japan and the Kuriles the convergence rate is about the same at 9–10 cm y⁻¹ (Gill, 1981). The dips of the slabs are similar at about 20–30° (Jarrad, 1986) as is the age of the subducting crust (Jurassic), and the timescale of subduction (≈100–125 Ma; Gill, 1981). The Cascades, however, is a relatively young arc (subduction initiated 50 Ma ago; Gill, 1981) with a slab dip of only 9° (Jarrad, 1986), a convergence rate of 2–3 cm y⁻¹ (Gill, 1981), and is subducting relatively warm, young crust (Leeman et al., 1990) formed at the Juan de Fuca Ridge. The slow convergence rate, warm slab, and shallow dip of the slab in the Cascades arc should allow for early or shallow release of volatiles and fluid-mobile elements. With these elements removed from the slab, sub-VF magmas will have no fluid-derived enrichments and B, As, Sb, and Pb will behave as typical incompatible elements. Thus, B/La, As/Ce, Sb/Ce, and Pb/Ce ratios should not change across the arc. These trends are reflected in the low overall abundances (≈ an order of magnitude) of these elements in the Cascades lavas relative to Japan and the Kuriles and in the across-arc traverses. Figure 7 shows that the dramatic decreases in these ratios observed for the Kuriles and Japan traverses are absent for the Cascades. For the Cascades traverse, most ratios decrease only slightly and then increase in the back-arc region resulting in little change in the ratio from VF to BAB as would be expected for magmatic processes.

The dip of the slab can also affect the enrichment of the mantle wedge. Steeply dipping slabs may cause the release of fluids to be focussed in a relatively narrow zone more directly beneath the VF resulting in more efficient metasomatism of the mantle wedge and greater enrichments of fluid-mobile elements. Slabs with shallow dips will release fluids over a broad region or lose volatiles beneath the forearc resulting in less-efficient transport of fluid mobile elements into the overlying wedge. Since the fluid-mobile elements will be dispersed over a broader region of the wedge or possibly lost

under the forearc there may be little or no perceptible enrichment in VF magmas. This has been noted for B in lavas from the Central American arc (Leeman et al., 1994). B/La ratios in lavas from Guatemala, Nicaragua, and El Salvador (where relatively old, cold crust is subducted steeply) are high. In contrast, B/La ratios in lavas from Costa Rica and Panama (where young, warm crust is being shallowly subducted) are low. Some Costa Rican lavas have B/La ratios identical to OIB indicating no sub-arc mantle metasomatism with respect to B (Leeman et al., 1994). Data from this study indicate that As/Ce, Sb/Ce, Pb/Ce, and some Mo/Ce ratios are also lowest in Costa Rican lavas (and overlap OIB values) and highest in Nicaraguan lavas (Table 2, Fig. 2). This implies efficient fractionation of B, As, Sb, and Pb (and Mo?) from the LREEs beneath Nicaragua (large slab component/fluid enrichment) but no fractionation or enrichment of these elements with respect to the LREEs beneath Costa Rica (little or no slab component/fluid enrichment). Sn/Sm and W/Th ratios in Costa Rican lavas overlap with Nicaraguan and other arc and OIB values indicating no significant enrichment of Sn or W relative to Sm and Th, respectively, (Table 2, Fig. 3) or, in other words, no fractionation of Sn and W from equally incompatible yet immobile lithophile elements irrespective of slab dip.

5.2. Enriched Element Sources, Enrichment Mechanisms, and the Production of Arc Magmas

5.2.1. Enriched element sources

The production of new oceanic crust and its return into the mantle via subduction zones can be considered the most important differentiation process occurring on the Earth today (Hofmann, 1990). This process has likely been occurring for >4 Ga. Concurrent with the production of new oceanic crust is the alteration of this crust by hydrothermal convection cells present along oceanic ridges. The presence of base metal-rich black and white "smokers," metalliferous sediments, and sulfide deposits along mid-ocean ridges (Hinkley and Tatsumoto, 1987; Ding and Seyfried, 1992; Hannington et al., 1992; German et al., 1993; Metz and Trefry, 1993; Mills et al., 1993; Rona et al., 1993; Puecker-Ehrenbrink et al., 1994), and sulfide mineralization as deep as the transition zone between the sheeted dikes and pillow basalts (Alt and Vanko, 1992) within the oceanic crust, attests to the enrichment of this new oceanic crust and overlying sediment in base-metals and other siderophile/chalcophile elements. In addition, the oceanic crust can be metamorphosed from low to mid greenschist facies shortly after formation resulting in the formation of a greater number of hydrous phases (e.g., Gillis and Thompson, 1993). Later, low temperature alteration and seawater interaction can also add elements (such as B, Rb, Cs, Ca, Pb, U, Sr, etc.) to the crust and increase $^{87}Sr/^{86}Sr$ ratios (Staudigel et al., 1981; Hart and Staudigel, 1982; Verma, 1992). Seawater may also be trapped in the upper portions of the crust and sediment pile. The deposition of pelagic (Wedephol, 1978; Hole et al., 1984), terrigenous (White and Dupré, 1986; Ben Othman et al., 1989), and metalliferous sediments (see above) on the seafloor adds additional trace elements, including Pb, and can dramatically alter the Sr, Nd, and Pb isotopic composition of the oceanic crust (altered MORB plus sediments). Conse-

quently, the composition of subducted oceanic crust differs significantly from typical MORB glasses and it is enriched in siderophile/chalcophile elements, LILE, and can have widely variable isotopic ratios depending on the degree and style of alteration and on the amount and type of sediments that are subducted.

Melting of depleted upper mantle will generally produce MORB (Saunders et al., 1988). Therefore, within subduction zones, the mantle wedge must be enriched in some way to become sources for arc magmas. Altered MORB plus sediments provide the reservoirs for the elements that are enriched in arc magmas, yet how the enrichment takes place is still obscure. Several possible mechanisms for enrichment of the mantle wedge include metasomatism of the wedge by hydrothermal fluids, incorporation of high-silica melts derived from the subducting slab (altered MORB plus sediments), and incorporation of bulk sediments into the mantle wedge. Hydrothermal fluids and/or melts have been invoked for years to account for the unique geochemistry of arc lavas (e.g., Gill, 1981; Zindler and Hart, 1986; Saunders et al., 1991). While slab melting may have been important in the Archean (Taylor and McLennan, 1985) and may play a role today where young, hot slabs are subducted (e.g., Bau and Knittel, 1993; Defant and Drummond, 1993; Sajona et al., 1993), recent studies of fluid mobile elements within subduction zones (Leeman, 1987; Morris and Tera, 1989; Morris et al., 1990; Noll et al., 1992a,b; Ryan and Langmuir, 1993; Leeman et al., 1994; Noll, 1994) and modelling of subduction zone geotherms calculated on the basis of heat transfer theory (Peacock, 1993a,b) argue against slab melting (and probably even against sediment melting) in most cases. Several researchers have shown that only very young (and thus relatively warm) lithosphere will melt and even then only within a few tens of millions of years after the initiation of subduction (Peacock, 1987, 1990, 1993a,b, 1994; Saunders et al., 1991; Sacks and Kinkaid, 1990; Vidal, 1992).

In addition to contributions from the slab itself (altered MORB), lead isotopic studies, Ce anomalies, and ^{10}Be-B systematics (White and Patchett, 1984; White and Dupré, 1986; Morris et al., 1990) of arc volcanics indicate that subducted sediment contributes to arc magmas though how this contribution is made is another topic of recent debate. In a study of the B-Be contents of Central American lavas, Leeman et al. (1994) presented mixing models between various mantle sources and bulk subducted sediment and a hydrothermal fluid. These models revealed little evidence that direct addition of bulk sediments into the mantle contributes to the production of arc magmas. Assuming that the relatively high slopes and correlation coefficients for Pb, As, and Sb with B (see Fig. 4) indicate that these elements are mobilized in like fashion to B, mixing models involving siderophile/chalcophile trace elements are presented here to place some general qualitative constraints on the mechanism of transfer of these elements within subduction zones.

5.2.2. Bulk Sediment-Fluid-Depleted Mantle Mixing Models

In order to evaluate the relative roles of sediment addition and hydrothermal fluids in the production of arc magmas, end-member compositions have been estimated (Table 4) for bulk

Table 4. Model parameters for mixing calculations. All values in μg/g.

