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Fluid influence on the trace element compositions of subduction zone magmas

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Subduction zones represent major sites of chemical fractionation within the Earth. Element pairs which behave coherently during normal mantle melting may become strongly decoupled from one another during the slab dehydration processes and during hydrous melting conditions in the slab and in the mantle wedge. This results in the large ion lithophile elements (e.g. K, Rb, Th, U, Ba) and the light rare earth elements being transferred from the slab to the mantle wedge, and being concentrated within the mantle wedge by hydrous fluids, stabilized in hydrous phases such as hornblende and phlogopite, from where they are eventually extracted as magmas and contribute to growth of the continental crust. High-field strength elements (e.g. Nb, Ta, Ti, P, Zr) are insoluble in hydrous fluids and relatively insoluble in hydrous melts, and remain in the subducted slab and the adjacent parts of the mantle which are dragged down and contribute to the source for ocean island basalts. The required element fractionations result from interaction between specific mineral phases (hornblende, phlogopite, rutile, sphene, etc.) and hydrous fluids. In present day subduction magmatism the mantle wedge contributes dominantly to the chemical budget, and there is a requirement for significant convection to maintain the element flux. In the Precambrian, melting of subducted ocean crust may have been easier, providing an enhanced slab contribution to continental growth.

1. Introduction

Subduction zones are the main tectonic setting where volatiles – particularly water – are returned to the mantle. These volatiles exert a major control on the melting relationships in the subducting slab and in mantle wedge of the over-riding plate. They also determine the nature of the fluxes that are responsible for transporting chemical elements from the slab into the wedge and, ultimately, into the island arc and calc-alkaline magmas which have contributed to continental growth throughout Earth history.

The chemical nature of, and pathways followed by, hydrous fluxes in the subduction zone environment are not well constrained. Many intraoceanic and continent-based arc magmas have high concentrations of large-ion lithophile (LIL) elements (Rb, Th, K and Ba) relative to high field strength (HFS) elements (Ti, Zr, Hf, Nb, Ta or P), and it has been suggested that breakdown of hydrous mineral phases in the subducted oceanic crust releases volatiles which preferentially transport the more water-soluble LIL-elements into the mantle wedge of the over-riding plate (Saunders *et al.* 1980; Pearce 1983; Gill 1981).

Slab dehydration may be only the first stage of a complex series of fractionation processes in subduction zones. As fluids enter the mantle wedge, hydration

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mechanisms serve to stabilize new minerals, such as hornblende or phlogopite, which themselves may become vulnerable to thermal breakdown as the thermal structure of the subduction zone evolves. Fluids migrating through the wedge will selectively scavenge incompatible elements from their more compatible partners. Such fluid migration and fractionation will lead to different chemical 'pathways' and different mantle wedge residence times for the various elements: for example, He, Rb, U, Be and Th may have particularly short residence times in the mantle wedge (Saunders *et al.* 1987; Sigmarsson *et al.* 1990). Moreover, the mantle wedge itself may be an important contributor of material to the ascending fluids or melts, and this could become a dominant supplier if induced convection effectively replenishes this wedge source.

At issue, then, is the relative importance of (i) the element flux derived from the slab (subducted ocean basalts plus sediments), which we shall term the *slab-derived flux*, and (ii) the element flux from the mantle wedge, which we shall term the *wedge-derived flux*. Recent studies have suggested that in oceanic arcs, which are underlain by young, depleted lithosphere and asthenosphere, the slab-derived flux may be dominant (Hole *et al.* 1984; Ewart & Hawkesworth 1987), whereas in continent-based arcs, a lithospheric or sub-lithospheric wedge-derived component is important (Saunders *et al.* 1980; Hawkesworth 1982; Pearce 1983; Hickey *et al.* 1986; Rogers & Hawkesworth 1989; Hawkesworth & Ellam 1989; Hickey-Vargas *et al.* 1989).

Continental flood basalts (and equivalent dyke swarms), erupted in tectonic settings far removed from contemporaneous subduction zones, often have trace element patterns similar to those of subduction zone magmas, possibly reflecting the magmas inheriting this signature from, or during ascent through, the continental lithosphere. This could imply that the suprasubduction zone trace element character occurs throughout extensive regions of the subcontinental lithosphere. If so, is this suprasubduction zone signature inherited by, or established at, subduction zones? If the former, how and where is the LIL-element enrichment achieved?

In this contribution, we assess the role of fluxes in the transport of trace elements in this environment. Crucial to any models of flux transport is the nature of the medium through which the fluids flow, and the mineral assemblages with which they equilibrate. It is the minerals which primarily control element fractionations, but their stability is critically dependent on the P–T–X conditions in different parts of the subduction zone. Thus we turn first to the postulated thermal structure of subduction zones.

