

GEOCHEMICAL TRACERS OF THE SLAB

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Introduction

In deciphering the complex geochemical signature in arc lavas, there is general agreement that there is an important slab component. Indeed the very presence of melting likely testifies to one part of such a component, namely water. Beyond the acknowledgement of its general presence, consensus rapidly evaporates on the nature, magnitude and associated transport processes of slab derived material. However, not only does a detailed understanding of the role of slab derived components in arc lavas place major constraints on the physical workings of the subduction zone, but the residue of elements after subduction zone processing is a first order variable in modelling the evolution of the mantle. Thus establishing a better fix on the key details of the addition of slab material should be a primary objective of the Subduction Factory initiative.

Much has been written on slab tracers, but there are significant recent developments that are worth taking stock. Unlike mid-ocean ridge and ocean island basalt (MORB and OIB) volcanism, in arcs there is not the common redundancy in elemental behaviour. Thus looking at a restricted elemental space can seriously affect the conclusions derived. The rapid development of high quality inductively coupled quadrupole mass-spectrometry (ICP-QMS) provides precise analyses for a wide range of elements of interest across the large span of concentrations experienced at arcs. The discussion here is based on recent ICP-QMS data sets to exploit this full range of tracers measured together, and to minimise questions as to data reliability. ICP-QMS analyses place vital context for the specific information yielded by isotopic analyses. The isotopic field itself has also seen a recent blooming, with new data on stable light isotopes ($^7\text{Li}/^6\text{Li}$ and $^{11}\text{B}/^{10}\text{B}$), high precision laser fluorination oxygen isotope data, and increasingly extensive data sets of ^{10}Be and Hf isotope measurements, in addition to continued, and increasingly precise, Sr-Nd-Pb work. Finally mass-spectrometric measurements of U-Th-Ra and U-Pa systems provide exciting dynamic information on the rates of transport of slab signatures.

A working model of arc lava geochemistry

There is not room here to justify in detail the general model in which the following discussion is framed. However, abundant evidence and argument in the literature supports general a "three component" model, in which the compositions of island arc lavas are dominantly accounted for by a (variable) mixture of:

- 1) depleted mantle wedge
- 2) subducted sediment
- 3) altered basaltic oceanic crust.

Conceptually this makes good sense. Upper mantle sampled in MORB worldwide is generally depleted (low incompatible element abundances e.g. Th, low relative light rare earth element abundances e.g. La/Sm and radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$) and the process of back-arc spreading is likely to further enhance the depleted nature of mantle feeding the subduction zone wedge (Woodhead et al 1993). Subducted material can be readily divided into two distinct slab components, the sediment cover and underlying altered basaltic oceanic crust. This material is observed to be subducted and transfer of this material into the depleted mantle wedge will have a

significant chemical effect. Possible additional influences such as an enriched, sub-arc mantle component (e.g. Morris and Hart 1983) and crustal contamination (e.g. Davidson 1987) may play a part in some localities, but I feel are of limited significance in determining the dominant chemical systematics of oceanic arcs.

Incompatible element systematics

An overview of a range of elemental behaviours can be gleaned from so called spidergrams. The ordering of elements on such spidergrams is empirical so as to generate 'smooth patterns for oceanic basalts (e.g. Hofmann 1988), although this basis is increasingly substantiated by experimental partitioning data. Thus marked 'spikes' on the plots illustrate suggest processes at work not operative in MORB and OIB genesis. Key features apparent in most island arcs include a negative Nb anomaly and clear positive Sr and Pb anomalies. The contrast between abundances in a depleted MORB source relative to a sediment are also clear. Much of the overall shape of arc lavas can be seen to reflect a typical sediment signature simply superimposed on depleted MORB, although there are notable exceptions, e.g. positive Sr anomaly. Clearly the budget of incompatible trace elements (i.e. those to the left of the plot) will be dominated by sediment addition even at the level of fractions of a percent addition by weight. Progressing to less incompatible elements on the right of the diagram, the influence of the mantle will be more marked. In gauging slab contributions, it therefore makes good sense to examine the high incompatible elements, that are peculiarly sensitive to slab additions. This has the additional advantage that mantle melting processes are highly unlikely to fractionate ratios of these elements.