	T&M PAAS	SIMS PAAS	NASC	Site 765	Calculated Site 765	Model Sediment	Model Fluid	Model DM	Model PM
B	100	-	-	-	-	100[a]	90[a]	0.03[a]	0.06[a]
La	38.0	-	31.1	24.0	24.0	23*	1[a]	0.31[a]	0.61[a,c]
Ce	80	-	67	56	51	48*	2.1[j]	0.95[i]	1.61[e]
Sm	5.6	-	5.6	4.5	3.5	3.4*	0.14[j]	0.32[i]	0.387[e]
Pb	20	-	-	-	-	26[c]	5[k]	0.06[g]	0.18[e]
As	-	6.6	28.4	5.8	-	4[b]	7.3[k]	0.014[f]	0.063[f]
Sb	-	0.54	2.1	0.9	-	0.4[b]	0.45[k]	0.002[f]	0.006[d,f]
Sn	4.0	-	-	-	-	2.4*	0.06[k]	0.10[h]	0.12[h]
Mo	1.0	1.2	-	-	-	0.6*	0.44[k]	0.045[f]	0.047[f]
B/La	3	-	-	-	-	4	90	0.10	0.10
Pb/Ce	0	-	-	-	-	0.5	2	0.06	0.11
As/Ce	-	-	0.4	0.1	-	0.08	3.5	0.015	0.04
Sb/Ce	-	-	0.03	0.02	-	0.008	0.21	0.002	0.004
Mo/Ce	0.01	-	-	-	-	0.013	0.21	0.047	0.030
Sn/Sm	0.7	-	-	-	-	0.71	0.43	0.31	0.31

T&M PAAS = Post-Archean average Australian Shale (TAYLOR and MCLENNAN, 1985). SIMS PAAS = Post-Archean average Australian Shale (SIMS et al., 1990). NASC = North American Shale Composite (GROMET et al., 1984). Site 765 = average concentrations for sediment column at DSDP site 765 (PLANK and LUDDEN, 1992). Calculated Site 765 = calculated concentrations for sediment column at DSDP site 765 (PLANK and LUDDEN, 1992). [a]LEEMAN et al. (1994); [b]mean of PAAS (SIMS et al. (1990)) and site 765 (PLANK and LUDDEN (1992)) multiplied by 0.6 (terrigenous content of average ocean sediment; see HAY et al. (1988) and PLANK and LUDDEN (1992)); [c]BEN OTHMAN et al. (1989); [d]WÄNKE et al. (1984); [e]HOFMANN (1988); [f]SIMS et al. (1990); [g]CHAUVEL et al. (1992); [h]JOCHUM et al. (1993); [i]WOOD (1979); [j]estimated from REE pattern (LEEMAN et al., 1994); [k]estimated using correlations in Figs. 4-5. * = PAAS x 0.6 as above.

subducted sediments (SED), hydrothermal fluids (FLUID), depleted mantle (DM), and primitive mantle (PM). For the sake of simplicity, variations in the endmembers are considered insignificant. The establishment of a "representative" sea floor sediment column ("Calculated Site 765"; see Table 4) to be used in elemental input-output calculations (Plank and Ludden, 1992; Plank and Langmuir, 1993) for subduction zones has lead to some generalizations regarding the chemical composition of seafloor sediments. For elements not contained in calcium carbonate (most trace elements with the exceptions of Pb, Sr, Ba, U, P, and Mn) the average subducted sediment can be modelled as a shale composite (North American Shale Composite, NASC or Post-Archean Australian Shale, PAAS; Gromet et al., 1984; Taylor and McLennan, 1985) diluted by biogenic phases. The worldwide distribution of seafloor sediments was recently evaluated by Hay et al. (1988) with the result that average seafloor sediment is approximately 40% carbonate with the rest being composed of pelagic clays and terrigenous material. For the present model, La, Ce, Sm, As, Sb, Sn, and Mo contents of the model sediment were estimated by multiplying their concentrations in PAAS by 0.6 (the noncarbonate percentage of average seafloor sediment). Lead concentrations were obtained from Ben Othman et al. (1989) and B from Leeman et al. (1994). The As and Sb contents of PAAS are from Sims et al. (1990).

The B and La contents of the model hydrothermal fluid are taken from Leeman et al. (1994). Cerium and Sm contents were estimated from a chondrite-normalized REE pattern of the model fluid given in Leeman et al. (1994). The model fluid B estimate was used in the equations for the regression lines in Figs. 4 and 5 to estimate the abundances of some of the siderophile/chalcophile elements (see Table 4). Surprisingly, the estimates for As, Sb, and Pb are comparable to average

contents of these elements in various geothermal waters listed in Weissberg et al. (1979) and Skinner (1979). The similarities may only be coincidental as these fluids are low temperature (most <100°C), shallow-level hot springs and probably not directly comparable to subduction zone systems. Unfortunately, there are very few data on the high temperature (>350°C)-high pressure solubilities and complexing capabilities of these elements. Since the concentrations of these elements can vary widely in hydrothermal fluids depending upon the chemical and physical properties of the fluids and the source(s) of the mobilized elements, the estimates of the concentrations of various elements in the model hydrothermal fluid are the least well constrained of the various endmembers given in Table 4. Estimates for depleted mantle (DM) and primitive mantle (PM) are referenced in Table 4. The DM and PM abundances of Sn were estimated using the Sn/Sm ratio of Jochum et al. (1993) and a DM value for Sm from Wood (1979) and a PM value for Sn from Hofmann (1988).

The mantle wedge possibly exists as an otherwise depleted matrix (DM) with variably enriched (e.g., E-MORB or OIB source) domains (Leeman et al., 1994). Since it is not possible to determine the exact nature of the mantle wedge and because the composition of the wedge is likely different from one arc to another, PM and DM are used as "generic" mantle compositions. DM can be considered depleted upper mantle or MORB-source. PM is generally considered to represent the upper mantle plus the continental crust; however, for current purposes PM can be considered an "enriched" mantle source.

Results of the mixing models are shown in Figs. 2 and 3. The equations used in the calculations are from Langmuir et al. (1978) for element-ratio plots. Bulk sediment (SED) and fluid (FLUID) are mixed with PM. DM is also plotted though, for clarity, mixing lines are not drawn to DM. The use of PM

instead of DM does not dramatically alter the results of the models. Evaluation of the siderophile/chalcophile elements follows that of Leeman et al. (1994) for B. Mixing curves for B, As, Pb, and Sb are similar. The data display an inverse correlation for B/La vs. La or X/Ce vs. Ce (X = As, Sb, or Pb) for volcanic arc lavas. This negative trend represents the changing chemical composition of the mantle wedge with distance from the VF as discussed previously. Bulk continental crustal estimates (Taylor and McLennan, 1985) plot near the sediment endmember. Pb/Ce, As/Ce, and B/La ratios in the sediment endmember are enriched relative to the upper mantle due to the enrichment of these elements in seafloor sediments. Arc lavas with ratios similar to PM or DM imply little, if any, subduction zone component (i.e., Cascades, Costa Rica). Melting of the various sediment-PM or fluid-PM mixtures would increase the La (or Ce) contents but the ratios of the siderophile/chalcophile-lithophile elements would remain relatively constant (Figs. 2, 3). Assuming that the bulk partition coefficient ($D^{mineral/melt}$) for La is approaching zero, Leeman et al. (1994) estimated that a melt fraction of <1% is required to produce some of the arc basalts (Fig. 2a). This is much too low for tholeiitic basalts and indicates that the mantle wedge is probably enriched (relative to MORB-source or PM) in incompatible elements. Such an enrichment would then allow for larger degree melts.

In the cases of B and Pb (Fig. 2a,b), most samples can be explained by mixing <5% sediment or fluid with PM followed by melting of the modified mantle and later fractional crystallization of the melts during ascent. The same conclusions were reached by Leeman et al. (1994) with a smaller database (Central American lavas only). While sediment mixing could not be ruled out, fluid mixing was preferred based on Be isotopic systematics combined with the B data. For example, to produce sources for the Nicaraguan lavas, incorporation of 5–10% sediment with unrealistic [10]Be/[9]Be and B/La is required. These large sediment contributions are inconsistent with low La/Yb and high Nd isotopic ratios of the lavas (Leeman et al., 1994). It is apparent in Fig. 2a,d that addition of more than 5% sediment will not produce the required change in the trace element ratios in the modified mantle wedge. In the case for As, the As/Ce ratio is similar in PM and SED; thus, sediment addition to arc magma source regions will not affect the As/Ce ratio.

The mixing models for As and Sb (Fig. 2c,d) indicate that numerous samples with X/Ce ratios (X = As or Sb) greater than SED cannot be explained by mixing bulk sediment with PM or DM. In fact, mixing of SED with DM (instead of PM) indicates that even fewer of the samples can be explained by incorporating bulk sediment into the arc magma source region. However, all of the samples can be modeled as fractionated melts derived from PM (or DM) with various additions of a fluid phase. In the cases of B and Pb, sediment mixing could not be ruled out. The new data for As and Sb, however, seem to indicate that fluid metasomatism is more plausible than addition of bulk sediment to the mantle wedge and is consistent with the conclusions reached by Leeman et al. (1994) based on B-Be systematics for the Central American arc.