2. Thermal and physical structure of subduction zones

The implications of whether or not subducted slabs melt beneath arc systems, or merely dehydrate and release an aqueous-rich fluid are considerable (Peacock 1990, 1991), as the compositions of the slab-derived component will vary accordingly. For example, melting of a high-pressure slab assemblage such as eclogite is likely to release a silicic melt substantially depleted in the heavy REE and Sc, elements strongly partitioned into garnet. On the other hand, dehydration during the breakdown of chlorite, amphibole or serpentine minerals will release a hydrous fluid phase capable of transporting substantial amounts of Si, K, light REE and LIL-elements from the slab (Boettcher & Wyllie 1968; Nakamura & Kushiro 1974; Tatsumi *et al.* 1986).

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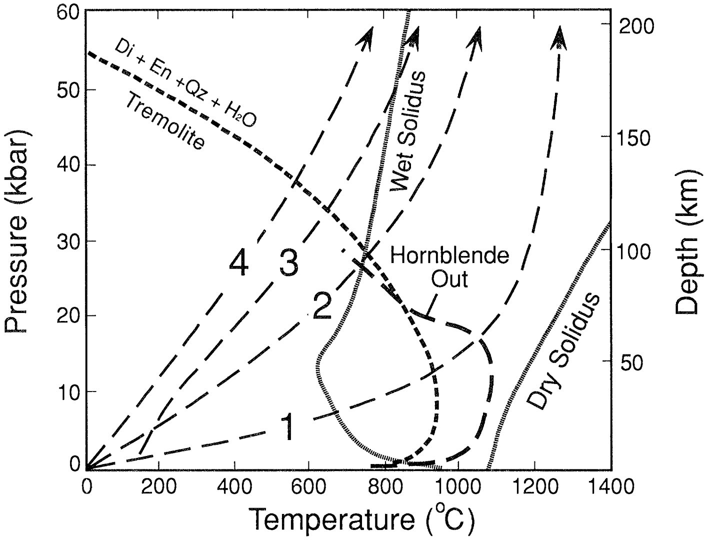

Figure 1. Pressure-temperature diagram illustrating the possible thermal conditions operative in subduction zone systems, modified from Peacock (1990). Lines 1–4 are representative thermal gradients along the top of the subducting oceanic slab in old, cold systems (line 4), through to subduction zones where there is induced mantle convection in the hanging wall. Phase relations in wet and dry basalt from Green (1982) and Lambert & Wyllie (1972); in wet and dry peridotite from Takahashi & Kushiro (1983), Mysen & Boettcher (1975). Hornblende and phlogopite stability curves are from Green (1973, 1982) and Wendlendt & Eggler (1980).

Peacock (1990, 1991) has shown that subducted oceanic crust is likely to intersect the wet basalt solidus only if the thermal gradient is high, as during the subduction of very young, hot oceanic crust, or during the initial stages of subduction (Tarney *et al.* 1981) when the adjacent mantle temperatures are still high; or during Archaean times when the geotherm was steeper (Tarney & Weaver 1987; Martin 1987) (figure 1). Trace element data for Archaean magmas are consistent with melting of a hydrous hornblende- or garnet-bearing mafic source (Tarney & Weaver 1987), but most modern arc volcanics do not have REE profiles consistent with extensive garnet fractionation. However, in areas of recent ridge subduction, where young (zero-age) oceanic crust has been subducted, such as Baja California, southern Chile and the Aleutian Islands (Rogers & Saunders 1989; Defant & Drummond 1990), the associated arc volcanics are unusually depleted in heavy REE, which might infer melting of eclogite under unusual thermal conditions. However, even under these conditions it is debatable whether the wet melting curve of eclogite is reached, and there are alternative explanations involving hornblende and garnet in the mantle wedge (Saunders *et al.* 1987; Rogers & Saunders 1989).

Slab-induced convection in the overhanging mantle wedge will influence the thermal structure of the subduction system, affect the stability of hydrous minerals, and influence the composition of the arc magmas. If the arc system is based on old and relatively thick continental lithosphere, and the angle of subduction is shallow, asthenosphere may be excluded from the subarc region. In this extreme situation, arc magmatism may not be possible. In arcs based on relatively young oceanic lithosphere, induced convection beneath the thin lithosphere could produce a deep asthenospheric wedge adjacent to the slab. These two 'end-member' wedge states will provide potentially quite different mantle source material for the arc magmas,

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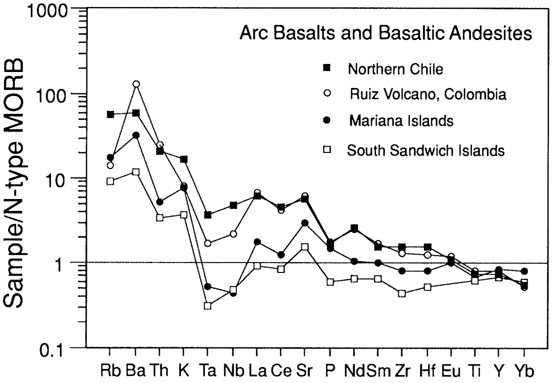

