TECTONIC IMPLICATIONS OF THE COMPOSITION OF VOLCANIC ARC MAGMAS

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INTRODUCTION

Volcanic arc magmas can be defined tectonically as magmas erupting from volcanic edifices above subducting oceanic lithosphere. They form a coherent magma type, characterized compositionally by their enrichment in large ion lithophile (LIL) elements relative to high field strength (HFS) elements. In terms of process, the predominant view is that the vast majority of volcanic arc magmas originate by melting of the underlying mantle wedge, which contains a component of aqueous fluid and/or melt derived from the subducting plate. Recently, opinions have converged over the key aspects of the physical model for magma generation above subduction zones (Davies & Stevenson 1992), namely:

- 1. that the mantle wedge experiences subduction-induced corner flow (e.g. Spiegelman & MacKenzie 1987);
- 2. that the subduction component reaches the fusible part of the mantle wedge by the three-stage process of (i) metasomatism of mantle lithosphere, followed by (ii) aqueous fluid release due to breakdown of hydrous minerals at depth (e.g. Wyllie 1983, Tatsumi et al 1983) and (iii) aqueous fluid migration, followed by hydrous melt migration, to the site of melting;

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3. that slab-induced flow may be locally reversed beneath the arc itself, allowing mantle decompression to contribute to melt generation (e.g. Ida 1983).

The simplified model in Figure 1 highlights the physical and chemical processes that have been invoked as being important in controlling the composition of volcanic arc magmas. Magma compositions (coupled with experimental data on element behavior) can help us gain further understanding of these physical and chemical processes. In this review, we first summarize knowledge of the behavior of elements in the subduction system. We then focus on compositional evidence for the processes illustrated in Figure 1, which we group as follows:

- 1. derivation of the subduction component,
- 2. transport of the subduction component to the melting column,
- 3. depletion and enrichment of the mantle wedge, and
- 4. processes in the melting column.

BEHAVIOR OF ELEMENTS IN SUBDUCTION SYSTEMS

Before considering the tectonic implications of arc magma composition, we need to consider the behavior of elements in the various parts of the subduction system. These determine whether the elements exhibit conservative or non-conservative behavior with respect to the source of the magma and how the elements behave in the melting column.

Conservative vs Nonconservative Elements

We can usefully make the following definitions:

A conservative element is one for which there is no detectable slab contribution to the source of arc volcanism.

A nonconservative element is one for which there is a detectable slab contribution to the source of arc volcanism.

Because the theoretical behavior of elements in fluids at high temperatures and pressures are poorly known, empirical methods provide the best indicators of nonconservative behavior at the present time. The identification of conservative elements can be made using one of the two elements widely thought to be least effectively transferred from slab to melting column, namely Nb or Ta. Of many possible projections, the most useful are graphs of the type M/Yb vs Nb/Yb, where M represents the element under study (Pearce 1983). Ytterbium is used as a denominator to minimize the effects of partial melting and fractional

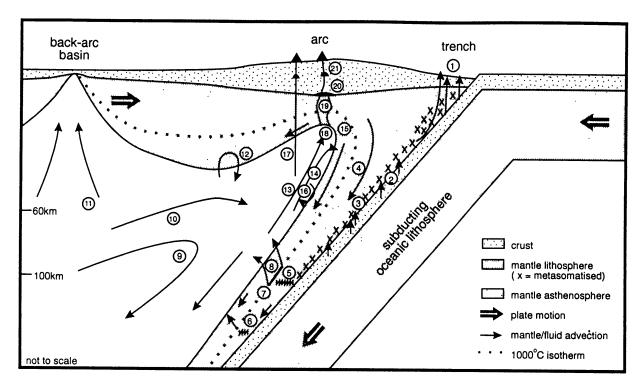


Figure 1 Schematic summary of the processes affecting arc magma composition.

Slab dehydration and melting 1. fluid loss via accretionary prisms and serpentinite seamounts, 2. dehydration \pm partial melting of subducting oceanic crust and sediment.

Transport of subduction component 3. hybridization of subduction component and downdragged mantle lithosphere, 4. slab-induced downward drag of hybridized mantle, 5. rerelease and lateral migration of aqueous fluids by amphibole breakdown at about 100 km depth, 6. rerelease of aqueous fluids by breakdown of other hydrous phases at greater depth, 7. initiation of hydrous melting of mantle at about 1000°C, 8. migration of small-volume hydrous melts through cross-fed mantle to the base of the melting column.

Mantle source processes 9. slab-driven "corner flow" of mantle into the mantle wedge, 10. replenishment of the melting column by mantle advection, 11. mantle source depletion by small-volume melt loss in back-arc region, 12. mantle source enrichment by delamination of sub-continental lithosphere.

Melting column processes 13. buoyancy-driven mantle counterflow, 14. decompression-melting of the mantle from about 60 km depth, 15. separation of residual mantle from the melting column aided by slab-induced downward drag, 16. column depletion by imperfect separation or reincorporation of residual mantle, 17. selective tapping of the melting column.

Lithosphere-melt interactions 18. melt segregation at the base of the lithosphere; 19. interaction with, and crystallization within, mantle lithosphere; 20. magma-assimilation-storage-homogenization at the base of the crust; 21. assimilation-fractional crystallization at shallower crustal levels.

crystallization and hence "see through" these processes to the composition of the mantle source. Other incompatible, conservative elements can be used instead of Yb when Yb itself is being investigated or when there is evidence from Sc depletion that a garnet residue has retained Yb. The idea is that, if M is conservative, the arc volcanic data will plot within a MORB (Mid-Ocean Ridge Basalt) array; if M is nonconservative, it will be displaced from the MORB array to higher M/Yb ratios. The assumption is that any slab component will not have the same vector as the MORB array on these plots.

Examples of conservative (M = Ti) and nonconservative (M = Th) behavior are shown in Figures 2a and 2b, respectively. The databases used, described by Pearce & Parkinson (1993), combine our own inductively coupled plasmamass spectroscopy analyses of Nb and other low-abundance trace elements in boninites and island are basalts with published data of known and comparable quality. In Figure 2a, the volcanic are lavas plot entirely within the MORB array. Ti is therefore an example of a conservative element. Note also that the volcanic are basalts have a spread of Nb/Yb ratios comparable to that of MORB, indicating that the mantle sources of volcanic are basalts may be both enriched and depleted with respect to an average N-MORB (Normal-MORB) source. In Figure 2b, the volcanic are lavas are invariably displaced to higher Th/Yb ratios than MORB, confirming the status of Th as a nonconservative element.

From other plots (not shown), it is apparent that most volcanic arc basalts plot in the MORB array only when M is Zr, Hf, Ti, heavy rare earth elements (HREE), Y, Sc, Ga, Ni, Cr, Co, or major and minor elements other than K, Na, or P. This result emphasizes the key point that ratios of conservative elements in volcanic arc basalts lie within the MORB array. McCulloch & Gamble (1991), Woodhead et al (1993), and Thirlwall et al (1994), among others, emphasize the principal implication of this observation, namely, that it is inconsistent with residual minor phases in the subarc melting column. This is because all the minor phases that might retain HFS elements, such as rutile, should also fractionate ratios of HFS elements in the melting column. This does not mean that there are no examples where residual garnet, amphibole, and perhaps other phases such as phlogopite have fractionated conservative element ratios, but these examples are rare and not associated with "normal" arc volcanism. Thus, for the vast majority of present-day volcanic arc magmas, the evidence is now extremely strong that the characteristic enrichment in LIL elements with respect to HFS elements must be explained by the fact that LIL elements are nonconservative while HFS elements are conservative with respect to the mantle source.