Similar models are presented for Mo and Sn (Fig. 3a,c). These elements are thought to be relatively immobile in fluid

phases. In Fig. 3a,c, the bulk of the samples can be explained as direct melts of PM or DM without the addition of either sediment or hydrothermal fluids. The uniform Sn/Sm ratio (Jochum et al., 1993) suggests that Sn is controlled by magmatic processes contrary to Noll et al. (1993). The constant Sn/Sm ratio across the Japan and Kurile arcs also supports this contention. The correlation of Mo/Ce with B/La and the general (though slight) decrease of the Mo/Ce ratio with distance across certain arcs suggests that some Mo is being mobilized. The low slope of the regression line (0.39), however, indicates that, in general, Mo is controlled by magmatic processes.

Tungsten is not modelled due to the difficulty of estimating W contents of hydrothermal fluids. Tungsten is thought to be relatively immobile in fluids and is often classified as an immobile HFSE such as Nb and Ta. The across-arc traverses also indicate that W is controlled dominantly by magmatic processes.

Obviously much more data are needed to improve these models yet it is apparent that the addition of bulk sediment into the mantle wedge is not an appropriate mechanism to produce enriched arc magma sources. This exercise also demonstrates the need for direct analysis of hydrothermal fluids, deep-sea sediments (terrigenous, pelagic, and metalliferous), and altered upper oceanic crust for fluid-mobile elements. Variations in the amount, type, and chemistry of sediment subducted combined with variations in the amount of sulfide present in altered oceanic crust as disseminated grains, massive sulfides, or stockwork ore can dramatically affect the overall budgets of the siderophile/chalcophile elements within subduction zones.

5.2.3. Sediment melting or hydrothermal fluids?

Several recent studies have evaluated, either directly or indirectly, the question of whether or not subducted sediments melt or dehydrate (Plank and Ludden, 1992; Plank and Langmuir, 1993; Pawley and Holloway, 1993; Peacock, 1993a,b; Nichols et al., 1994; Ryan et al., 1995). While sediment melting is an attractive explanation for transporting certain elements into arc magma source regions there are several problems with this proposed transport mechanism. Most calculated P-T paths for subducting slabs are subparallel to the wet sediment (clay) solidus, not to mention the wet gabbro solidus, (e.g., see Peacock, 1993a,b; Peacock et al., 1994; Nichols et al., 1994) at 100–120 km depth. It is unclear if the P-T paths intersect the solidi at deeper depths. Nichols et al. (1994) point out, however, that only a slight temperature increase is needed to allow subducted sediments to melt at depths of 100–120 km. Nonetheless, the subducting slab plus sediment has likely been undergoing dehydration over an extensive range of P-T conditions. The work of Peacock (1987, 1990, 1993a,b) and Pawley and Holloway (1993) has demonstrated that continuous blueschist → eclogite reactions in the slab can cause the release of large amounts of water over a broad range of depths (<20 to >100 km) depending on the P-T path, age, original water content, and the mineralogy of the slab. If such is the case, then these fluids are likely to scavenge fluid-mobile elements and transport them up the dip-slope of the subduction zone or into the overlying mantle wedge. In fact, the meta-

morphic phase transitions within the downgoing slab modeled by Peacock (1993a) for a convergence rate of 10 cm/y, a slab dip of 20°, and various amounts of shear stress show that at least the upper half of the slab is converted to eclogite (essentially anhydrous) at depths of 70 km except for subduction zones with shear stresses of 33 MPa or less. It is unclear at what depth the slab will be converted to eclogite with these lower amounts of shear stress. However, with much of the water removed from the slab before it reaches the average depth of arc magma generation (nominally 100 km) it seems likely that most of the fluid-mobile elements will also be removed. In addition, since the slab may very well be essentially anhydrous at 100 km depth, any subducted pelagic clay or terrigenous sediment will not melt since the dry sediment solidus requires much higher temperatures than are expected for the top of the slab at these depths. Thus, it is unlikely that subducted sediments will melt and, even if they did, they would not have the necessary composition to mass balance the arc magma outputs of the fluid-mobile elements (B, As, Sb, Pb, etc.).

The B contents of metamorphic rocks analogous to subducted oceanic crust plus sediments lends credence to the above conclusions. Moran et al. (1992) showed that B is extracted by fluids released by devolatilization reactions upon progressive heating of a subducting slab. A similar study on the Catalina Schist showed that reductions in B and Cs contents with increasing metamorphic grade correlate with decreases in N and H_2O contents (Bebout et al., 1993). At 650°C, >90% of the original B (and probably H_2O) in basaltic and pelitic rocks has been removed from the slab (see Table 2 in Moran et al., 1992). This is also the approximate temperature at which hydrous red clay starts to melt at 100 km depth (Nichols et al., 1994). It is unlikely, given the large reduction in B contents (and H_2O) of the slab and sediments associated with temperatures ≥650°C, that sediment melting would occur and if it did, that incorporation of these melts into the mantle wedge will produce arc magma sources with B contents high enough to match the arc magma outputs.

5.2.4 The production of arc magmas

Many researchers have advocated large-scale hydration of the mantle wedge (e.g., Gill, 1981; Zindler and Hart, 1986; Tatsumi, 1989; Tatsumi et al., 1991; Peacock, 1993a,b; and others) by fluids released during metamorphic dehydration reactions occurring within the subducted slab (oceanic crust plus sediments). These fluids may also be directly linked to the production of arc magmas in that they lower the solidus temperature of the mantle wedge and promote melting (e.g., Ringwood, 1975, and references therein; Pawley and Holloway, 1993). The production of silica-saturated magmas (quartz tholeiites and basaltic andesites) and the development of calc-alkaline differentiation trends typical of volcanic arcs are directly related to the involvement of water (Kushiro, 1972; Nicholls and Ringwood, 1973; Nicholls, 1974; Sisson and Grove, 1993). Additionally, the liberation of fluids from the subducting altered oceanic crust plus sediments by dehydration reactions provides a vehicle for the transport of fluid-mobile elements within subduction zones.

Regardless of where the dehydration of the slab and hydration of the mantle takes place, the fact remains that in most subduction zones, the position of the volcanic front on the surface roughly corresponds to a depth to the Wadati-Benioff zone of 100 km. The lack of volcanism in the region between the trench and the volcanic front (the arc-trench gap), in most arcs, suggests that arc magmas do not originate at depths of less than about 100 km. This observation lends credibility to the models of Tatsumi (1989), Sudo and Tatsumi (1990), and Tatsumi et al. (1991) whereby mantle peridotite (wedge material) can be hydrated at shallow depths (but does not melt) and is "dragged down" with the subducting slab by convection. This hydrous peridotite later dehydrates through pressure-dependent decomposition reactions at roughly 110 km depth (pargasitic amphibole + orthopyroxene → phlogopite + clinopyroxene + olivine + garnet + H_2O and chlorite + orthopyroxene → garnet + olivine + H_2O) and 180 km depth (phlogopite + clinopyroxene + orthopyroxene → K-richterite + garnet + olivine + H_2O + K_2O). Any amphibole, chlorite, or phlogopite remaining in the slab will also dehydrate at these depths. These reactions can account for the decrease in melt fraction from the volcanic front to the back-arc as amphibole (and chlorite) can supply a larger amount of water than phlogopite (Sudo and Tatsumi, 1990). The enrichment of the wedge in fluid-mobile elements is likely occuring over a wide range of depths as temperature and pressure increase and blueschist → eclogite reactions occur. It is the pressure dependent decomposition of amphibole and chlorite within this metasomatized mantle at 110 km that accounts for arc magma production and enrichment of the magmas in fluid-mobile elements (B, As, Sb, Pb) beneath the volcanic front.

5.3. Nature of the Fluids

Based on the suite of elements mobilized (B, As, Sb, Pb, Cu?, Zn?, and Tl?) and the lack of enrichments of Sn, W, and Mo, together with studies of hydrothermal ore deposits and the direct analysis of hydrothermal fluids from mid-ocean ridges, it might be possible to place some constraints on the nature of the fluids involved in subduction zone processes. It has been known for decades that certain metals can be transported as chloride and/or sulfide complexes depending on the character of the fluids. In many ore deposits the elements Cu, Ag, Pb, Zn, Cd, Hg, and Fe are thought to have been transported as chloride complexes in relatively oxidizing, moderate salinity fluids. Fluids low in Cl but high in H_2S can transport Au, Ag, Hg, As, Sb, Pb, and Zn.

Most hydrothermal solutions are generally mildly alkaline to acidic. Solutions from the East Pacific Rise (EPR) (Michard et al., 1983) range in pH from <3.8 to 6.9. Many gangue minerals from banded iron formations and other hydrothermal ore deposits have positive Eu anomalies suggesting that the fluids were reducing leading to the reduction of Eu^{3+} to Eu^{2+}. Hydrothermal solutions sampled from the EPR also display large positive Eu anomalies (Michard et al., 1983). Using Fe/Cu ratios to calculate the log f_{O_2} of hot spring fluids from 21°N on the EPR, Ding and Seyfried (1992) estimate a redox state slightly more reducing than in equilibrium with the hematite-magnetite buffer. The solutions sampled from 21°N on the EPR registered temperatures between 280 and 350°C (Michard et al., 1983). However, in the subduction zone environment temperatures and pressures are much higher.