Figure 2. Representative analyses of basalts and basaltic andesites from oceanic arcs (South Sandwich Islands and Mariana Islands) and continent-based arcs. Nb and Ta are positioned according to their relative incompatibility in four-phase mantle peridotite. Note that the magnitude of the Nb and Ta anomaly decreases in the continent-based arcs, and that the abundance of most elements, including the HFS elements, increases in these lavas. Data sources: Northern Chile-sample A791 from Cerro Overo (Thorpe *et al.* 1984); Colombia-sample MB 260 from Ruiz Volcano (Marriner & Millward 1984); Mariana Islands-sample AS1 from Ascuncion Island (Hole *et al.* 1984); South Sandwich Islands, SSM4.1 from Montague Island (P. E. Baker and I. Luff, unpublished data). Normalizing values from Sun & McDonough (1989).

and result in different residence times for slab-derived material: for example, asthenospheric source material can be continually replenished, and removed, by mantle flow; whereas lithospheric mantle provides a more permanent storage for slab-derived components. The rheological state of the lower lithosphere boundary is critical. Importantly, Falloon & Green (1990) have shown that, in carbonated subcontinental lithosphere, carbonatitic melts could coexist with residual phlogopite and garnet at depths greater than 100 km. So it is possible that induced mantle flow could occur in old sub-continental lithosphere, and this would have the effect of circulating new mantle material, that had suffered earlier metasomatism, into the source regions of continental arcs.

3. Trace element characteristics of subduction-related magmas

Trace element comparisons are best made using multielement mantle- or MORB-normalized diagrams or 'spiderdiagrams' (Wood *et al.* 1979*a*, *b*; Tarney *et al.* 1979, 1980; Sun 1980; Thompson *et al.* 1983, 1984). For reference purposes, we plot a range of basalts and andesites from oceanic island arcs and continental-margin arcs in figure 2. Included in this compilation are data for post-subduction magmas from Mexico. The following features are apparent: all of the patterns exhibit a pronounced, but variable, trough or anomaly at Nb (and Ta); the HFS elements to the right of the diagrams have much lower abundances than the LIL elements to the left; there are considerable variations in inter LIL-element ratios (e.g. Rb/Ba, K/Ba; or Rb/Th); and continental magmas have higher LIL- and HFS-element abundances than their oceanic counterparts.

In these diagrams the elements are arranged in order of increasing incompatibility (right to left) for a normal upper mantle spinel peridotite mineral assemblage (Sun 1980; Tarney *et al.* 1980, 1981; Thompson *et al.* 1983, 1984; Sun & McDonough 1989).

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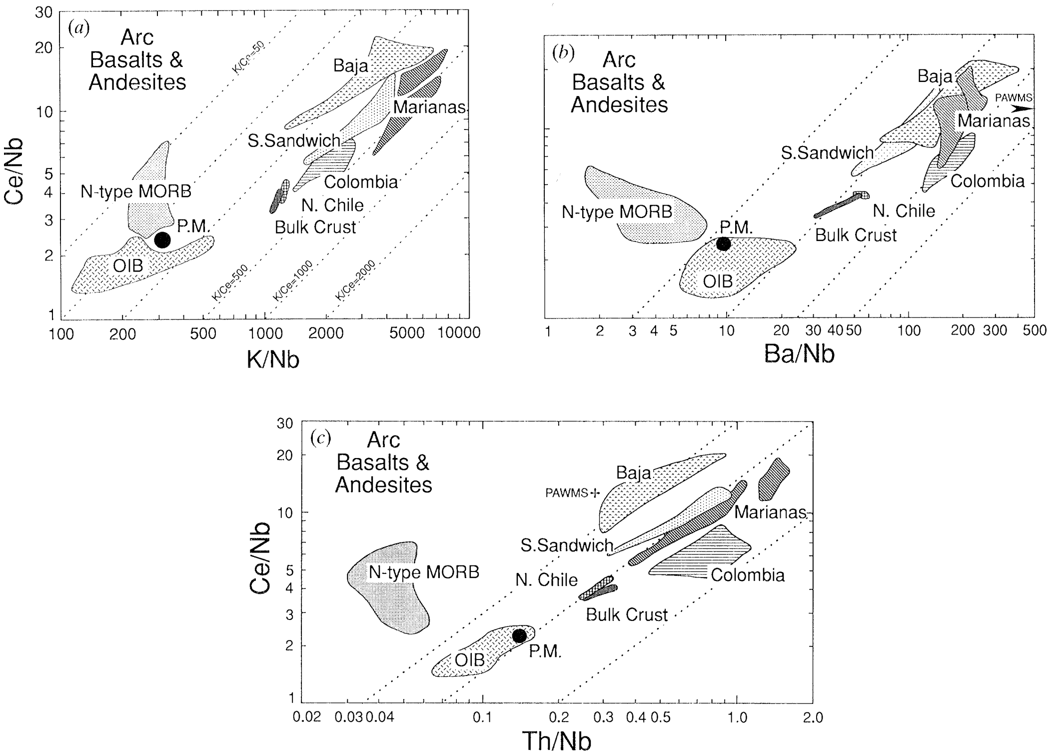