There are, nonetheless, some caveats that need to be made. In particular, evidence is growing that at least some of the "conservative" elements become nonconservative when crust or subducted sediment undergoes melting rather

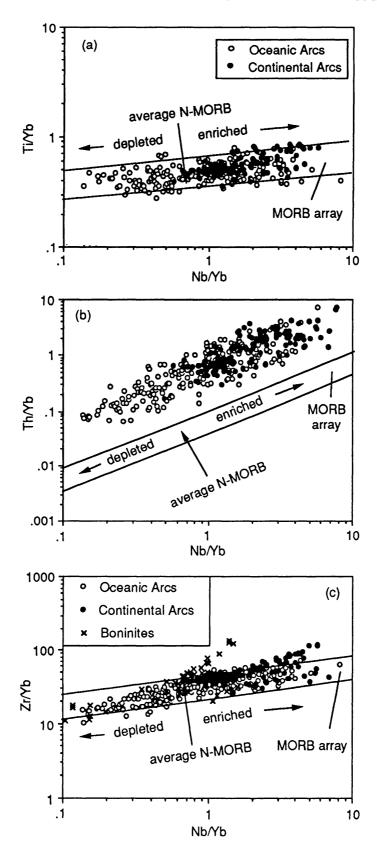


Figure 2 Diagrams of the form M/Yb vs Nb/Yb used to distinguish between conservative behavior [(a) M = Ti], nonconservative behavior [(b) M = Th], and variable behavior [(c) M = Zr].

than dehydration. Key elements are Zr and Hf. Figure 2c shows the plot for M = Zr. It is apparent that, although the great majority of samples plot within the MORB array (within error), a significant number plot toward high Zr/Yb ratios. Anomalous samples include the subset of the boninite database that is associated with arc initiation and earliest arc evolution in the Western Pacific. Some continental arc samples (from southern Chile and the Philippines) also have anomalously high Zr/Yb ratios. These areas are associated with ridge subduction and continent-arc collision, respectively.

The arguments for and against a slab-melting origin for these ratios are laid out in the next section. At this stage, we raise the real possibility that the behavior of at least Zr, Hf, Nb, and Ta depends strongly on whether the subduction component is a siliceous or an aqueous fluid.

The distinction between conservative and nonconservative elements is also apparent on MORB-normalized plots of volcanic arc basalts, some typical examples of which are reproduced in Figure 3. The three patterns in Figures 3a-c represent basalts with Nb/Yb ratios less than, equal to, and greater than MORB, respectively. The pattern in Figure 3d represents one of the boninites described above in which many HFS elements are enriched as a possible result of melt, rather than aqueous fluid, extraction from the subducting slab.

Quantification of Nonconservative Behavior

We can obtain a simple measure of nonconservative character from the geochemical patterns in Figure 3 by taking the abundances of the nonconservative elements above a baseline extrapolated from the abundances of the conservative elements. For any element, the value obtained, expressed as a percentage of total concentration, gives the percentage of the subduction component (%sz) in the mantle source of the volcano (Pearce 1983). Note that %sz is a relative measure of subduction input, which is dependent on whether the mantle is depleted or enriched relative to an N-MORB source when the subduction component is added. However, an absolute measure of nonconservative character cannot be obtained unless the nature and degree of partial melting and fractional crystallization are also known.

The original description of this method treats the enrichment above the base-line as entirely slab derived. Hawkesworth et al (1991) reassess this approach from an isotopic perspective for elements with isotope_ratios (Sr, Nd, Pb, Th). They find that the extent of enrichment is, in some cases, significantly less than that estimated by the approach of Pearce (1983). They conclude that a high proportion of these elements are derived not from the slab but from the mantle. They argue that aqueous fluids derived from the subduction zone are able selectively to leach these elements from the mantle *en route* to the melting zone. This conclusion is evaluated further in the next section. To accommodate their results, the description of the subduction contribution has been changed from the original

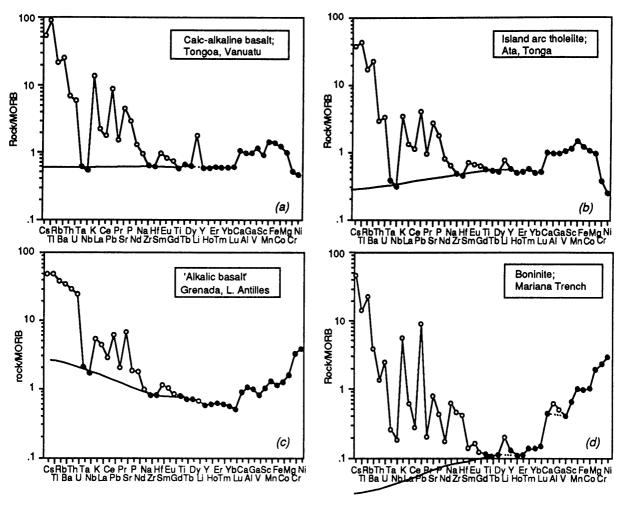


Figure 3 MORB-normalized patterns for a range of volcanic arc lavas. Solid circles refer to conservative elements, open circles to nonconservative elements. The lines are the "baselines" that link the compositions the elements would have had without subduction. The elements increase from left to right in compatibility during spinel-lherzolite melting.

"slab-derived" to "slab-related" to permit inclusion of both elements stripped from the slab and elements stripped from the mantle by slab-derived fluid.

Subduction component patterns for the nonconservative elements in the Tongoa and Ata volcanoes in Figure 3 are shown in Figure 4. Although there is considerable variability within and between arcs (as discussed later), the elements shown in Figure 3 can be divided as follows for most volcanic arc magmas:

- highly nonconservative (%sz > 80): Rb, Ba, K, Pb, Th, U, Sr
- moderately nonconservative (%sz = 40-80): P, LREE
- slightly nonconservative (%sz = detection limit—40): MREE, Na

• conservative (%sz < detection limit): Zr, Hf, Ti, (HREE), Y, Sc, Ga, Ni, Cr, Co, major and minor elements other than K, Na, or P.

Here, LREE and MREE refer to light and middle rare earth elements, respectively. Li is highly variable, possibly for analytical reasons, and is not plotted in Figure 4. Note that studies of other elements have indicated, for example, that B, Sb, and Au are highly nonconservative, Be moderately nonconservative, Cu slightly nonconservative, and Zn conservative. Note also that redox conditions in the subduction system may play a part in explaining the behavior of elements such as U and Ce. For example, the oxidizing nature of hydrous fluids may contribute to the development of negative Ce anomalies (with respect to La and Nd) in many volcanic arc magmas (Ben Othman et al 1989).

Reasons for Conservative vs Nonconservative Behavior

An element may behave as conservative for several reasons: It may be buffered by a high concentration in the mantle source; it may be retained in the subducting slab; or it may be retained in the metasomatized mantle. Important parameters are, respectively:

- 1. the mantle/melt bulk distribution coefficient,
- 2. the slab/fluid (aqueous and siliceous) bulk distribution coefficient,
- 3. the mantle/fluid (aqueous and siliceous) bulk distribution coefficient.

The mantle-melt coefficients are broad measures of the relative concentrations of the element in the mantle and the crust. Elements with high coefficients have the highest relative concentrations in the mantle and are therefore less likely

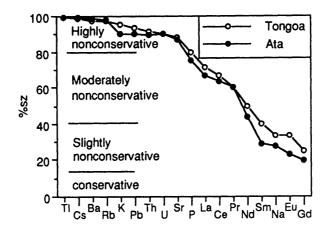


Figure 4 Inferred subduction zone contribution for nonconservative elements (as %sz—see text) to the mantle source of Ata (Tofua arc) and Tongoa (Vanuatu arc) volcanoes.

to be influenced by the subduction component. There are sufficient experimentally determined values for these coefficients that the relative incompatibilities of the elements are well known. For fertile mantle, they decrease from right to left in the order shown in Figure 3. Most of the elements to the right of Yb in this plot are effectively conservative because of their high concentrations in the mantle compared with the subduction component. For example, the LIL element Ca is almost certainly mobile in subduction fluids but is unable to generate detectable enrichments except in the most depleted mantle sources.

Values for the slab/aqueous fluid coefficients are very poorly defined, and this is compounded by the potential variability of slab residues, which makes unmeasured coefficients difficult to predict theoretically. Serpentinite-aqueous fluid coefficients obtained by Tatsumi et al (1986) show an increase in coefficient with increasing ionic radius. However, we cannot be certain that the same relationships hold when residual phases such as amphibole or biotite are involved. Most HFS elements are concentrated in the minor phases. Ayers & Watson (1991) investigate minor phase solubility in supercritical aqueous fluids in the temperature range $T=800-1200^{\circ}\mathrm{C}$ for pressures P=1-3 GPa. They find that zircon has a very low solubility, that apatite and monazite have low solubilities that increase with decreasing pH, but that rutile has a significant solubility. The potential solubility of rutile implies that Ti and Nb may be mobilized more effectively than hitherto predicted in subduction-derived aqueous fluids.