A recent study of volcanogenic seafloor sulfide deposits in Australia (Davidson, 1992) reveals that the Cu-Au mineralization there is due to mobilization of these elements as chloride complexes in moderate temperature (260–380°C), oxidizing, acidic, and H_2S deficient fluids. In addition, increased salinity favored the transport of W, Sn, Mo, and Co. These deposits are also markedly deficient in Pb and Zn. Experimental solubility measurements for Sb, Pb, and Zn (among others) by Wood et al. (1987) indicate that at temperatures higher than 300°C in low-Cl solutions Zn is present as a bisulfide complex $(Zn(HS)^0_2)$. This is because the H_2S concentration in equilibrium with pyrite + pyrrhotite + magnetite increases with increasing temperature. Given the presence of sulfide mineralization throughout the altered oceanic crust (Alt and Vanko, 1992), the presence of magnetite within the oceanic crust, and the presence of sulfides and magnetite in subducted sediments, it is probable that subduction zone fluids are relatively high in H_2S. In addition, Pb was also shown to be complexed as $Pb(HS)^0_2$ at temperatures higher than 300°C in low-Cl solutions (Wood et al., 1987). Neither Sb, Pb, or Zn were shown to be transported as chloride complexes at high or low temperature in low-Cl solutions. Lead and Zn can, however, readily form chloride complexes in Cl-rich solutions. Antimony is predominantly transported as $Sb(OH)^0_3$ in both Cl-rich and Cl-poor solutions (Wood et al., 1987). This may imply that B and As are also transported as OH⁻ complexes. Ryzhenko et al. (1993) have shown that H_2S plays a negligible role in the transport of Sn in hydrothermal solutions at temperatures > 200°C.

It has been proposed that chloride complexes may be responsible for the mobilization of Pb in subduction zones (e.g., Chauvel et al., 1992). However, the complexing capabilities of H_2S, HS⁻, and Cl⁻ (and other ligands such as CO_3^{2-}, F⁻, NH_3, OH⁻, SO_4^{2-}, etc.) are relatively unknown under conditions of high and variable temperature and pressure. The ability of a fluid to transport siderophile/chalcophile elements as complexes also depends on the relative concentrations of the complexing components, the oxygen and/or sulfur fugacity, temperature, pressure, whether or not the fluids are supercritical, and the pH, all of which may vary during progressive metamorphism of the slab.

The above discussion coupled with the following observations leads to some general conclusions regarding subduction zone fluids: (1) As, Sb, B, Pb, Zn, Cu, Tl(?), and Mo(?) appear to be mobilized and Sn, W, and Mo(?) are not (based on analysis of arc lavas); (2) subduction zone fluids are likely to be rich in H_2S due to the breakdown of sulfides contained within the altered crust and sediments (Cl is probably lost early due to the expulsion of trapped seawater); (3) because of the abundance of H_2S (and evidence such as positive Eu anomalies) the fluids are likely reducing; (4) at temperatures > 200°C, H_2S plays a negligible role in the transport of Sn (note that Sn is not enriched in arc magmas which is consistent with the presence of H_2S); (5) Sb, Pb, and Zn are not transported as chloride complexes in Cl-poor solutions at any temperature (these elements are enriched in arc magmas suggesting that the fluids are rich in Cl and/or S); (6) W, Mo, Sn can be transported as Cl complexes in high salinity, Cl-rich, oxidizing fluids but not generally as sulfide complexes (these elements are not enriched suggesting that Cl is not the dom-

inant complexing agent); and (7) As, Sb, and B may be transported as OH⁻ complexes.

Based on these observations, the mobility of As, Sb, B, Pb, Cu, Zn, Tl(?), and Mo(?) within subduction zones is consistent with H_2S-rich and Cl-poor, reducing, acidic, high temperature (>300°C) hydrothermal fluids. The immobility of Sn, W, and Mo(?) is also consistent with these same fluids. It is also possible that B, As, and Sb are transported as OH⁻ complexes whereas the other elements are transported as sulfide complexes. Alternatively, it is possible that the nature of the fluids changes as subduction progresses from shallow, low temperature, Cl-rich, oxidizing fluids to deep, high temperature, H_2S-rich, reducing fluids. Thus, common enrichments of Pb, As, and Sb (and Cu?, Zn?, and Tl?) and lack of enrichments of Sn, W, and Mo observed in arc basalts are consistent with enhanced solubility due to siderophile/chalcophile element complexing probably involving S and/or OH⁻. However, chloride (and/or other ligands) complexing cannot be ruled out.

5.4. Implications for Crust-Mantle Evolution

The mobilization of certain elements within subduction zones has important implications regarding crust-mantle evolution. Lead is perhaps the most important of the elements studied here because of its role in U-Pb isotopic systematics used to constrain the origins of various mantle and crustal reservoirs. One of the outcomes of U-Pb studies of oceanic rocks is the so-called "Pb-Paradox." The Pb-Paradox refers to the observation that MORB and OIB, almost without exception, have Pb that is more radiogenic than the 4.55 Ga bulk Earth geochron (Zindler and Hart, 1986). If the age of the Earth is 4.55 Ga (the age of chondritic meteorites), then the bulk Earth must lie on this geochron. Since most mantle derived rocks plot to the right of the geochron on $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plots (enriched in radiogenic Pb), there must be some other reservoir of nonradiogenic Pb. The problem is that no such reservoir can be unambiguously identified (Zindler and Hart, 1986). In addition, McCulloch (1993) argues that the Pb-Paradox requires a relatively recent U fluxing of the mantle (at the end of the Archean). Apparently, near the end of the Archean, subduction styles changed (as a result of the Earth's cooling) allowing subducted slabs to penetrate into the deep mantle without melting. Because it is likely that subducted slabs melted during the Archean, there was no mechanism to deliver U back into the deep mantle. Also at the end of the Archean the Earth's atmosphere changed from reducing to oxidizing. This allowed for the mobility of U as UO_2^{2+} during weathering at the Earth's surface and its subsequent transport into trenches (Asmerom and Jacobsen, 1993; McCulloch, 1993). According to McCulloch (1993), this addition of U to subducted sediments at the end of the Archean coupled with the fluid-mobility of U within subduction zones accounts for the increased U/Pb and U/Th ratios in subducted slabs and the U over abundance in arc rocks. In this model it is argued that U is mobilized from the slab by hydrothermal fluids and into the arc magma sources whereas Th is not. The amount of U mobilized is significant relative to Th but insignificant relative to the total U subducted. In this way the slab retains high U/Pb and U/Th while at the same time arc mag-

mas also have high U/Th (McCulloch, 1993). The data presented here, however, suggest that Pb is extremely mobile in subduction zone fluids due to base-metal complexation. In addition, it is argued that these fluids are reducing which greatly reduces the solubility of U (Bailey and Ragnarsdottir, 1994), though it is still more soluble than Th. Therefore, an alternative explanation for the high U/Pb of subducted slabs is that, in reducing fluids, U is relatively immobile compared to Pb. This is still in agreement with the model of changing subduction styles and atmospheric conditions at the end of the Archean. Uranium is still transported into trenches because of its enhanced mobility (UO_2^{2+}) during surficial weathering in an oxidizing atmosphere. The increase in subducted U at the end of the Archean also accounts for the high U/Th ratios in subducted, highly processed slabs (McCulloch, 1993).

The change in subduction styles at the end of the Archean also allows for the recycling of these U/Pb and U/Th enriched slabs into the deep mantle (McCulloch, 1993). These recycled slabs have the necessary chemical signatures (high HFSE concentrations relative to MORB) for the production of many OIB sources (Hofmann and White, 1982; Weaver, 1991; Vidal, 1992). However, since MORBs also plot to the right of the geochron, the MORB source (depleted upper mantle) must also become enriched in U/Pb and U/Th but not in HFSE. Therefore, there must be some way to get U into the upper mantle as well as the deep mantle at the end of the Archean to account for both OIB and MORB sources. McCulloch (1993) proposes mixing of the mantle wedge with depleted upper mantle, injections of OIB blobs into mid ocean ridges, and mixing of subducted slabs into the upper mantle. Mixing of the wedge with depleted upper mantle requires that the wedge be enriched in U more so than Pb and Th. This presents two problems: (1) based on the above arguments, the wedge should be enriched in Pb more so than U and (2) the solubility of U^{4+} hydroxide species is too low to account for the observed enrichment of U and U/Th ratios in arcs (Bailey and Ragnarsdottir, 1994). Uranium (VI) solubilities are higher and could account for the U enrichment and U/Th ratios in arc magmas (Bailey and Ragnarsdottir, 1994) but only if the fluids are oxidizing, which appears unlikely. What is needed is a mechanism, or mechanisms, to create a wedge that, after the production of arc magmas, has high U/Pb and high U/Th.