Figure 3. Ce/Nb ratio versus K/Nb, Ba/Nb and Th/Nb ratio, for subduction-related basalts and andesites, N-type mid-ocean ridge basalts (N-type MORB) and ocean island basalts (OIB). Fields for MORB and OIB, and primordial mantle (PM) values, from Saunders *et al.* (1988). Data sources for subduction-related volcanics given in figure 2, plus Baja California from Saunders *et al.* (1987) and Rogers & Saunders (1989); southern Chile data from Hickey-Vargas *et al.* (1989). 'Bulk crust' refers to average continental crustal estimates from Taylor & McLennan (1985) and Weaver & Tarney (1984); PAWMS (Pacific authigenic weighted mean sediment) from Hole *et al.* (1984). For most samples, and to improve precision at low abundances in arc basalts, Nb is calculated from Ta using a Nb/Ta ratio of 16.

Entry of another mineral into the fractionating assemblage with specific affinity for one or more elements can effectively change its position on the incompatibility scale, resulting in a prominent positive or negative anomaly on the spiderdiagram. Such is the case for Nb in most subduction-related magmas; that the high distribution coefficient indicated is a consequence of deep-level processes is shown by the fact that, say, K and Nb behave coherently in shallow-level magmas. We are left with the fundamental observation (Saunders *et al.* 1980) that Nb, along with other HFS elements like Ta and Ti, is strongly depleted relative to the LIL elements, in arc parental magmas. This feature can be illustrated in larger numbers of samples using ratio–ratio diagrams. By using Nb as a denominator, and adjacent LIL elements (e.g. La, Ce, K, Ba or Th) as numerators, we can produce a useful and immediate representation of the 'magnitude' of the anomaly (figure 3) in comparison with representative data for MORB and ocean island basalts. Note that all of these elements are considered to have low partition coefficients in olivine, pyroxene, plagioclase, spinel and garnet. Consequently, we would not expect individual magmatic suites to show much dispersion on the ratio–ratio plots, and this is, on the whole, observed.

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The exceptions mainly reflect analytical uncertainty at the low abundances of Nb and Ta in primitive arc tholeiites.

There is only limited variation in Ba/Ce, K/Ce or Th/Ce ratios in the various arc lavas, which is perhaps surprising considering the range of values which are found in possible source rocks. For example, subducted pelagic sediments have low Th/Ce ratios (*ca*. 0.002) and high Ba/Ce ratios (*ca*. 140), in addition to high LIL/Nb ratios. Note also that all recent arc rocks, for which data are available, have LIL/Nb ratios greater than that of average continental crust compositions estimated by Weaver & Tarney (1984) and Taylor & McLennan (1985).

4. Mineral phases which may fractionate Ti, Nb, Ta, Zr, Hf and P

Mineral phases which are likely to sequester significant amounts of HFS elements, either in the slab or the mantle wedge, are clearly important in the petrogenesis of subduction zone magmas. Phases which contain significant Nb and Ta are the titaniferous minerals ilmenite, sphene, rutile and perovskite. Some amphiboles can contain significant Nb, Ta, Ti and Zr. Zircon and apatite contain stoichiometric Zr and P respectively. At high pressures, Zr, Ti and P may have enhanced solubilities in garnet and pyroxene. Pyrochlore contains stoichiometric Nb, but this mineral is normally restricted to rocks with very high Nb contents (e.g. carbonatites) and its behaviour and stability in a subduction zone environment are unknown.

Amphibole megacrysts have measured distribution coefficient (*D*) values for Nb and Ta ranging from 0.2 to 0.6 (Irving & Frey 1984). Values increase for intermediate and acid rocks, reaching 4.0 (Pearce & Norry 1979). Green & Pearson (1986) investigated the distribution of Nb and Ta between various magmas and magnetite, ilmenite, rutile and sphene. For Nb, the reported *D* value for magnetite was 0.7, for ilmenite values are in the range 2–5, sphene in the range 3–8, whereas rutile shows the highest values at 26–30. Reported *D* values for Ta are correspondingly higher, especially for sphene and rutile. As with hornblendes, *D* values rise markedly with increasing silica content of the associated liquid. Although there are no published *D* values for perovskite, concentrations of Nb in this mineral in igneous rocks reach 5000 p.p.m. (Wedepohl 1970) implying that *D* values must be high for most magma compositions. However, because perovskite is only stable in equilibrium with magmatic liquids with very low silica activities (Carmichael *et al*. 1970) it is unlikely that perovskite would able to equilibrate with orthopyroxene under subsolidus conditions in the subarc mantle, and would more likely react to form another Ti-bearing phase.