Slab-siliceous fluid (melt) coefficients are somewhat better defined. LIL element coefficients are largely controlled by major residual phases and are almost always <1, i.e. the elements are concentrated in the melt. HFS elements are controlled in part by major residual phases such as amphibole and garnet and in part by minor phases such as zircon. Experiments by Watson and coworkers (e.g. Watson & Harrison 1984) have established minor phase solubilities in siliceous melts as functions of temperature and melt composition. Summarizing their work briefly, low temperature, hydrous melts will have the lowest contents of HFS elements because of the relative insolubility of zircon, monazite, apatite, and rutile. However, higher temperature melts can contain substantial quantities of these elements. Yttrium and the heavy rare earth elements may be most compatible because they are accommodated not only in minor phases, but also in amphibole and garnet. All data suggest that melts are more effective than aqueous fluids in transferring elements from slab to wedge.

Our knowledge of the mantle-hydrous fluid coefficients is dependent almost entirely on the olivine-fluid partition coefficients determined experimentally by Brenan & Watson (1991). Hawkesworth et al (1993) use a function based on ionic radius to extrapolate from these coefficients to the coefficients of elements not studied experimentally. They then multiply their set of olivine-fluid coefficients by pyroxene-melt coefficients to obtain pyroxene-fluid and

hence peridotite-fluid bulk coefficients. Until more experiments are carried out this is probably the best that can be done.

Mantle-hydrous melt coefficients are not known but can be assumed to lie between values for mantle-melt and those for mantle-hydrous fluids. It is likely that the incompatibility of HFS elements will show little change, but that the incompatibility of LIL elements will increase with increased water content of the melts.

As many scientists have noted, there is a relationship between the selective enrichments of nonconservative elements in volcanic arc magmas (Figure 4) and the slab-fluid and peridotite-fluid partition coefficients. Figure 5 summarizes how element behavior is related to ionic radius (an approximate indicator of partitioning into aqueous fluids) and bulk distribution coefficient between mantle and melt (an appropriate indicator of mantle relative to crustal abundance), based on experiment and observation. Figure 5a applies to a hydrous slab component; Figure 5b applies to a siliceous melt slab component.

Note that the distinction between "mobile" LIL elements and "immobile" HFS elements is really an oversimplification because ions of very high field strength are also stable (as complex ions) in aqueous solution. However, we have chosen to retain this frequently used terminology in this review. The main point is that the different behavior of elements in melts and aqueous fluids is capable of generating the patterns observed in Figure 3, at least to a first approximation. The question then is which processes are most important in determining element behavior and hence explaining in detail the composition of volcanic arc magmas. These processes are discussed in the sections that follow.

IMPLICATIONS FOR MAGMA GENERATION PROCESSES

Slab Dehydration and Melting

RELATIONSHIP TO SUBDUCTION INPUT One of the most sensitive indicators of the presence of a subduction component in volcanic arc magmas is water itself (Stolper & Newman 1994), derived both from altered oceanic lithosphere (hydothermally modified by ridge processes and by longer-term aging of the lithosphere) and from its sediment cover. Of the other elements, boron is one of the most diagnostic (Morris et al 1990) as it is strongly enriched in both oceanic sediments and altered oceanic crust. This leads, for example, to much higher B/Be ratios in the mantle wedge compared with other mantle reservoirs. The most compelling, and now well-established, pieces of evidence for a sediment contribution to the subduction component come from isotopic tracers, such as ¹⁰Be and ²⁰⁷Pb (e.g. Brown et al 1982, Tera et al 1986, Woodhead 1989). In some arcs such as New Britain, the presence of an elemental subduction signature without a lead isotope anomaly is generally taken as good evidence

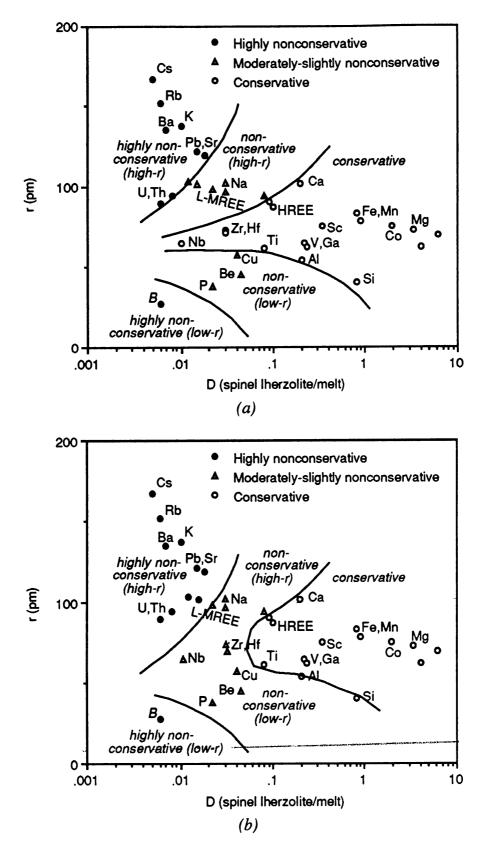


Figure 5 Element behavior in the subduction system as a function of ionic radius and bulk mantlemelt distribution coefficient for (a) hydrous fluids and (b) siliceous melts.

for the involvement of altered MORB in the subduction component (Woodhead & Johnson 1993, Gill et al 1993).

The signature of the nonconservative elements in arc lavas has provided some of the most useful information on the nature of the subduction component. Plank & Langmuir (1993) calculate the subducted sediment flux of a number of nonconservative elements (Ba, Sr, K, Rb, Cs, La, Th, U) for eight arc systems. For many of these elements, these fluxes vary by more than an order of magnitude. Significantly, the sediment flux correlates with the magnitude of the enrichment seen in the arc magmas, once the magma compositions have been corrected for the effects of crustal processes and melting. Figure 6a shows the example for Ba from Plank & Langmuir (1993). Fractional crystallization is taken into account by taking Ba concentrations at MgO = 6.0 wt% (written as Ba6.0), while division by Na concentrations at MgO = 6.0 wt% (Na6.0) removes the effect of partial melting and thus highlights source variations.

Plank & Langmuir (1993) also link the trace element features of a particular arc to the type of sediment being subducted at that arc. For example, they point out that Guatemalan arc magmas have high Ba (Ba6.0 = 397) relative to K (K6.0 = 0.71)—a feature also characteristic of the biogenic oozes being subducted at the Guatemalan trench, which average Ba = 3250 ppm and $K_2O = 0.67$ wt%. These oozes have high Ba concentrations because of barite precipitation onto biogenic material but have low K concentrations because the K-poor biogenic components dilute the K-rich clay components. In contrast, Vanuatu arc magmas tend to have high K (K6.0 = 0.95) relative to Ba (Ba6.0 = 206)—a feature characteristic of the K-rich volcaniclastic sediments ($K_2O = 2.29$ wt%) that dominate the subducted sediment in this arc (Briqueu & Lancelot 1983; DW Peate et al, in preparation). Plank & Langmuir (1993) also find that, for certain elements, the calculated sediment flux is insufficient to balance the observed output from the arc magmas. They attribute the difference to a contribution from altered basaltic crust within the downgoing slab.

Extending this approach from a global scale to the scale of individual arcs has thus far been hampered by the limited sampling of sediments near trenches.

Figure 6 Diagrams showing some key lines of evidence for slab melting and dehydration processes. (a) = Ba6.0 vs Na6.0 plot of Plank & Langmuir (1993) showing correlation between Enflux and Ba content of arc volcanics. (b) $Na_2O = TiO_2$ plot of Pearce et al (1992) showing the distinctive enrichment in Na for some boninite glasses that helps indicate a tonalitic slab-melt component in their mantle sources. (c) MORB-normalized patterns for metasomatized mafic rocks from the Santa Catalina subduction complex (unmetasomatized rocks have flat patterns) showing how the aqueous fluids that have metasomatized the metabasalt have a different composition from the siliceous melts that metasomatized the migmatites.

Some convincing along-arc compositional variations have, however, been identified in which the terriginous sediment flux increases in response to continental proximity. From south to north along the North Luzon (Philippines) arc (McDermott et al 1993) and from west to east along the Sunda-Banda arc (Vroon 1992), the approach of a continent collision zone is accompanied by what both authors identify isotopically as "bulk sediment assimilation," implying wholesale melting of large volumes of terrigenous sediment. Similarly, the magnitude of the subduction component southward along the Lesser Antilles arc increases in response to the nearby terrigenous sediment input from South America (White & Dupré 1986), and Gamble et al (1993) recognize a similar southward increase in the Kermadec-Taupo arc with proximity to New Zealand. By contrast, Arculus et al (1991) provide evidence that mantle composition rather than subduction input best explains chemical changes along the transect from Japan to the Izu islands.