It has been proposed that highly fluid-mobile elements such as B have very short residence times in the upper mantle (Morris et al., 1990). Boron and other fluid-mobile elements are quickly recycled through subduction zones via arc magmatism. As amphibole and chlorite dehydrate at approximately 110 km the released fluids transport the fluid-mobile elements to the area of partial melting. The relative mobilities of certain groups of elements may play an important role here. The highly fluid-mobile elements (B, As, Sb, and Pb) may be much more efficiently incorporated into arc magmas relative to U, Th, ^{10}Be, etc. This effectively removes fluid-mobile elements (including Pb) from the wedge but could leave significant quantities of U behind. This could explain high U/Pb ratios in wedge material that is mixed with depleted upper mantle and also the low U/Pb ratios of arc lavas; however, a mechanism is still required for the fractionation of U from Th within the wedge.

The most obvious explanation for the fractionation of U from Th is that the mantle wedge is depleted in Th ($D_{Th} < D_U$; Sun and McDonough, 1989) due to previous melting events whereas U is continually being added to the wedge by fluids. This fluid addition of U is relatively minor compared to, for example, B, As, Sb, or Pb but large compared to Th. Another possibility for enriching the wedge in U relative to Th, proposed earlier, is that the nature of the fluids may change as subduction progresses. It is quite possible that at shallow levels within subduction zones the fluids released are dominantly pore fluids (seawater) at relatively low temperatures ($<300°C$). These fluids may be oxidizing, rich in Cl, and could transport U in the U^{6+} hydroxide form which is 10 orders of magnitude more soluble than Th^{4+} (Bailey and Ragnarsdottir, 1994). Lead and other metals could be transported as chloride complexes and B, As, and Sb as hydroxide complexes into the mantle wedge. As pore fluids are expelled and temperature and pressure increases, hydrous minerals start to dehydrate in the presence of sulfides. This could result in reducing, H_2S-rich, higher temperature fluids capable of transporting base metals and other elements as sulfide complexes. The change from oxidizing to reducing conditions within the subduction zone fluids would greatly reduce the transport of U (reduced to 4^+) yet continue to transport elements such as B, As, Sb, Pb, Tl, etc. In this way the wedge can become enriched in U relative to Th at a shallow depth and is subsequently dragged down by convection to depths of arc magma generation or mixed with depleted upper mantle.

All of the above processes contribute to the occurrence of the Pb-Paradox. The model of changing subduction styles and atmospheric conditions at the end of the Archean (McCulloch, 1993) combined with the proposed enhanced mobility of Pb due to complexing, the limited mobility of U within subduction zone fluids, the enhanced mobility of U during surficial weathering, the changing nature of the subduction zone hydrothermal fluids from oxidizing to reducing with depth, the short residence time of highly fluid-mobile elements within the mantle wedge, and the models of continuous dehydration of the slab and mantle wedge melting triggered by pressure-dependent decomposition of amphibole and phlogopite at specific depths (Tatsumi, 1989; Tatsumi et al., 1991; Sudo and Tatsumi, 1990) all play important roles in an evolving crust-mantle system.

If slab melting was indeed dominant in the Archean then one might expect that the bimodal compatibility seen in modern arcs for B, As, Sb, and Pb (which is a direct result of the fluid-mobility of these elements) would not be present in Archean samples. In other words, As/Ce, Sb/Ce, Pb/Ce, and B/La ratios in Archean continental crust and arc lavas would be similar to those in Archean mantle-derived magmas because the dominant mechanism of element transport would be silicate melts instead of hydrothermal fluids. In actuality, however, As and Sb (Sims et al., 1990), and Pb do display bimodal compatibility in Archean samples just as for Phanerozoic arc lavas and continental crustal materials. In some cases it appears that the ratios may be even more enriched in Archean samples relative to modern crust and arc lavas. For example, the Pb/Ce ratio averages 0.30 for modern arc lavas (Noll, 1994), 0.31 for average upper continental crust, and 0.24 for bulk continental crust (Taylor and McLennan, 1985).

Yet in Archean metasediments from West Greenland and Proterozoic metasediments from Northwest Scotland the Pb/Ce ratios average 0.35 and 0.51, respectively (McLennan et al., 1984; Floyd et al., 1989). Average Archean mudstone, which is representative of the Archean upper continental crust has an average Pb/Ce ratio of 0.48 (Taylor and McLennan, 1985). These limited data may suggest a greater enrichment of Pb (and other fluid mobile elements?) in the Archean and Proterozoic. Puecker-Ehrenbrink et al. (1994) have shown that a substantial fraction of the excess Pb ultimately found in arc lavas is delivered to subduction zones in metalliferous sediments formed at mid-ocean ridges. Thus, the fractionation of siderophile/chalcophile elements and boron from the LREE and U in the Archean may have taken place at the mid-ocean ridges and the elevated ratios were transferred "en masse" from subducted altered oceanic crust to arc magma source regions by melting of the slab. Today the fractionation takes place in both tectonic regimes but is dominant within subduction zones and is controlled by hydrothermal activity as opposed to slab or sediment melting.

6. CONCLUSIONS

The data presented here, combined with that of previous workers, have demonstrated that the continental crust is enriched in B, Pb, As, and Sb relative to LREEs when compared to oceanic rocks (MORB and OIB). This enrichment is most likely due to the transport of these elements in subduction zones from the slab to the arc magma source region by hydrothermal fluids. This is supported by statistically significant, strong correlations (slopes of the regression lines approach one) of Pb/Ce, As/Ce, and Sb/Ce with B/La. In addition, these ratios decrease from the volcanic front towards the back-arc-basin reflecting the declining role of fluids with distance and thus, depth. Tin, Mo, and W on the other hand, do not seem to be as easily mobilized by hydrothermal fluids. The fact that correlations of Mo/Ce, Sn/Sm, and W/Th with B/La are not as strong and that these ratios do not decrease systematically with distance from the volcanic front, suggests that the behavior of these elements is governed by magmatic processes. The uniform Mo/Ce and Sn/Sm ratios in nearly all terrestrial rocks indicates that Ce and Mo, and Sn and Sm are not fractionated with respect to each other and the ratios may reflect that of the Earth's primitive mantle (Sims et al., 1990; Newsom et al., 1992; Jochum et al., 1993). Copper may show a slight enrichment in arc magmas relative to MORB-OIB but Zn contents of arc volcanics, the continental crust, MORB, and OIB are similar ($D_{Zn} \approx 1$) suggesting no enrichment of Zn in the continental crust relative to oceanic crust. These reservoirs do, however, have higher Zn contents than the upper mantle which implies that magma sources are enriched in Zn prior to melting. Data for Tl are lacking but crystal chemical considerations suggest that Tl is an incompatible element in magmatic systems and is also mobilized by hydrothermal fluids, especially those that mobilize Pb, As, and Sb.

Pressure-temperature considerations suggest that melting of subducted sediment and/or altered basaltic oceanic crust within subduction zones is restricted to a very limited set of conditions; usually during the initiation of subduction or when the subducting lithosphere is relatively hot. The data pre-sented here combined with previous studies on the fluid-mobility of B suggest that hydrothermal fluids are the main vehicles for the transport of B, Pb, As, and Sb into the source regions of arc magmas. Mixing models between a primitive and/or depleted mantle source and bulk sediment or hydrothermal fluids indicate that not all arc magmas can be explained by melting sources that have been modified by the addition of bulk sediment. However, derivation of arc magmas from mantle modified by the addition of fluids is possible and is the favored model.

Much of the B, Pb, As, and Sb (and possibly Cu, Zn, and Tl) was probably enriched in the oceanic crust before subduction. This early enrichment is most likely related to hydrothermal convection cells established in new oceanic crust at mid-ocean ridges which produce sulfide mineralization throughout the oceanic crust and deposit metalliferous sediments onto the oceanic crust (black smokers) (Puecker-Ehrenbrink et al. 1994). Within the subduction zone, however, conditions are such that hydrothermal mobilization of B, Pb, As, and Sb is favored whereas mobilization of Sn, W, and Mo is not.

Little data exists on the complexing capabilities of siderophile/chalcophile elements in hydrothermal fluids at high temperatures and pressures. Nevertheless, by analogy with ore deposits, examination of ridge-crest hydrothermal systems, and experimental data it appears that sulfide and/or OH⁻ complexing may be more important than chloride complexing. Given the lack of data and the large number of variables involved it can only be stated that common enrichments of B, Pb, As, and Sb and lack of enrichments of Sn, W, and Mo in arc magmas are consistent with enhanced solubility due to complexation involving S, OH⁻, and/or Cl.