Pargasitic amphibole could be stable in the downgoing slab or in the mantle wedge, provided that the water pressure did not exceed about 30 kbar (3 GPa) (Allen *et al*. 1975). K-rich amphiboles are stable to rather greater depths (Sudo & Tatsumi 1990). Survival of amphibole in the mantle wedge could confer negative Nb and Ta anomalies on the equilibrium liquids. However, the *D* values for Nb and Ta in amphibole are relatively small, and substantially less than Zr, Ti, P (?) and the HREE, which would result in a strong decoupling between these elements and Nb, which is not observed in subduction-related magmas. Moreover, post-subduction magmatic suites, whose unusual compositions (particularly their high K/Rb ratios (greater than 3000)) are attributed to breakdown of amphibole (Saunders *et al*. 1987; Rogers & Saunders 1989), also show strong negative Nb and Ta anomalies, but should

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show the reverse. Amphibole, though an ideal mineral in many other respects to be involved in arc magma petrogenesis, does not yet appear to be able to account for Nb and Ta distributions.

A phase (or phases) which will sequester Nb, Ta and possible Ti without causing larger depletions in other HFS elements is required. Sphene, ilmenite and rutile almost certainly meet this criterion because of their high D values for Nb and Ta; garnet and pyroxene provides the means to retain other HFS elements such as Zr, P and Ti.

5. Potential sites for HFS element retention

Two fundamentally different series of models have been proposed to account for the low HFS element characteristic of arc magmas. In one model, the abundances are controlled by melting of mantle with residual titaniferous minerals ('titanites') which retain the HFS elements in the mantle source region (Saunders *et al.* 1980; Foley & Wheller 1990). In the other model, HFS elements are retained in the subducting oceanic crust (Saunders *et al.* 1980, 1988). The low abundance of HFS elements in the arc magmas is a consequence of this retention and of previous episodes of melt extraction from the wedge (Green 1972). In both models LIL-element abundances are significantly enhanced relative to that of the HFS elements because hydrous fluids selectively mobilize and transport LIL elements from the slab into the wedge and also within the wedge.

(*a*) *Titanite, zircon and apatite stability in the mantle wedge*

Titanium, being a stoichiometric component of rutile, sphene and ilmenite, is buffered at a specific activity in any liquid with which these minerals may equilibrate. In basalt or basaltic andesite, the natural melting products of lherzolite, the activity constant for Ti is low (Watson 1976; Ryerson & Watson 1986). This allows the TiO_2 content of the basic magma to increase to substantial concentrations before it is removed by fractionating phases such as titanomagnetite or ilmenite. Similarly, during melting, the first-formed melt in equilibrium with a Ti-bearing phase will be rich in TiO_2 and this concentration will not fall until all of the Ti-rich phase has been consumed in the melting process. To create a Nb or Ta anomaly, the modal abundance of the Ti-rich phase in the melting assemblage will have to be sufficient to survive melting to the point where the melt can separate from the residue and the mineral be left as a site for element sequestration. Moreover, before a TiO_2-rich phase can begin to equilibrate with a liquid, the other phases in the assemblage must be saturated with Ti. For instance both garnet and clinopyroxene can contain substantial Ti, especially at the high temperatures of the lherzolite solidus.

Green & Pearson (1986) showed that silica contents of liquids have a strong effect on titanite saturation, with higher silica liquids achieving saturation at lower TiO_2 contents. Indeed tholeiitic basalts require at least 1.5% TiO_2, and possibly as much as 8% TiO_2 in the source before saturation is achieved. Foley & Wheller (1990) have re-interpreted the experiments of Green & Pearson (1986) and Ryerson & Watson (1986) to suggest that at the predicted low solidus temperatures, high water content, high pressure and high fO_2 conditions accompanying arc magma formation, titanite saturation could be achieved in the mantle source regions, even at the low predicted TiO_2 concentrations. Residual apatite or zircon are unlikely to survive in the residue during normal melting of mantle lherzolite, although if melting occurs at sufficiently

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low temperatures (less than 1100 °C), and perhaps under hydrous conditions (as in the subarc environment), small amounts of apatite may survive melting (Watson 1980).

Critical to the stability of titanites and related phases in the mantle wedge is the nature of the melting process in the subarc region. For example, in the periphery of the melt régime, where the extent of melting may be very small (McKenzie 1984, 1985), minor phases, if initially present, may not be exhausted and this could lead to major LIL/HFS element fractionation in the extracted liquids. This process may be amplified if the melts are hydrous, as suggested by Foley & Wheller (1990). However, titanite phases must still exist in the mantle before melting. The minor phases could be inherited from earlier, presubduction lithospheric enrichment events (cf. McKenzie 1989), an apparent prerequisite for accounting for the LIL and HFS contents, and Sr- and Nd-isotope systematics, of continent-based arcs (Rogers & Hawkesworth 1989; Hawkesworth & Ellam 1989). Lithosphere-derived xenoliths, the MARID suite, which actually contain rutile, are found in kimberlite pipes, and were used by Saunders *et al.* (1980) as indirect support for their suggestion that titanite minerals might exist in the subarc wedge. Waters (1987) has subsequently argued that these xenoliths represent mantle material infiltrated by lamproitic magmas; alternatively that some may represent cumulates.