Even taking into account the errors inherent in estimating sediment compositions and fluxes, it is apparent from the work cited above that volcanic arc magmas respond to differences in the subducted material regardless of modifications that might take place during transport and in the melting column. This does not, however, mean that the melting column receives a component with the same composition as the subducted material. The behavior of individual nonconservative elements during slab dehydration and melting will be controlled not only by the composition and flux of the subducted material but also by their partitioning into the subduction-derived fluid and by their behavior during transport. Differences in nonconservative element ratios between island arc basalts and subducted oceanic basalts and sediments indicate that all these factors must operate.

Ratios of LIL elements to LREE (e.g. Ba/La) are particularly diagnostic. Island arc basalts, in general, have higher Ba/La ratios than oceanic basalts. However, Ben Othman et al (1989) report that the Ba/La ratios of the lavas from the Lesser Antilles are considerably higher than the average Ba/La ratio in the sediments subducted beneath the arc. Similarly, our own work (DW Peate et al, in preparation) shows that Vanuatu arc volcanic rocks have high Ba/La ratios (20 to 85), whereas the sediments supplied to the trench have relatively low Ba/La ratios (8 to 32) and the altered crust has insufficiently high ratios to redress the balance.

Cesium-enrichment relative to Rb and K is another diagnostic feature of arc magmas. Marine sediments do have high Cs/Rb ratios relative to both midocean ridge and ocean-island basalts (Ben Othman et al 1989) but, again, bulk incorporation of sediment cannot account for the high ratios in arc magmas. Hart & Reid (1991) demonstrate that fluids or melts removed from feldspar-bearing subduction assemblages under high-grade metamorphic conditions should be enriched in Cs relative to Rb and K.

The experimental studies summarized earlier suggest that the high Ba/La and Cs/Rb ratios in volcanic arc lavas reflect the preferential partitioning of Ba and Cs, respectively, into water-rich fluids. The unresolved issue, however, is the relative extent to which the fractionation of these elements takes place during slab dehydration and melting or during transport. As we summarize in the next section, chromatographic effects during transport could also contribute to an increase in these ratios.

RELATIONSHIP TO THE THERMAL STATE OF THE SUBDUCTION SYSTEM One aspect of arc volcanism that has developed rapidly over the past few years is that of the relationship between the thermal state of the subduction system and the fate of the subducted slab and its sediment cover. From a modeling standpoint, Peacock, in particular, emphasized in a series of papers (e.g. Peacock et al 1994) that, although dehydration is likely to be the dominant mechanism in mature arcs, slab melting is the likely fate of subduction of young lithosphere.

The petrological link with the thermal models was first made by Defant, Drummond, and coworkers (Defant & Drummond 1990, Drummond & Defant 1990), stimulated by the work of Kay (1978), who identified possible slab melts (subsequently termed *adakites*) on Adak island in the Aleutians. The geochemical characteristics of adakites include low values of Y and HREE, high Sr and Zr values, and MORB-like rather than arc-like isotope ratios. Defant & Drummond (1990) note the sporadic, but worldwide, occurrence of this chemically distinct rock type in parts of the arc system where ridges are or were recently subducting, such as the Cascades, Central America (Defant et al 1991), and the Austral Andes (Stern et al 1990, Kay et al 1993). This association thus supports the hypothesis that these rocks are derived by melting of subducted crust. The geochemistry supports the hypothesis that the melt residue is metamorphosed in eclogite facies, the requirement for water suggesting that the melt was generated probably during the metamorphic transformation from amphibolite to eclogite facies.

Similarly unusual geochemical characteristics (high Zr relative to Y, HREE, and Ti; Pb isotopes on the Northern Hemisphere Reference Line) characterize most of the Eocene boninites of the Western Pacific that erupted within a few my of the time of plate reorganization in the Western Pacific. Pearce et al (1992) interpret this composition as resulting from a subduction component made up of the product of melting subducted oceanic crust in amphibolite facies. This component, according to their model, causes melting of depleted mantle to produce boninites. Their finite-difference modeling demonstrates that shallow slab melting is likely if both subducting plate and mantle wedge are hot, as they might be if subduction initiated at an active transform fault.

Scientists are still, however, some way from reaching consensus with their interpretations. If adakites are slab melts, it is difficult to envisage how they could rise, unmodified, from depths of 100 km or more to the surface without

interacting with the mantle or crust. If the high-Zr boninites contain a slab-melt component, this is difficult to reconcile with other ideas on boninite genesis. For example, Stern et al (1991) prefer the slab component to be an aqueous fluid rather than a melt and explain its unusual chemistry in terms of extensive modification (as discussed in the next section) by chromatographic processes during transport to the melting zone. Hickey-Vargas (1992) prefers migration of small-volume asthenospheric melts of HIMU isotopic character (high U/Pb ratio) to explain the Pb isotope signature. These models explain the isotope variations, but not the high-Zr contents of the rocks relative to the REEs. The theory summarized in the previous section suggests that neither chromatographic processes nor small-volume asthenospheric melts can achieve the relative enrichment in Zr seen in the boninites in question. However, there are sufficient gaps in the theory that these processes cannot be ruled out, nor are they and slab melting mutually exclusive.

Pursuing the slab melting argument, the Zr/Yb vs Nb/Yb plot presented earlier (Figure 2) demonstrates that the volcanic arc lavas postulated to have a slab-melting origin plot outside the MORB array, toward higher Zr/Yb ratios. Other elements and element ratios also behave in unusual ways. Of particular note is the fact that Na becomes strongly nonconservative in the boninitic rocks, in marked contrast to its slightly nonconservative behavior in most arcs. This is demonstrated in the Na₂O-TiO₂ plot in Figure 6b, where boninitic glasses are displaced off the MORB and island-arc trends to high Na₂O contents. We argue that aqueous fluids, even when saturated in NaCl, can only transport small masses of Na to the zone of melting. By contrast, a slab melt can (if tonalitic) contain up to 5 wt% of Na, enough to have a much more dramatic effect on the mantle source. If slab melting is the cause of the unusual compositions, we can infer that Zr (and Nb) are no longer conservative elements once thermal conditions allow slab melting.

McDermott et al (1993) present particularly convincing evidence for this difference in behavior of HFS elements between aqueous fluids and melts ("bulk sediment additions" in their terminology) derived from the subducting plate. They identify two subduction components, one with the typically high LIL/HFS element ratios of aqueous fluids, the other with the composition of the terrigenous trench sediments. Their data show that the Ta/Yb (and hence Nb/Yb) and Zr/Yb ratios both correlate well with the proportion of terrigenous subduction component (as inferred from Nd isotope ratios) and therefore that Ta and Zr exhibit nonconservative behavior. These data help form the continental-arc basalt trends toward high Zr/Yb ratios in Figure 2c.

EVIDENCE FROM SUBDUCTION COMPLEXES Subduction complexes—mélanges formed at depth at or near subduction plate boundaries—provide an alternative perspective on the nature of the subduction component. The best studied is located on Santa Catalina Island (California) (e.g. Sorensen & Grossman

1989, Bebout & Barton 1993), which formed at a depth of 15–45 km at an Early Cretaceous subduction zone. Geochemical studies of metasomatized rocks from this locality (e.g. Figure 6c) suggest that elements were mobilized in both aqueous and siliceous (pegmatitic and granitic) fluids. The data suggest that the elements released most effectively from the downgoing plate are silicon, the alkaline and alkaline earth elements (Na, K, Rb, Cs, Sr, Ba), and elements of very high ionic potential (e.g. B). Thorium, LREE, and HFS elements were also mobilized, but mainly by siliceous, rather than aqueous, fluids.

As Sorensen & Grossman point out, the Santa Catalina complex may be characteristic of subduction initiation rather than of a mature subduction zone. Nonetheless, the results match very well both the theoretical behavior of the elements and the observations from volcanic arc magmas. Cs/Rb and Ba/La ratios are, for example, both high in the subduction component, and HFS elements are mobilized much more effectively by melts than by aqueous fluids.

EVALUATION OF RESULTS There seems little doubt from isotopic and elemental data that both sediments and altered oceanic crust contribute to the subduction component in volcanic arc lavas. There is equally little doubt that the component added to the mantle rarely has the composition of the subducted material itself, but has enhanced concentrations of the elements most strongly partitioned into aqueous fluids. Less certain is whether the change in composition is due mainly to the dehydration and melting of the subducted material or to transport of the subduction component to the melting column.