The transfer of fluid-mobile elements into the continental crust via subduction zone processes throughout Earth history may explain certain aspects of mantle geochemistry. The anomalously low U/Pb ratio of arc magmas may be produced by the preferential transport of Pb over U from the slab into the mantle wedge via base-metal complexation in hydrothermal fluids. The Pb within the wedge is further transported into newly produced arc magmas. This, combined with a late U fluxing of the mantle (McCulloch, 1993), could leave the wedge with a high U/Pb ratio. Mixture of this wedge material with depleted upper mantle may provide an explanation for the high U/Pb ratio of the upper mantle and the excess radiogenic Pb commonly found in MORBs. In addition, the hydrothermal transport of Pb from the slab into the wedge can potentially leave the slab with an unusually high U/Pb ratio which may eventually become a component of ocean island basalts. Thus, recycled oceanic crust may impart a HIMU signature and low Pb/Ce ratios to parts of the mantle (Vidal, 1992). Recycled oceanic crust provides a large reservoir with a chemistry similar to many OIBs (Hofmann and White, 1982; Hofmann, 1990; Weaver, 1991; Vidal, 1992) with variations in isotopic ratios and trace elements due to variable amounts of subducted pelagic, metalliferous, and/or terrigenous sediment and variations in the amount of fluid and fluid-mobile elements removed from the slab. In addition, late enrichment of the mantle in U relative to Th (McCulloch, 1993) may explain why oceanic basalts commonly have higher U/Th and

U/Pb ratios than suggested by the time-integrated lead isotopic signature.

Lead/Ce ratios for volcanic arcs and continental crustal estimates are identical, within error, strengthening the tie between subduction zone processes and continental crustal formation. Since Archean crust displays similar enrichments of siderophile/chalcophile elements as Phanerozoic crust, it is probable that subduction processes have been involved in continental crust formation throughout geologic time. Some Archean and Proterozoic metasediments have Pb/Ce ratios that are higher than modern continental crust. This may indicate a greater enrichment of siderophile/chalcophile elements in the Precambrian due to steeper geotherms, more rigorous hydrothermal activity, and a more primitive mantle.

Editorial handling: A. N. Halliday

REFERENCES

Alt J. C. and Vanko D. A. (1992) Hydrothermal alteration of the lower sheeted dike complex, ODP Hole 504B: Approaching the dike-gabbro transition. *Eos* 73, 255 (abstr.).

Asmerom Y. and Jacobsen S. B. (1993) The Pb isotopic evolution of the Earth: Inferences from riverwater suspended loads. *Earth Planet. Sci. Lett.* 115, 245–256.

Bailey E. H. and Ragnarsdottir K. V. (1994) Uranium and thorium solutilities in subduction zone fluids. *Earth Planet. Sci. Lett.* 124, 119–129.

Bau M. and Knittel U. (1993) Significance of slab-derived partial melts and aqueous fluids for the genesis of tholeiitic and calc-alkaline island-arc basalts: Evidence from Mt. Arayat, Philippines. *Chem. Geol.* 105, 233–251.

Bebout A. E., Graham C. M., and Leeman W. P. (1992) Trace element distribution and mobility during prograde metamorphism of sediments: ion-microprobe study of the Pelona schist, California. *Eos* 73, 327 (abstr.).

Bebout G. E., Ryan J. G., and Leeman W. P. (1993) B-Be systematics in subduction-related metamorphic rocks: Characterization of the subducted component. *Geochim. Cosmochim. Acta* 57, 2227–2237.

Ben Othman D., White W. M., and Patchett J. (1989) The geochemistry of marine sediments, island arc magma genesis, and crust-mantle recycling. *Earth Planet. Sci. Lett.* 94, 1–21.

Carr M. J., Feigenson M. D., and Bennett E. A. (1990) Incompatible element and isotopic evidence for tectonic control of source mixing and melt extraction along the Central American arc. *Contrib. Mineral. Petrol.* 105, 369–380.

Caulcutt R. and Boddy R. (1983) *Statistics for Analytical Chemists.* Chapman and Hall.

Chauvel C., Hofmann, A. W., and Vidal, P. (1992) HIMU-EM: The French Polynesian connection. *Earth Planet Sci. Lett.* 110, 99–119.

Cotton F. A. and Wilkinson G. (1980) *Advanced Inorganic Chemistry.* Wiley.

Davidson G. J. (1992) Hydrothermal geochemistry and ore genesis of sea-floor volcanogenic copper-bearing oxide ores. *Econ. Geol.* 87, 889–912.

Defant M. J. and Drummond M. S. (1993) Mount St. Helens: Potential example of the partial melting of the subducted lithosphere in a volcanic arc. *Geology* 21, 547–550.

Ding K. and Seyfried W. E. (1992) Experimental determination of Cu-Cl speciation at the T-P conditions relevant to ridge crest hydrothermal activity: Implications to log (fO_2) in the hot spring fluids. *Eos* 73, 254.

Doe B. R. (1992) Importance of source rocks in the genesis of metallic sulfide deposits: ocean ridge environment. V. M. Goldschmidt Conf. A-29 (abstr.).

Domanik K. J., Hervig R. L., and Peacock S. M. (1993) Beryllium and boron in subduction zone minerals: an ion microprobe study. *Geochim. Cosmochim. Acta* 57, 4997–5010.

Edwards C. M. H., Morris J. D., and Thirlwall M. F. (1993) Separating mantle from slab signatures in arc lavas using B/Be and radiogenic isotope systematics. *Nature* 362, 530–533.

Floyd P. A., Winchester J. A., and Park R. G. (1989) Geochemistry and tectonic setting of Lewisian clastic metasediments from the early Proterozoic Loch Maree group of Gairloch, NW Scotland. *Precamb. Res.* 45, 203–214.

German C. R., Higgs N. C., Thomson J., Mills R., Elderfield H., Blusztajn J., Fleer A. P., and Bacon M. P. (1993) A geochemical study of metalliferous sediment from the TAG hydrothermal mound, 26°08'N, Mid-Atlantic Ridge. *J. Geophys. Res.* 98, 9683–9692.

Gill J. B. (1981) *Orogenic Andesites and Plate Tectonics.* Springer-Verlag.

Gillis K. M. and Thompson G. (1993) Metabasalts from the Mid-Atlantic Ridge: new insights into hydrothermal systems in slow-spreading crust. *Contrib. Mineral. Petrol.* 113, 502–523.

Gladney E. S. (1978) Determination of arsenic, antimony, molybdenum, thorium, and tungsten in silicates by thermal neutron activation and inorganic ion exchange. *Anal. Lett.* 5, 429–435.

Gladney E. S. and Roelandts I. (1988) 1987 compilation of elemental concentration data for USGS BHVO-1, MAG-1, QLO-1, RGM-1, SCo-1, SDC-1, SGR-1, and STM-1. *Geostand. Newsl.* 12, 253–362.

Gladney E. S., O'Malley B. T., Roelandts I., and Gills T. E. (1988) Compilation of elemental concentration data for NBS clinical, biological, geological, and environmental standard reference materials. *NBS Spec. Pub.* 260-111.

Gladney E. S., Jones E. A., Nickell E. J., and Roelandts I. (1990) 1988 compilation of elemental concentration data for USGS basalt BCR-1. *Geostand. Newsl.* 14, 209–359.

Gromet L.P, Dymek R. F., Haskin L. A., and Korotev R. L. (1984) The "North American shale composite": Its compilation, major and trace element characteristics. *Geochim. Cosmochim. Acta* 48, 2469–2482.

Gurney J. J. and Ahrens L. H. (1973) The zinc content of some ultramafic and basic rocks. *Geol. Soc. S. Afr., Trans.* 76, 301–307.

Hannington M. D., Herzig P. M., Tivey M. K., Thompson G., and Rona P. A. (1992) Hydrothermal reworking of sulfide deposits in the TAG field, Mid-Atlantic Ridge: Evidence from the distribution of gold. *Eos* 73, 530.

Hart S. R. and Staudigel H. (1982) The control of alkalies and uranium in seawater by ocean crust alteration. *Earth Planet. Sci. Lett.* 58, 202–212.

Hay W. W., Sloan J. L., and Wold C. N. (1988) Mass/age distribution and composition of sediments on the ocean floor and the global rate of sediment subduction. *J. Geophys. Res.* 93, 14,933–14,940.

Hinkley T. K. and Tatsumoto M. (1987) Metals and isotopes in Juan de Fuca hydrothermal fluids and their associated solid materials. *J. Geophys. Res.* **92**, 11,400–11,410.

Hofmann A. W. (1988) Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust. *Earth Planet. Sci. Lett.* **90**, 297–314.

Hofmann A. W. (1990) Recycled ideas on the origin of OIB. *Geol. Soc. Australia*, 7th Intl. Conf. Geochron. Cosmochron. and Isotope Geol. **27**, 47 (abstr.).

Hofmann A. W. and White W. M. (1982) Mantle plumes from ancient oceanic crust. *Earth Planet. Sci. Lett.* **57**, 421–436.

Hofmann A. W., Jochum K. P., Seufert M., and White W. M. (1986) Nb and Pb in oceanic basalts: New constraints on mantle evolution. *Earth Planet. Sci. Lett.* **79**, 33–45.