(b) *Titanite stability in the subducting slab*

The initial melting product of the wet, basaltic subducting slab is a silica-rich liquid similar to dacite (Green & Ringwood 1967). The activity coefficient for TiO_2 in such a liquid is higher than that in a basaltic liquid (Watson 1976); consequently TiO_2 concentrations required to saturate the dacitic liquid with respect to a Ti-rich phase will be lower than in the case of basalt produced from a lherzolite (Green & Pearson 1986). Moreover, the TiO_2 concentration in a basaltic source could be higher by a factor of 5–20 than that in a depleted lithosphere harzburgite. The lower melting temperatures also mean that less Ti is required to saturate the accompanying clinopyroxene and/or garnet, leading to higher modal proportions of the residual Ti-rich phase.

In most modern subduction zones, however, temperatures within the downgoing slab are too low to permit melting, although dehydration reactions will occur (Anderson *et al.* 1978; Peacock 1990). At high pressures, K, Rb, Ba and probably La and Ce can dissolve in water-rich fluids, whereas Ti, Nb, Ta and other HFS elements are likely to be highly insoluble (Mysen 1979; Tatsumi *et al.* 1986). This is the situation where the greatest decoupling of LIL from HFS elements will occur, providing the fluid can escape to transfer the LIL elements into the overlying mantle wedge, leaving Nb, Ta and Ti in the basaltic slab. Because most subduction-related basalts, basaltic andesites and boninites cannot easily be produced as direct melts of the slab, material must be transported into the mantle wedge, where it hybridizes with the mantle component (Wyllie & Sekine 1982): the MgO, Ni and Cr and other compatible elements being provided by the mantle wedge, with the slab providing the LIL elements and also the fingerprint of equilibration with a Ti-rich (and possibly other) minor phase.

Melting experiments carried out in basaltic systems confirm that ilmenite, rutile and sphene are stable above the solidus (Allan *et al.* 1975; Thompson 1975; Helz 1973; Hellman & Green 1979). Rutile replaces ilmenite with increasing pressure (Thompson 1975) and in wet melting experiments has been seen to replace sphene

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with both increasing pressure and temperature, sphene being stable to only 15 kbar (1.5 GPa) (Hellman & Green 1979). The phase ultimately responsible for the retention of Nb and Ta within the slab will then depend on the pressure and temperature experienced when the melt or fluid escapes from the slab. Zr, Hf and P, may be retained in garnet and clinopyroxene at high pressures, or of course in zircon and apatite at lower temperatures if their saturation points are reached.

HFS element retention in the slab cannot, alone, account for the low absolute abundances of these elements found in some primitive island arcs (Tonga: Ewart & Hawkesworth 1987; South Sandwich Islands: figure 3). Green (1972), Hole *et al.* (1984) and Ewart & Hawkesworth (1987) have proposed that the sources of these arc basalts had suffered previous melt extraction. Replenishment by LIL elements from the slab then produces the characteristic high LIL/HFS ratios in these magmas.

6. Fluxes in the subduction zone environment

Arc systems are a paradox in being voluminous zones of magmatism yet being regions where cool lithosphere is being returned to the mantle and isotherms are depressed. Hydrous fluids are clearly vital in lowering the solidus temperatures of slab and/or mantle wedge to enable melting to occur, but it is widely recognized that degrees of melting must be low and that the processes of segregation of these small melt fractions must be efficient. Fluids serve another important function in stabilizing hydrous mineral phases such as hornblende and phlogopite, which may exert significant control on the pathways followed by trace elements passing through the system.

Much fluid is lost from the oceanic lithosphere at relatively high levels in the subduction zone, as porosity is reduced and low-grade minerals dehydrate. However, fluids incorporated in hydrous minerals such as hornblende in the mantle wedge may be transferred down-dip to the site of arc-magma genesis by induced flow (drag) of metasomatized mantle adjacent to the slab. Water trapped in the cooler interior of the slab in amphiboles, or as high pressure forms of serpentine, may survive to be released at greater depths (perhaps to *ca.* 300 km; Ringwood 1990), thus extending the zone through which fluid fluxing and separation of LIL from HFS elements may occur.

There is conclusive proof from the presence of ^{10}Be that subducted young sedimentary material is being incorporated in the source of some arc magmas (Tera *et al.* 1986); Pb-isotopic ratios and the presence of negative Ce anomalies in some arc lavas strongly support a subducted sediment input into the magma source (Hole *et al.* 1984; Barreiro 1983; Woodhead & Fraser 1988); and the high volatile content in undegassed back-arc magmas indicates subduction of hydrous material (Muenow *et al.* 1980). However, most of these authors stress that the proportion of such subducted material involved in the formation of arc magmas is actually very small. For example, Hawkesworth & Ellam (1989) estimate that only about 3% of subducted Sr is required to satisfy the requirement of newly formed crust. Much of the subducted material must therefore bypass the magma-production zone to be carried down into the deep mantle, or it is efficiently removed beneath the forearc region.