The nature of the subduction component is also controversial. Some scientists favor dehydration as the sole mechanism, while others favor melting of sediments but dehydration of altered crust. There is also some evidence that sediment fusion rather than dehydration commonly accompanies subduction of large volumes of terrigenous sediments, e.g. when collision zones are approached. We speculate that terrigenous sediments fuse more easily than pelagic sediments because their high concentrations of quartz and feldspar produce "minimum melts" at lower temperatures (650°C or less). To the authors, as to those who have constructed thermal models of subduction systems, there is now also good evidence that both slab and sediments can fuse when the subducting crust is very young, whereas dehydration may be more important than melting when the subducting plate is older and cooler.

Transfer of Elements from Slab to Melting Column

INTERACTION BETWEEN SUBDUCTION COMPONENT AND MANTLE As noted earlier, there is a consensus of opinion toward the general mechanism that a fluid component from the subduction zone enriches a mechanical boundary layer of mantle peridotite directly above the slab, creating a hornblende-peridotite. This layer is dragged downwards above the slab until hornblende breaks down at a

depth of about 100 km. The fluids released by this reaction then migrate into the hot mantle wedge where melting initiates (Figure 1).

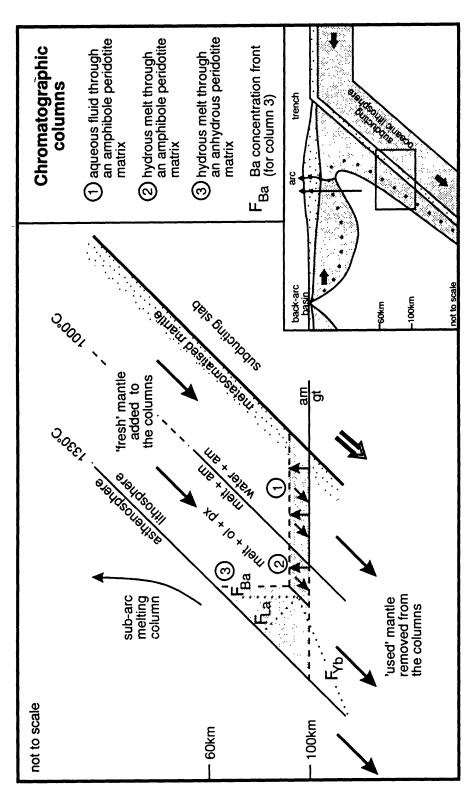
The first stage in this process is therefore the hybridization of slab component and mantle. Although only a transient stage in the transfer of elements from slab to melt zone, it is important because the minerals produced and the behavior of these minerals during descent of the metasomatized mantle determine the extent to which elements can be accommodated in the fluid released. Most evidence comes from the experiments of Wyllie and coworkers (e.g. Wyllie et al 1989). Their experiments on the interaction between peridotite and a hydrous, granitic melt at 15 and 30 kb pressure reveal that garnet and pyroxene are the common products of this interaction. The presence of these minerals would help to explain the conservative behavior of Y and the HREE during both slab melting and slab dehydration.

Subduction complexes provide some feel for the real-world complexities of the hybrid zone. On Santa Catalina island, the zone is a mélange of veined and metasomatized blocks of ultramafic, mafic, and sedimentary rocks, in which hybridization has taken place by mechanical mixing as well as chemical reactions.

EVIDENCE FROM SEPARATION SCIENCE Several arguments have been put forward linking the composition of volcanic arc magmas to processes taking place between the zone of fluid release and the melting column. These have been stimulated by such papers as McKenzie's (1984) and Navon & Stolper's (1987) in which the mantle is described as behaving like a chromatographic column during two-phase flow. These authors emphasize that the fluid may be constantly interacting with the mantle during its passage to the zone of melting. The likely effect, as indicated earlier, is that elements partitioned into the fluid phase will be stripped from the mantle "column" and enriched in the fluid. Because the fluid is aqueous, elements of high and very low ionic radius are preferentially removed.

The separation column that might apply above a subduction zone is shown in Figure 7. Its distinctive feature is that, unlike a separation column in the laboratory, new mantle is constantly fed into the top of the column and "used" mantle removed from its base, the so-called matrix cross-feeding of Navon & Stolper (1987).

If chromatographic effects are an important feature of the interaction of the slab fluid with the mantle wedge material, then the convective regime within the wedge might be a critical factor in explaining the pattern of enrichment of nonconservative elements seen in the volcanic arc magmas. Theory suggests that each cation will develop its own concentration front, which then moves through the mantle at a rate determined by the bulk distribution coefficient between the fluid (aqueous or siliceous) and the mantle. However, because the subducting plate induces a downward drag on the overlying mantle wedge material, elements with slow-moving concentration fronts will be swept away



of hydrous melts released above the temperature of amphibole breakdown. The zigzag paths in columns 1 and 2 result from the fact that fluids Figure 7 Diagram showing chromatographic processes during transport of the subduction component to the melt column (after Navon & amphibole breakdown, 2. during lateral migration of hydrous melts released at the "damp" peridotite solidus, and 3. during upward migration released from metasomatized peridotite can be reincorporated into amphibole on upward migration (Davies & Bickle 1991). Chemical fronts Stolper 1987, Stern et al 1991). Chromatographic processes could take place 1. during lateral migration of aqueous fluids released by or Ba, La, and Yb are shown schematically for the third column only.

to depth and not reach the melting source of subduction zone magmatism (Navon & Stolper 1987). Thus, the "critical Kd," which divides elements whose concentration fronts move faster than the convecting mantle (and thus become involved in arc magmagenesis) from those whose concentration fronts move slower (and thus tend to get removed from the subduction system), varies inversely with subduction velocity (Stern et al 1991, Hawkesworth et al 1993).

As noted above, this process provides another mechanism for fractionating ratios such as Cs/Rb and Ba/La. One way to test whether slab dehydration or chromatography is responsible for the high Ba/La ratios in arcs might be to compare these ratios between arcs above slow- and fast-subducting slabs. Other things being equal, one might expect magmas with the highest ratios to erupt above fast-subducting slabs as the rate of mantle cross-feeding should then be greater. From the data in Plank & Langmuir (1993), it is apparent that island arc tholeites with high Ba/La ratios are indeed common in oceanic arcs with high convergence rates (e.g. Tonga). On the other hand, the North Lesser Antilles arc has low convergence rates yet high ratios. We therefore view the case for chromatographic fractionation of nonconservative element ratios as likely but, as yet, unproven.

EVIDENCE FROM COUPLED ISOTOPE-ELEMENT DATA Hawkesworth et al (1991) and Stern et al (1991) point out that, for elements with isotope ratios, the apparent subduction zone input of nonconservative elements, as calculated from element abundances, exceeds estimates of input based on isotope ratios. They suggest that the difference between the two sets of values means that the selective enrichments in the nonconservative elements are due not just to the slab contribution, but also to the extraction of these elements from the mantle by aqueous, subduction-derived fluids.

This argument is a powerful one, although it generates two related problems. Because the subduction component may have much higher concentrations of LIL elements than the mantle, and because the fluid-peridotite partition coefficients are not particularly high, these elements could be lost to, rather than extracted from, the mantle unless the coefficients are in error (Hawkesworth et al 1993). Moreover, the isotopes may simply exchange, rather than extract, elements from the mantle, in which case elements would be *expected* to give higher flux estimates than isotopes. Theoretically, one would expect that the apparent flux of an element estimated from arc magma compositions could be overestimates or underestimates of the real subduction flux depending on the behavior of the element in the separation column.

EVIDENCE FROM COUPLED WATER-ELEMENT DATA Stolper & Newman (1994) use water contents of Mariana Trough glasses to infer the composition of the migrating fluid phase. They combine their water data with elemental data from the same samples to estimate the composition of the hydrous component. The composition they obtain has, as expected, high ratios of LIL to HFS elements

compared to MORB, but its LIL element contents are less than might be expected from studies of volcanic arc compositions and its HFS element contents are significantly greater.

Stolper & Newman (1994) argue that the subduction component is unusual because the subduction zone does not overlie the Mariana Trough. Thus, the fluid pathway must be longer than that affecting volcanic arc sources, losing much of its slab signature and gaining more of a mantle signature. From this, they infer the fluid component must have changed its composition by extensive interaction with the mantle. The principal question is whether water reached the melting column directly from the subduction zone. Volpe et al (1990) suggest that the enriched components in the Mariana Trough had accumulated in the lithosphere over a period of time and had been released when the back-arc basin propagated into this enriched lithosphere. If Volpe et al are correct, the component correlating with water content may have had a more complicated origin than Stolper & Newman assume in their interpretation. Nonetheless, their study provides the only estimate of the nature and composition of small-volume fluids in supra-subduction zone settings.