Hole M. J., Saunders A. D., Marriner G. F., and Tarney J. (1984) Subduction of pelagic sediments: Implications for the origin of Ce-anomalous basalts from the Mariana islands. *J. Geol. Soc. London* **141**, 453–472.

Jarrad R. D. (1986) Relations among subduction parameters. *Rev. Geophys.* **24**, 217–284.

Jarvis K. E., Gray A. L., and Houk R. S. (1992) *Handbook of Inductively Coupled Plasma Mass Spectrometry*. Chapman and Hall.

Jenner G. A., Longerich H. P., Jackson S. E., and Fryer B. J. (1990) ICP-MS—A powerful tool for high-precision trace-element analysis in Earth sciences: Evidence from analysis of selected U. S. G. S. reference samples. *Chem. Geol.* **83**, 133–148.

Jochum K. P., Hofmann A. W., and Seufert H. M. (1993) Tin in mantle-derived rocks: constraints on Earth evolution. *Geochim. Cosmochim. Acta* **57**, 3585–3595.

Kushiro I. (1972) Effect of water on the composition of magmas formed at high pressures. *J. Petrol.* **13**, 31–334.

Lambert D. D., Morrison C. A., Ahlers W. W., Losada-Calderon A. J., Bloom M. S., and Keays R. R. (1992) Quantitative analysis of trace elements in pyrite by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS): Applications in mineral exploration. *V. M. Goldschmidt Conf.* A-62–A-63 (abstr.).

Langmuir C. H., Vocke R. D., Jr., and Hanson G. N. (1978) A general mixing equation with applications to Icelandic basalts. *Earth Planet. Sci. Lett.* **37**, 380–392.

Leeman W. P. (1987) Boron geochemistry of volcanic arc magmas: Evidence for recycling of subducted oceanic lithosphere. *Eos* **68**, 462 (abstr.).

Leeman W. P., Smith D. R., Hildreth W., Palacz Z., and Rogers N. (1990) Compositional diversity of Late Cenozoic basalts in a transect across the southern Washington Cascades: Implications for subduction zone magmatism. *J. Geophys. Res.* **95**, 19,561–19,582.

Leeman W. P., Carr M. J., and Morris J. D. (1994) Boron geochemistry of the Central American volcanic arc: Constraints on the genesis of subduction-related magmas. *Geochim. Cosmochim. Acta* **58**, 149–168.

Metz S. and Trefrey J. H. (1993) Field and laboratory studies of metal uptake and release by hydrothermal precipitates. *J. Geophys. Res.* **98**, 9661–9666.

Metz S., Trefrey J. H., and Butterfield D. B. (1994) Arsenic, gallium, indium, and thallium in hydrothermal solutions from the southern Juan de Fuca Ridge. *Eos* **75**, 176 (abstr.).

McCulloch M. T. (1993) The role of subducted slabs in an evolving earth. *Earth Planet. Sci. Lett.* **115**, 89–100.

McCulloch M. T. and Gamble J. A. (1991) Geochemical and geodynamical constraints on subduction zone magmatism. *Earth Planet. Sci. Lett.* **102**, 358–374.

McLennan S. M., Taylor S. R., and McGregor V. R. (1984) Geochemistry of Archean metasedimentary rocks from West Greenland. *Geochim. Cosmochim. Acta* **48**, 1–13.

Michard A., Albarède F., Michard G., Minster J. F., and Charlou J. L. (1983) Rare-earth elements and uranium in high-temperature solutions from the East Pacific Rise hydrothermal vent field (13°N). *Nature* **303**, 795–797.

Miller D. M., Goldstein S. L., and Hofmann A. W. (1994) Ce/Pb and Pb isotope ratios in arc magmas and the enrichment of Pb in the continents. *Nature* **368**, 514–520.

Miller J. C. and Miller J. N. (1984) *Statistics for Analytical Chemistry*. Wiley.

Mills R., Elderfield H., and Thomson J. (1993) A dual origin for the hydrothermal component in a metalliferous sediment core from the Mid-Atlantic Ridge. *J. Geophys. Res.* **98**, 9671–9681.

Moran, A. E., Sisson V. B., and Leeman W. P. (1992) Boron in subducted oceanic crust and sediments: Effects of metamorphism and implications for arc magma compositions. *Earth Planet. Sci. Lett.* **111**, 331–349.

Morris J. D. and Tera F. (1989) [10]Be and [9]Be in mineral separates and whole rocks from volcanic arcs: Implications for sediment subduction. *Geochim. Cosmochim. Acta* **53**, 3197–3206.

Morris J. D., Leeman W. P., and Tera F. (1990) The subducted component in island arc lavas: Constraints from Be isotopes and B-Be systematics. *Nature* **344**, 31–36.

Newsom H. E., White W. M., Jochum K. P., and Hofmann A. W. (1986) Siderophile and chalcophile element abundances in oceanic basalts, Pb isotopic evolution and growth of the Earth's core. *Earth Planet. Sci. Lett.* **80**, 299–313.

Newsom H. E., Noll P. D., Jr., Slane F., and Beserra T. B. (1992) Siderophile Element Abundances and Behavior. *Lunar Planet. Sci. Conf.* **23**, 983–984 (abstr.).

Nicholls I. A. (1974) Liquids in equilibrium with peridotitic mineral assemblages at high water pressures. *Contrib. Mineral. Petrol.* **45**, 289–316.

Nicholls I. A. and Ringwood A. E. (1973) Effect of water on olivine stability in tholeiites and the production of silica-saturated magmas in the island-arc environment. *J. Geol.* **81**, 285–300.

Nichols G. T., Wyllie P. J., and Stern C. R. (1994) Subduction zone melting of pelagic sediments constrained by melting experiments. *Nature*. **371**, 785–788.

Noll P. D., Jr. (1994) Siderophile and chalcophile trace element concentrations in young subduction-related volcanics: Implications for continental crust formation and crust-mantle evolution. Ph.D. dissertation, Univ. New Mexico.

Noll P. D., Jr., Newsom H. E., and Leeman W. P. (1992a) Pb/Ce ratios in island arc basalts: Implications for the genesis of ocean island basalts. V. M. Goldschmidt Conf. A-77 (abstr.).

Noll P. D., Jr., Newsom H. E., Leeman W. P., and Garcia S. R. (1992b) Siderophile and chalcophile trace element concentrations in arc volcanics: Implications for element transfer. *Eos* **73**, 342 (abstr.).

Noll P. D., Jr., Newsom H. E., Leeman W. P., and Ryan J. (1993) Lead and tin in subduction-related lavas: Fluid-mobility, cross-arc variations, and the origin of Pb enrichments in the continental crust. *Eos* **74**, 674 (abstr.).

Pawley A. R. and Holloway J. R. (1993) Water sources for subduction zone volcanism: new experimental constraints. *Science* **260**, 664–667.

Peacock S. M. (1987) Thermal effects of metamorphic fluids in subduction zones. *Geology* **15**, 1057–1060.

Peacock S. M. (1990) Fluid processes in subduction zones. *Science* **248**, 329–337.

Peacock S. M. (1993a) The importance of blueschist → eclogite dehydration reactions in subducting oceanic crust. *GSA Bull.* **105**, 684–694.

Peacock S. M. (1993b) Large-scale hydration of the lithosphere above subducting slabs. *Chem. Geol.* **108**, 49–59.

Peacock S. M., Rushmer T., and Thompson A. B. (1994) Partial melting of subducting oceanic crust. *Earth Planet. Sci. Lett.* **121**, 227–244.

Plank T. and Langmuir C. H. (1993) Tracing trace elements from sediment input to volcanic output at subduction zones. *Nature* **362**, 739–743.

Plank T. and Ludden J. N. (1992) Geochemistry of sediments in the Ago abyssal plain at site 765: A continental margin reference section for sediment recycling in subduction zones. *Proc. Ocean Drill. Prog., Sci. Results.* **123**, 167–189.

Puecker-Ehrenbrink B., Hofmann A. W., and Hart S. R. (1994) Hydrothermal lead transfer from mantle to continental crust: the role of metalliferous sediments. *Earth Planet. Sci. Lett.* **125**, 129–142.

Ringwood A. E. (1975) *Composition and Petrology of the Earth's Mantle*. McGraw-Hill.

Rona P. A., Bogdanov Y. A., Gurvich E. G., Rinski-Korsakov N. A., Sagalevitch A. M., Hannington M. D., and Thompson G. (1993)

Relict hydrothermal zones in the TAG hydrothermal field, Mid-Atlantic Ridge 26°N, 45°W. *J. Geophys. Res.* **98**, 9715-9-30.

Ryan J. G. and Langmuir C. H. (1993) The systematics of boron abundances in young volcanic rocks. *Geochim. Cosmochim. Acta* **57**, 1489-1498.