The problem of quantifying the chemical flux from the slab is especially difficult in continent-based arcs, where there may be a significant chemical component from the mantle wedge, and where crustal contamination of magmas may be important.

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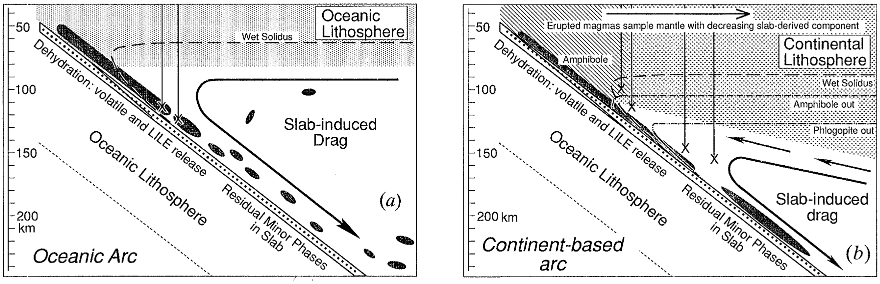

Figure 4. Schematic diagrams illustrating the alternative processes in (*a*) youthful, oceanic subduction systems, where the arc is underlain by asthenospheric and depleted lithospheric mantle, and where the trace element and isotopic compositions of the arc magmas are dominated by the slab-derived chemical flux; and (*b*) a mature continent-based arc system, where a wedge-derived flux is dominant over the slab-derived flux. The ultimate origin of the wedge-derived component is unclear; it may be inherited in the form of small-degree melts percolating from the asthenosphere, far removed from any subduction zone; or it may be inherited from ancient subduction zone systems. Light stipple: oceanic lithosphere; intermediate stipple: subcontinental lithosphere; dark stipple: immediate zone of metasomatism of mantle by slab-derived fluids; diagonal ornament: zone of amphibole formation; large crosses; zones of initial magma generation. In either case (*a*) or (*b*), fluids must play an important role in fractionating the LIL and HFS elements, either at the slab-mantle interface, or in the mantle wedge.

With primitive oceanic arcs, Ewart & Hawkesworth (1987) estimated that 84% of the Sr in basalts from Tafahi, in the Tonga Island, is from the slab, and Hole *et al.* (1984) estimated that 50% of the Sr in Mariana arc magmas may be slab (oceanic crust plus sediments) derived, the remainder coming from the mantle wedge.

A possible scenario for young oceanic arcs is summarized in figure 4*a*. HFS elements are retained in the subducting slab: for Ti, Nb and Ta initially in sphene and, at greater depths, in rutile; Zr, Hf, and P enter zircon and apatite or clinopyroxene and garnet. Dehydration alone will permit mobile LIL elements, but not insoluble HFS elements, to be transported from the slab to the mantle wedge, thus producing the required decoupling from LIL elements with or without minor phases. Slab melting will not decouple the LIL and HFS elements unless residual minor phases are present. The fact that voluminous Archaean crustal compositions have marked negative Nb and Ta anomalies (Weaver & Tarney 1984), and were generated through hydrous melting of a basaltic source, suggests that these minor phases are commonly stable during wet melting.

Fluids from the slab interact with and metasomatize the mantle wedge, which initially may have been depleted by previous melt extraction, and this may then melt under the influence of fluids to form parental arc basalts. The fluids and their associated chemical flux enable growth of hornblende (and at a deeper level, phlogopite: Sekine & Wyllie 1982), but if there is slab-induced convection dragging down the metasomatized mantle, there may be continual pressure-induced breakdown of hornblende, releasing fluids for melting or for further fluxing the wedge, or promoting ascent of low-density diapirs. In intraoceanic arcs the asthenospheric nature of the wedge facilitates slab-induced convection and replenishment of the arc mantle source, although being oceanic it may not have a high content of LIL elements, and continual fluxing at the wedge-slab interface may be required to achieve the progressive LIL element enrichments observed with time in such arcs (cf. Tarney *et al.* 1981; Saunders & Tarney 1984).