TIME SCALES OF THE FLUID TRANSFER PROCESS Uranium-thorium disequilibria studies have been used to provide constraints on the time scales involved in the fluid transfer process from subducted slab to the arc-magma source region. In the Southern Volcanic Zone of Chile, Sigmarsson et al (1990) show that 238 U/ 232 Th ratios are correlated with 10 Be/ 9 Be ratios, indicating that uranium and 10 Be were added to the source by fluids derived from subducted sediments very recently (<20 ka). By contrast, in Central America (Condomines & Sigmarsson 1993) and the Bismark arc (Gill et al 1993), 10 Be/ 9 Be ratios correlate with 230 Th/ 232 Th ratios, which implies a longer transfer time (>100 ka). These differences could be explained by the different subduction rates, and hence different rates of mantle advection, in the two areas: slow in Chile but rapid in New Britain (Gill et al 1993).

EVALUATION OF RESULTS If Hawkesworth et al (1991, 1993), Stern et al (1991), and Stolper & Newman (1994) are correct, and we have noted some caveats above, element fractionation during transport is an important process in understanding the composition of volcanic arc lavas. One difficulty with simple acceptance of this model is the absence of consistent observations. For example, Hawkesworth et al (1991) require gain of nonconservative trace elements by the slab-derived fluids from the mantle, whereas Stolper & Newman (1994) require loss of these elements by the fluids to the mantle. As Stolper & Newman (1984) themselves state, this contradiction need not mean that the two sets of results are incompatible, as chromatographic columns can both extract and concentrate elements. However, it does reinforce the fact that fluid-mantle interactions at high temperatures are very poorly understood. Clearly, there is room for further experimentation on this important topic.

Depletion and Enrichment of the Mantle Wedge

EVIDENCE FOR WEDGE DEPLETION AND ENRICHMENT Mantle wedge depletion has been recognized as a feature of many intraoceanic arcs. The clearest evidence for wedge depletion comes from ratios of conservative elements of different compatibilities during melting. For example, we can use the Ta/Yb ratio (Pearce 1982, 1993), the Zr/Nb and Ti/Zr ratios (McCulloch & Gamble 1991), the Sc/Y and V/Ti ratios (Woodhead et al 1993), or patterns of these elements (Pearce & Parkinson 1993). The basic idea is that differences in degrees of partial melting (assuming pooled, fractional melting) or of fractional crystallization cause only small variations in these ratios. In contrast, the loss of small melt fractions from the mantle will cause the more incompatible element to be depleted much more rapidly than the less incompatible element. In Figure 2, the fact that many Nb/Yb ratios are less than that of average N-MORB highlights the importance of source depletion.

Conservative element ratios made up of elements of different compatibilities also provide evidence for enrichment. Thus, in Figure 2, samples that plot to significantly higher Nb/Yb ratios than N-MORB can be taken to have enriched sources. This group includes parts of many intraoceanic arcs, notably the southern Lesser Antilles, parts of the Aleutians, north-central Vanuatu, the north Marianas (Volcano arc), and parts of most intracontinental arcs.

CAUSES OF MANTLE DEPLETION AND ENRICHMENT Given that there is consensus over the existence of mantle depletion in some arcs, the question then arises as to its cause and whether that cause has any relationship to the subduction process. Three possibilities are discussed in the literature (Figure 1):

- 1. depletion prior to advection into the wedge, probably as a result of back-arc basin extension;
- 2. processes of melt extraction within the melting column; and
- 3. inefficient removal of melting residues from the mantle wedge or inefficient replenishment of the wedge by asthenospheric flow.

Several possible causes of mantle enrichment are also discussed in the literature. These include:

- 1. introduction of low-volume asthenospheric melts into the source region,
- 2. incorporation of enriched lithosphere,
- 3. advection of plume-enriched mantle into the wedge, and
- 4. processes of melt extraction within the melting column.

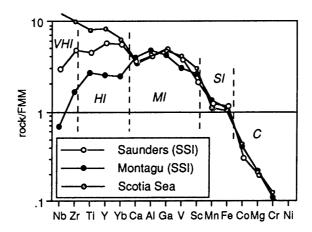


Figure 8 Diagram showing a Fertile MORB Mantle (FMM)-normalized plot (from Pearce & Parkinson 1993). Pattern from the Scotia Sea back-arc basin is compared with two Scotia arc islands and shows how the latter could only be derived from depleted mantle. The elements are ordered according to incompatibility during mantle melting. VHI = very highly incompatible; HI = highly incompatible; MI = moderately compatible; SI = slightly incompatible; C = compatible.

EVIDENCE FOR WEDGE DEPLETION IN ARCS WITH BACK-ARC BASINS To investigate whether depletion is related to the subduction process, comparison of the composition of volcanic arc basalts with basalts from their associated backarc basins is a necessary exercise. The comparison, first made for the Tonga arc-basin system by Ewart & Hawkesworth (1987), has been done in most detail by Woodhead et al (1993). They demonstrate that, compared with their associated back-arc basins, the Tonga, Kermadec, Mariana, and Vanuatu arcs have lower average abundances of HFS elements and higher ratios of Ti/Zr, V/Ti, and Sc/Y. These features are all characteristic of mantle depletion, as explained above.

The fertile MORB mantle—normalized plot (Figure 8) highlights the general conclusions reached by Woodhead et al (1993) for the Scotia arc-basin system. Melting of an undepleted MORB mantle source must produce enrichments in the order VHI > HI > MI for low-moderate degrees of melting changing to a flat pattern at high degrees of melting (where VHI = very highly incompatible, HI = highly incompatible, MI = moderately incompatible). This type of pattern is apparent in the Scotia Sea back-arc basin, which thus can be inferred to have a typical MORB mantle source. Element orders of VHI < HI = MI or VHI < HI < MI as seen in the two Scotia arc volcanoes plotted in Figure 8 cannot, however, be generated directly from an undepleted MORB mantle source. An episode of mantle depletion must therefore have stripped out the most incompatible elements.

Although there are several ways to explain the depleted sources required by the patterns in Figure 8, it is apparent from the data set that arcs without proximal back-arc basins (the continental arcs, the Aleutians, northern Vanuatu,

Lesser Antilles) all exhibit MORB-like or enriched sources. Despite the small sample size, therefore, the inferences of Woodhead et al (1993) seem to survive the scrutiny made possible by our independent data set.

EVIDENCE FROM CONTINENTAL ARCS FOR WEDGE ENRICHMENT An overall comparison of intraoceanic and intracontinental arcs shows a difference between the two, but some overlap, for ratios that are independent of the subduction component (Figure 2). Thus, oceanic arcs are predominantly derived from mantle similar to, or more depleted than, average MORB mantle, but with some enriched portions, as pointed out above. Continental arcs are predominantly derived from MORB-mantle sources or sources more enriched than these. Pearce (1983) concludes that enriched subcontinental lithosphere may play a part in the chemical distinction between oceanic and continental arcs. On a regional scale, Saunders et al (1980) attribute the transverse geochemical variations in arc lavas across the Antarctic peninsula to enriched sub-continental mantle. Rogers & Hawkesworth (1989) argue that the temporal trend of eastward increasing ⁸⁷Sr/⁸⁶Sr ratios within the Central Andes is caused by increasing mobilization of late-Proterozoic sub-continental mantle lithosphere as the locus of volcanism migrated eastwards.

Recently, however, isotope systematics have shown that crustal contamination is also capable of generating the distinctive characteristics of continental arcs previously attributed to the sub-continental lithosphere. In some arcs, such as Banda (Margaritz et al 1978) and the Philippines (McDermott et al 1993), the hyperbolic trend on an oxygen-strontium isotope plot indicates bulk sediment addition to the mantle source. In others, for example the Central Volcanic Zone of the Andes (Davidson et al 1990), isotope systematics enable the enriched lithosphere hypothesis to be rejected in favor of contamination and homogenization with lower crustal melts at the base of thickened crust. In a further set of arcs, such as the Lesser Antilles, interaction with the upper crust appears to be important (Davidson 1987). Thus, although there are no data to suggest that the mantle wedge beneath any continental arc is depleted, there are few areas where the presence of enriched mantle can be demonstrated unambiguously.