Ryan J. G., Morris J. D., Tera F., Leeman W. P., and Tsvetkof A. (1995) The slab effect as a function of depth: Evidence from across-arc geochemical variations in the Kurile arc. *Science* **270**, 625-627.

Ryzhenko B. N., Kovalenko N. I., and Prisyagina N. I. (1993) The role of sulfur in the transport of tin by supercritical fluids. *Geochem. Intl.* **30**, 1-9.

Sacks I. S. and Kincaid C. (1990) On slab melting in subduction zones. *Eos* **71**, 1714 (abstr.).

Sajona F. G., Maury R. C., Bellon H., Cotten J., Defant M. J., and Pubellier M. (1993) Initiation of subduction and the generation of slab melts in western and eastern Mindanao, Phillippines. *Geology* **21**, 1007-1010.

Saunders A. D., Norry M. J., and Tarney J. (1988) Origin of MORB and chemically-depleted mantle reservoirs: trace element constraints. *J. Petrol.* (Special Lithosphere Issue), 415-445.

Saunders A. D., Norry M. J., and Tarney J. (1991) Fluid influence on the trace element compositions of subduction zone magmas. *Phil. Trans. Roy. Soc. London* **335**, 377-392.

Sims K. W. W. and Gladney E. S. (1991) Determination of arsenic, antimony, tungsten, and molybdenum in silicate materials by epithermal neutron activation and inorganic ion exchange. *Anal. Chimica. Acta* **251**, 297-303.

Sims K. W. W., Newsom H. E., and Gladney E. S. (1990) Chemical fractionation during formation of the Earth's core and continental crust: Clues from As, Sb, W, and Mo. In *Origin of the Earth* (ed. H. E. Newsom and J. H. Jones), pp. 291-317. Oxford Univ. Press.

Sisson T. W. and Grove T. L. (1993) Experimental investigations of the role of H$_2$O in calc-alkaline differentiation and subduction zone magmatism. *Contrib. Mineral. Petrol.* **113**, 143-166.

Skinner B. J. (1979) The many origins of hydrothermal mineral deposits. In *Geochemistry of Hydrothermal Ore Deposits*, pp. 1-21. Wiley.

Staudigel H., Hart S. R., and Richardson S. H. (1981) Alteration of the oceanic crust: Processes and timing. *Earth Planet. Sci. Lett.* **52**, 311-327.

Sudo A. and Tatsumi Y. (1990) Phlogopite and K-amphibole in the upper mantle: Implication for magma genesis in subduction zones. *Geophys. Res. Lett.* **17**, 29-32.

Sun S. S. and McDonough W. F. (1989) Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes. In *Magmatism in Ocean Basins* (ed. A. D. Saunders and M. J. Norry), pp. 313-345. London Geol. Soc. Spec. Publ.

Tatsumi Y. (1989) Migration of fluid phases and genesis of basalt magmas in subduction zones. *J. Geophys. Res.* **94**, 4697-4707.

Tatsumi Y., Murasaki M., Arsadi E. M., and Nohda S. (1991) Geochemistry of Quaternary lavas from NE Sulawesi: transfer of subduction components into the mantle wedge. *Contrib. Mineral. Petrol.* **107**, 137-149.

Taylor S. R. and McLennan S. M. (1985) *The Continental Crust: Its Composition and Evolution.* Blackwell.

Verma S. P. (1992) Seawater alteration effects on REE, K, Rb, Cs, Sr, U, Th, Pb, and Sr-Nd-Pb isotope systematics of mid-ocean ridge basalt. *Geochem. J.* **26**, 159-177.

Vidal Ph. (1992) Mantle: More HIMU in the future? *Geochim. Cosmochim. Acta* **56**, 4295-4299.

Wänke H., Dreibus G., and Jagoutz E. (1984) Mantle chemistry and accretion history of the Earth. In *Archaean Geochemistry* (ed. A. Kröner et al.), pp. 1-24. Springer-Verlag.

Weaver B. L. (1991) The origin of ocean island basalt end-member compositions: Trace element and isotopic constraints. *Earth Planet. Sci. Lett.* **104**, 381-397.

Weberling R. P. and Cosgrove J. F. (1965) Flame emission and absorption methods. In *Trace analysis, physical methods.* Wiley.

Wedepohl K. H. (1978) *Handbook of Geochemistry* (ed. K. H. Wedepohl), Vols. II-1-II-5. Springer-Verlag.

Weissberg B. G., Browne P. R. L., and Seward T. M. (1979) Ore metals in active geothermal systems. In *Geochemistry of Hydrothermal Ore Deposits*, pp. 738-780. Wiley.

White W. M. and Dupré B. (1986) Sediment subduction and magma genesis in the Lesser Antilles: Isotopic and trace element constraints. *J. Geophys. Res.* **91**, 5927-5941.

White W. M. and Patchett J. (1984) Hf-Nd-Sr isotopes and incompatible element abundances in island arcs: Implications for magma origins and crust-mantle evolution. *Earth Planet. Sci. Lett.* **67**, 167-185.

Wood D. A. (1979) A variably veined suboceanic upper mantle—genetic significance for mid-ocean ridge basalts from geochemical evidence. *Geology* **7**, 499-503

Wood S. A., Crerar D. A., and Borcsik M. P. (1987) Solubility of the assemblage pyrite-pyrrhotite-magnetite-sphalerite-galena-gold-stibnite-bismuthinite-argentite-molybdenite in H$_2$O-NaCl-CO$_2$ solutions from 200 to 350°C. *Econ. Geol.* **82**, 1864-1887.

Zindler A. and Hart S. (1986) Chemical geodynamics. *Ann. Rev. Earth Planet. Sci.* **14**, 493-571.

APPENDIX

Table 1A. Summary of rock standard analyses by RENA, ICP-MS, and AA. All values in μg/g.

RENA

A.	NBS SRM 1633a			
	As	Sb	W	Mo
n	24	23	24	24
Mean	146	8.3	5.8	33
Std. Dev.	9	2.1	1.1	4
Consensus	145	7.0	5.7	30
Std. Dev.	15	0.5	0.7	3
Range	130-160	6.5-7.5	5.0-6.4	27-33

AA

C.	USGS BHVO-1	
	Zn	Cu
n	17	17
Mean	109	137
Std. Dev.	9	9
Consensus	105	136
Std. Dev.	5	6
Range	100-110	130-142

B.	USGS BHVO-1			
	As	Sb	W	Mo
n	8	8	8	8
Mean	0.55	0.16	0.3	1.0
Std. Dev.	0.04	0.04	0.2	0.1
Consensus	0.40	0.16	0.3	1.0
Std. Dev.	0.22	0.04	0.1	0.1
Range	0.18-0.62	0.12-0.20	0.2-0.4	0.9-1.1

D.	USGS AGV-1	
	Zn	Cu
n	10	10
Mean	92	64
Std. Dev.	4	6
Consensus	88	60
Std. Dev.	2	6
Range	86-90	54-66

ICP-MS

E.	USGS BHVO-1									
	St. Add. Pb	3-pt. Pb	St. Add. As	3-pt. As	St. Add. Sb	3-pt. Sb	St. Add. Sn	3-pt. Sn	St. Add. Tl	3-pt. Tl
n	11	16	11	9	10	7	1	12	11	12
Mean	2.24	1.97	0.48	0.45	0.15	0.15	1.2	1.8	0.043	0.045
Std. Dev.	0.54	0.27	0.14	0.09	0.02	0.03	-----	0.2	0.004	0.005
Consensus	2.60	2.60	0.40	0.40	0.16	0.16	2.1	2.1	0.058	0.058
Std. Dev.	0.90	0.90	0.22	0.22	0.04	0.04	0.5	0.5	0.012	0.012
Range	1.70-3.50	1.70-3.50	0.18-0.62	0.18-0.62	0.12-0.20	0.12-0.20	1.6-2.6	1.6-2.6	0.046-0.070	0.046-0.070

F.	USGS AGV-1									
	St. Add. Pb	3-pt. Pb	St. Add. As	3-pt. As	St. Add. Sb	3-pt. Sb	St. Add. Sn	3-pt. Sn	St. Add. Tl	3-pt. Tl
n	5	10	5	5	6	8	2	8	7	10
Mean	36	34	0.92	1.00	5.0	3.9	3.9	4.3	0.322	0.281
Std. Dev.	5	1	0.11	0.34	0.4	0.3	-----	0.2	0.027	0.016
Consensus	36	36	0.84	0.84	4.4	4.4	4.2	4.2	0.340	0.340
Std. Dev.	5	5	0.27	0.27	0.4	0.4	1.1	1.1	0.060	0.060
Range	31-41	31-41	0.57-1.11	0.57-1.11	4.0-4.8	4.0-4.8	3.1-5.3	3.1-5.3	0.280-0.400	0.280-0.400

Std. Add. = Standard addition
3-pt. = 3-point calibration curve.
References for consensus values: GLADNEY et al. (1988a, 1988b, 1990).