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Continent-based arcs, on the other hand, are associated with a foundation of thick, variably old, lithospheric mantle (figure 4*b*). Neither the thickness nor the thermal profile are well constrained. Melting of this lithosphere is much more difficult than with the asthenospheric mantle wedge of intraoceanic arcs, and indeed is most likely where extensional decompression permits uprise of asthenosphere into the lithosphere. It may be for this reason that emplacement of calc-alkaline granitoids is normally associated with extensional activity at Cordilleran margins, and with the extensional collapse of collisional orogenic belts. Although crustal contamination does occur, there is now good evidence that the magmas have inherited a significant proportion of their trace element budget from the subcontinental lithosphere. For instance, the systematic correlation between increasing $^{87}Sr/^{86}Sr$ ratio, Sr abundances and decreasing ϵ_{Nd} in arc magmas from northern Chile cannot readily be explained by adding a high Sr/Nd component from the slab (Hawkesworth 1979) as this would produce a convex-upward mixing trend on the $^{87}Sr/^{86}Sr$–ϵ_{Nd} isotope plot, which is not observed. Secondly, arc magmas from northern Chile show a progressive increase in HFS/REE ratio (e.g. Nb/Sm) with time which correlates positively with $^{87}Sr/^{86}Sr$ and negatively with ϵ_{Nd} (Rogers & Hawkesworth 1989). Again, these data are difficult to reconcile with crustal contamination, or input into the source solely from the subducted slab. Note, that this apparent temporal variation in northern Chile is also spatial; the oldest magmas in the west have the lowest $^{87}Sr/^{86}Sr$ ratio. Moreover, Hickey-Vargas *et al.* (1989) and Stern *et al.* (1990) describe similar spatial variations in Quaternary to Recent volcanic rocks from S. Chile. The primary control on these variations may therefore be spatial rather than temporal and reflect mineralogical control and/or increasing involvement of the subcontinental lithosphere.

The consistently lower LIL/Nb ratios of continental arc magmas relative to oceanic ones (figure 3) implies that the magmas have tapped mantle source material with an ocean island basalt (OIB) component. This trace element signature is most unlikely inherited from the slab since, as pointed out by Hickey-Vargas *et al.* (1989), the OIB-like signature becomes pronounced in those parts of the system furthest from the trench. Magmas generated closest to the trench will inherit a greater proportion of slab-derived flux; this is consistent with the lower $^{87}Sr/^{86}Sr$, lower Nb/REE ratios and higher ϵ_{Nd} values in these magmas. Those generated more distally will have a progressively diminished slab-derived component, until they become fully OIB-like, as in the Patagonian basalts of southern S. America (Stern *et al.* 1990).

An important constraint on the lithosphere contribution is that continental margin arcs like the Andes have been producing voluminous magmas continually for several hundred million years, so the supply of trace element and major element components must continually be replenished, and on a massive scale. This is most easily accomplished if subduction does induce convection in the mantle wedge so that subcontinental lithosphere is continually drawn into the melting zone. Because mantle-enrichment processes, some carbonatitic, are continually adding new OIB components to the base of the lithosphere through hot-spot plume activity (Saunders *et al.* 1988; Hawkesworth *et al.* 1990), the replenishment problem is readily satisfied. The trace element and isotopic differences observed between oceanic and continental arcs (Hawkesworth 1979) then reflects the fact that enrichment processes have affected subcontinental lithosphere over a considerably longer period than oceanic lithosphere. Interestingly, many island arc and continental margin volcanics have the isotopic and trace element characteristics of PREMA (prevalent mantle in the

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terminology of Hart & Zindler (1989)) rather than MORB, which either reflects the mixture of OIB components (EM1, EM2, HIMU) which have been added to the base of the lithosphere, or that PREMA is indeed a prevalent component that is being continually released from the lower mantle (Hart & Zindler 1989) and rises to underplate the lithosphere. The major element differences between the dominantly mafic compositions of primitive arc magmas and the silicic compositions of continental margin arc magmas may be a function of the higher degrees of melting provided by the hotter asthenospheric mantle in oceanic regions.

Finally, because mantle enrichment processes generally occur through veining of the refractory harzburgitic lithosphere by much more fertile carbonatitic fluids or OIB material, this may enable a titanite phase to remain stable in the residue during hydrous melting-out of calc-alkaline magmas. A consequence would be that it is not only the slab itself, but also the lithospheric mantle dragged down by the subducting slab, which carries the positive Nb anomaly that compensates for the negative Nb anomalies in subduction-related magmas (cf. Saunders *et al.* 1988).

7. Summary

Critical points from the above arguments are as follows.

1. Although sediments are subducted in significant volumes at subduction zones, and their presence in the magma source regions can be detected in arc chemistry, the more surprising fact is that the sediment contribution is usually relatively minor. This argues against a major contribution to modern arc volcanism through melting of the slab, though slab melting may occur at the initiation of subduction, and it may have been more common in the early Precambrian.

2. The lithosphere is the dominant material source of subduction magmas, induced convection continually dragging in new lithospheric material into the melting zone. This most easily accounts for the compositional differences between oceanic and continental arcs. OIB components added to the lithosphere play an important role in replenishing the source regions for arc magmatism.

3. Hornblende and phlogopite are important minor phases which control some aspects of the chemistry of subduction zone magmas.

4. Titanite phases, stabilized by the hydrous environment in the slab and probably in the wedge, confer a characteristic chemical signature on all subduction-related magmas. These residual minerals are carried deep into the mantle.

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