EVIDENCE FOR WEDGE ENRICHMENT ASSOCIATED WITH ARC RIFTING Enriched compositions are often encountered during and immediately after arc rifting. The Sumisu Rift in the Izu-Ogasawara arc is a good example of an arc undergoing rifting (Hochstaedter et al 1990). Here, the isotope and trace element data are consistent with mixing of an enriched-MORB source and a MORB-like, subduction-affected mantle source. The enriched rocks of the Volcano arc in the northern Marianas are located where the arc is starting to reform following arc rifting (Lin et al 1990). Isotopic data again suggest a two-component mixing model. These authors describe the two components as 1. a MORB-like, subduction-affected source and 2. a source similar to that of ocean-island basalts (OIB).

Scientists studying these two parts of the otherwise "normal" Izu-Mariana system attribute the enriched (OIB or MORB) component to asthenospheric processes. Hochstaedter et al (1990) argue that rifting causes new, fertile mantle to invade the mantle wedge. The enriched component in the arc lavas could then have a similar origin to the enriched component in rifts unrelated to subduction, such as by the preferential tapping of enriched mantle domains. This source could still be present while normal arc volcanism reestablishes itself (as in the Volcano arc). Once arc volcanism is reestablished, however, the mantle wedge reverts to its more-depleted composition.

Evidence from the Lau islands of Fiji reinforce these conclusions. They carry a record of Lau arc volcanism prior to, during, and following arc rifting (Gill 1984). Whereas the mantle was depleted prior to rifting, the rifting event that caused the remnant arc to move away from the subduction zone caused magmas of OIB character to erupt in the remnant arc. These postrifting lavas may contain the "OIB" mantle component inferred for the Izu-Mariana region.

The central region of the Vanuatu arc presents a different type of arc rifting. It has experienced major tectonic disruption as a result of the ongoing collision with an Eocene arc complex, which began at about 2 my. Recent data from ODP Leg 134 (Laporte & Briqueu 1993) indicate that the arc underwent a major compositional change in this area at that time. Our own isotope data (DW Peate et al, in preparation) reveal that the islands facing the collision zone acquired a signature dominated by Indian-MORB mantle Pb, rather than by Pacific-MORB and sediment, subduction-derived Pb. Thus, it seems that the collision caused an influx of fertile, perhaps deeper, mantle from the back-arc region into the mantle wedge.

EVIDENCE FOR THE TIMING OF ENRICHMENT AND DEPLETION EVENTS tion that can be addressed geochemically is the relative timing of the mantle depletion/enrichment event and the addition of the subduction component. In some of the arc-basin systems investigated above, the volcanoes within the arc itself exhibit variable depletion. The Scotia arc is a good example, containing two groups of volcanoes of tholeitic composition, one having significantly less potassium than the other (Pearce et al 1994). Such variations can be used to test whether depletion predates or postdates addition of the nonconservative elements. For this, the Th/Yb-Nb/Yb projection is effective (Figure 2b). Depletion in the back-arc prior to fluid addition gives a trend in which the most depleted source is, by virtue of mass balance, the most affected by the subduction component. In contrast, depletion in the melting column subsequent to fluid addition gives a trend parallel to the MORB array. In most intraoceanic arcs, such as the Scotia arc, MORB-parallel trends are observed, demonstrating that at least some of the mantle depletion can be explained by loss of small melt fractions in the melting column after addition of the slab component.

EVALUATION OF RESULTS As Figure 2 shows, for conservative elements, the mantle wedge has a range of compositions that is broadly comparable to the range shown by MORB mantle, with both depleted and enriched domains. However, the causes of this range of source compositions are not always the same. Depleted sources (relative to an N-MORB source) are rare at ocean ridges and probably owe their origin to melting dynamics. This process of mantle depletion may also operate beneath volcanic arcs, as discussed in the next section. However, depleted sources are also more common beneath volcanic arcs, where they are restricted (according to existing data) to intraoceanic arcs with active back-arc spreading centers such as the Scotia and Tonga arcs. Models that require depletion of the mantle by melt loss prior to advection into the wedge are thus favored at present. It is difficult to see how recycling of depleted mantle can be as effective as melt loss. For example, the depletion by melt loss of a very highly incompatible element such as Nb is so effective that about a 50% mixing of mantle totally depleted in Nb would be needed to have the same effect as a 1% melt loss from the mantle source.

Although enriched parts of the mid-ocean ridge system are often related to hot-spot activity, only rarely (e.g. North Tonga) do hot spots directly influence the composition of volcanic arc basalts. The most common cause of enrichment in oceanic arcs is intraarc rifting, which could result from collision of an edifice with the arc, as in the Vanuatu arc, or from the early stages of back-arc spreading, as in the Izu-Marianas arc. Evidence to date points to the addition of small-volume asthenospheric melts to the mantle wedge in these environments as part of a general process of wedge replenishment whereby new, fertile mantle can advect into the wedge. Once the arc establishes itself, this supply of fertile mantle is cut off.

The Partial Melting Process: Constraints and Degree

MAJOR ELEMENTS Plank & Langmuir (1988) use major elements to constrain the melting process. They use variation diagrams for most of the world's arcs to obtain oxide values for MgO = 6.0 wt% (denoted as Na6.0 etc) and plot the values obtained against crustal thickness. Their best correlations are of Na6.0 (positive) (Figure 9a) and Ca6.0 (negative). They show that variations in the heights of melting columns beneath thin and thick lithosphere could account for this difference, i.e. the extent of melting decreases as lithosphere thickness increases. They infer degrees of melting between 10% (thick crust) and 25% (thin crust), taking melting parameters from Jacques & Green's (1980) experiments and assuming a primitive upper-mantle composition. They note that the correlations obtained are the reverse of those reported from mid-ocean ridges, where Na8.0 correlates inversely with lithosphere thickness owing to the effect of temperature.

conservative elements in volcanic arc basalts to study the melting process. Because element ratios highlight source rather than degree of melting, they use a Nb-Yb plot, which effectively separates source depletion from degree of melting. This plot can be contoured for extent of mantle depletion/enrichment and pooled fractional melting (Figure 9b). Because the degree of melting and fractional crystallization (and crystal cumulation) form subparallel trends on this plot, the Nb and Yb values must be normalized to a given MgO content (9.0 wt%). The results of this study yield values that are slightly higher than those of Plank & Langmuir (1988), ranging from about 15% (thick lithosphere) to just over 30% partial melting (thin lithosphere). Although Plank & Langmuir did not consider variable source composition, they considered a much greater number of arcs, so this difference may not be very significant.

water-element covariations Stolper & Newman (1994) use the correlation between water and element concentrations in Mariana Trough glasses to estimate the degree of melting. They use a least-squares method to relate the proportion of their water-rich component in the source of their glasses to degree of melting. Their key plot, shown in Figure 9c, shows that a 0.2 wt% increase in water content causes the degree of melting to increase by about 12%. Hydrous melting experiments in progress at the University of Tokyo (K Hirose & I Kushiro, personal communication) confirm that this estimate is broadly correct. Assuming that decompression melting causes 15–20% melting, and that 0.2 wt% water is in the mantle wedge, one discovers that a typical arc on thin lithosphere could be the product of about 30% melting. However, the further implication of Stolper & Newman's work is that parameters affecting subduction fluxes (e.g. convergence rate, subduction input) may have as great a bearing as lithospheric thickness on degree of melting.

PERIDOTITE COMPOSITIONS Comparison of suprasubduction zone peridotites with mid-ocean ridge (abyssal) peridotites provides another line of evidence for the difference in degree of melting between the two environments. Figure 9d shows a plot of Ti against Y (Parkinson et al 1992; JA Pearce, unpublished data) in peridotites from mid-ocean ridges and suprasubduction zone (forearc) settings. We modeled the compositional trend according to degree of fractional melting assuming 1% melt retention. This plot gives an estimated degree of melting of 25–30% for the suprasubduction zone peridotites. The latter are unlikely, however, to represent the residue from melting beneath volcanic arcs. More likely, they represent the residues from the melting event that produced boninites. However, analysis of boninite glasses from the same area indicates a water content of about 0.2 wt% in their mantle source (Newman & Van der Laan 1992). The fact that this water content has increased melting by some 10% relative to abyssal peridotites is in good agreement with Stolper & Newman's (1994) estimate of a 12% increase in degree of melting for a 0.2 wt% water input.

INTRA-ARC COMPOSITIONAL VARIATIONS The discussion above treats arc melting on a global (whole-arc) scale. However, most arcs exhibit local variations in the degree of melting that cannot simply be related to the length of the melting column. These variations may be both along-arc and across-arc.

Umnak Island in the Aleutian arc provides a good example of along-arc variations. Here, two adjacent volcanoes have substantial inferred differences in

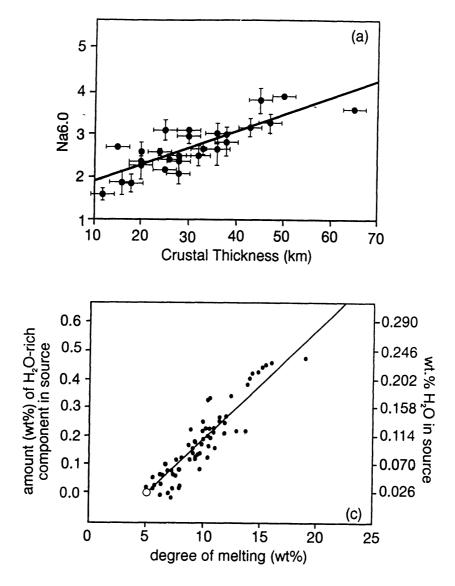
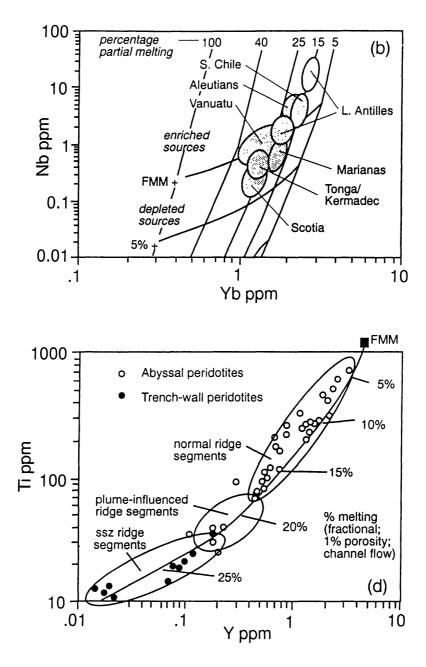


Figure 9 Diagrams showing some of the key lines of evidence for the degree of melting during genesis of arc volcanics. (a) Plank & Langmuir's (1988) correlation between Na6.0 and crustal thickness. (b) Pearce & Parkinson's (1993) plot of Nb9.0 against Yb9.0 contoured for source depletion and degree of melting. (c) Stolper & Newman's (1994) correlation between water content of Mariana trough glasses and inferred degree of melting. (d) Unpublished data (JA Pearce) on Ti and Y contents of peridotites from mid-ocean ridge and supra-subduction zone settings showing the degrees of melting required to explain their compositions.

the extent of partial melting, despite similar crustal thicknesses beneath each (Miller et al 1992). These are Okmok (tholeiitic trend with 20% inferred melting) and Recheshnoi (calc-alkaline trend with 5% inferred melting). Because the most nonconservative elements, such as Cs and Ba, are enriched in Okmok compared with Recheshnoi, Miller et al attribute the higher degrees of melting beneath Okmok to a greater slab flux and hence greater water content. Within the Aleutian arc as a whole, tholeiitic volcanoes are often associated with fracture zones on the subducting plate (Kay et al 1982, Marsh 1982). Miller et al (1992) suggest that fracture zones, by acting as sediment traps and by virtue of



more extensive crustal alteration, could generate a greater subduction flux than normal subducted crust. If correct, this provides some of the best evidence for spatial variations along an arc being controlled by variations in the nature of the subducting plate.

Several studies of across-arc variations have concluded that, in general, reararc volcanoes are the product of lower degrees of melting than those of the magmatic front, despite the longer mantle column arising from the increased depth to the Benioff Zone. Examples include New Britain (Woodhead & Johnson 1993), Sangihe (Tatsumi et al 1991), Marianas (Stern et al 1993), Scotia (Pearce et al 1994), and Izu (Onuma et al 1983, Tatsumi et al 1992). For the Sangihe arc, Tatsumi et al (1991) further suggest that the rear-arc magmas segregate from the mantle at deeper levels than magmas beneath the main volcanic front (as depicted in Figure 1). However, Stern et al (1993) attribute the lower degrees of melting in the Mariana rear-arc to an alternative explanation: that the proportion of slab-derived water in the mantle decreases with increasing distance from the trench.

The various approaches used to estimate degree of OVERALL ASSESSMENT melting in volcanic arcs from lava compositions give very similar results: 10-30% melting, with lithospheric thickness and water content as the prime controls. Interestingly, Davies & Bickle (1991) use the 1970s experiments of Green (1973, 1976) to investigate mantle melting above subduction zones and obtain a value of 2-8% melting. However, Green's experiments relate to in situ melting, and these conclusions may simply emphasize the point that decompression is as (or more) important than water in generating melt. The observation made by Gill (1981)—that tholeitic lavas (the assumed products of high degrees of melting) dominate those arcs with thin crust (<20 km) and high (>7 cm/yr) convergence rates—further emphasizes the combined role of decompression and volatile content in determining degree of melting. Combining all the results, we would ascribe in the order of $10 \pm 5\%$ melting to volatile addition and the remainder to decompression. On the scale of single arcs, there is evidence for selective tapping of the lower parts of the melting column, which feeds rear-arc volcanoes. These arcs are thus the products of lower degrees of partial melting than the volcanoes of the main volcanic front. There is also evidence of variable subduction fluxes causing variable degrees of melting along arcs.

SUMMARY AND CONCLUSIONS

The steady accumulation of new and better data on volcanic arc lavas has led to a consensus in some aspects of arc magmagenesis while fueling conflict in others. The following points emerge from this review:

- 1. Volcanic arc magmas owe their compositions to many factors, including the fertility of the mantle wedge, the composition of subducted material, the generation of a subduction component and its transport to the zone of melting, processes in the melting column, and magma-lithosphere interaction. Because these factors vary systematically with tectonic setting, so the setting of an arc volcano governs its composition.
- 2. The compositions of most volcanic arc lavas support, to a certain extent, the widely held view that the HFS elements are conservative and the LIL elements are nonconservative with respect to their mantle source. However, the HFS-LIL element distinction is a simplistic one. Elements of very high field strength are also nonconservative, while large ion lithophile elements that are major elements can exhibit conservative behavior because their high concentration in the mantle masks the effect of any added component.
- 3. The abundances of the nonconservative elements in volcanic arc magmas vary systematically with sediment flux, which is in turn dependent on the nature and thickness of the subducted sediment column and the rate of subduction.
- 4. The thermal state of the subduction system is important in determining whether aqueous fluids or melts are generated. While aqueous fluid generation may be the norm, there are many exceptions. Thus, subduction of very young lithosphere appears to provide the necessary conditions for slab melting, while sediment melting is favored by subduction of thick sequences of terrigenous sediment. Melting rather than dehydration influences the behavior of the elements. In particular, Zr and Nb now become nonconservative elements.
- 5. Fractionation of nonconservative elements can take place during generation of the subduction component and during transport of fluids and melts to the melt zone. These two processes have similar effects. However, fractionation during dehydration and melting of the subducting slab is well-substantiated experimentally and from studies of subduction complexes. Fractionation by chromatographic processes during transport is likely theoretically, but its precise effect is difficult to quantify.
- 6. Loss of small melt fractions from the mantle source, both beneath backarc spreading centers and deep in the sub-arc melting column itself, may deplete the mantle source of intraoceanic volcanic arc lavas in incompatible elements. By contrast, the mantle sources for both oceanic and continental volcanic arc magmas with no back-arc basins are at least as fertile as N-MORB mantle sources.

- 7. Arc rifting may be an effective way of refertilizing the mantle wedge by permitting advection of fertile mantle into the mantle wedge. Several independent lines of evidence suggest that generation of small-volume asthenospheric melts during rifting gives the resulting magmas alkalic compositions.
- 8. Enriched lithosphere may become incorporated in the source of volcanic arc magmas, especially in continental settings. However, more important ways of enriching continental volcanic arc magmas may be by subduction and melting of terrigenous sediment and by interactions between magma and the crust.
- 9. Melting beneath island arcs takes place in response to a combination of volatile-addition and decompression. There is a direct relationship between added water and degree of volatile-induced melting with several independent lines of evidence all suggesting that $10 \pm 5\%$ of melting (10% per 0.2 wt% water in the mantle source) is volatile-related. The decompression component depends on lithospheric thickness and varies from 15–20% in primitive intraoceanic arcs to only small amounts at Andean-type margins.
- 10. The melting column under volcanic arcs may differ from that beneath ridges, allowing small melt fractions to be lost prior to pooling of the melt generated. This melt may feed rear-arc calc-alkaline volcanoes and cause the main arc volcanoes to have more tholeitic, depleted compositions.

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