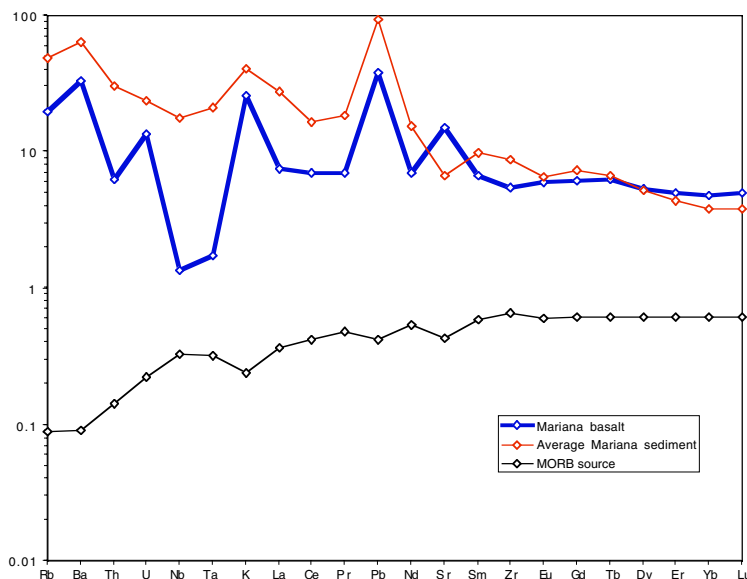


Fig. 1 Primitive mantle normalised trace element abundances of typical Mariana basalt, average Mariana sediment and average MORB source

Before delving into the world of trace element ratios, it is worth considering variations in absolute elemental abundances. Although to interpret these in detail requires assessment of variable mantle depletion, degree of melting and fractional crystallisation, the overall variability is so large that some important first order observations can be made. Unlike the MORB-OIB sample, the biggest variability is not in the most incompatible elements (i.e. those at the left of the spidergram). For example Th varies by some two and half orders of magnitude whereas Ba (more incompatible both empirically and from experiment) varies by less than two orders of magnitude (Fig 2a). Likewise it is well documented that Ce and Pb vary similarly in the MORB-OIB environment but evident differ greatly in the global arc database (Fig 2b).

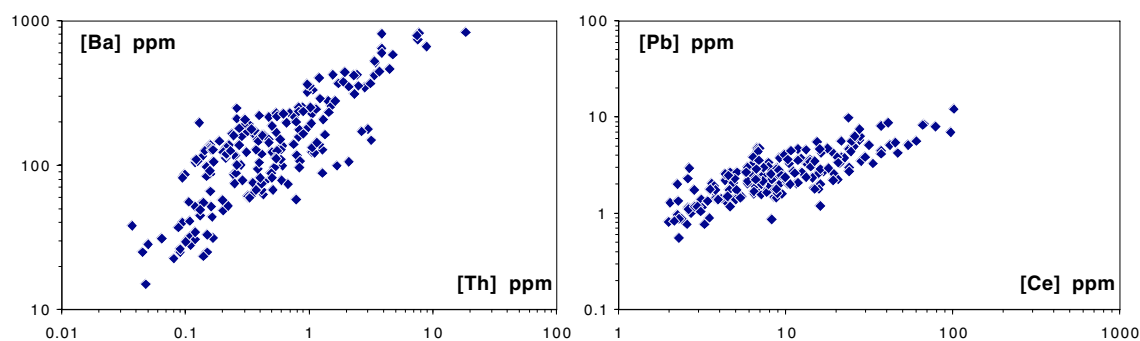


Fig 2 Plots of a) Th vs Ba and b) Ce vs Pb concentrations in $\mu\text{g/g}$ for a dataset of oceanic island arcs analysed by ICP-MS (same data set as used in Fig 3 below). Note the much bigger variations of Th and Ce relative to Ba and Pb respectively. In MORB and OIB the latter element pairs vary as much or more than the former elements. This is interpreted to reflect the addition of a fluid component which notably increases the concentrations of the elements in the y-axis in the most elementally depleted lavas but leaves the fluid immobile elements plotted on the x-axes unaffected.

In traditional melting models, a smaller variation would be attributed to buffering of an element in a phase in which it was relatively more compatible. It might thus be argued that variable melting of the mantle wedge with residual amphibole would dampen variability of Ba relative to Th. However, this would be notable in terms of a negative concentration anomaly rather than the positive spikes associated with the elements marked by diminished variability (Fig 1). Despite this important detail, it is nevertheless noticeable that there is a dominant overall trend of 'enrichment', from depleted arcs (such as the Izus and Tonga) to enriched arcs (such as the Volcano and Lesser Antilles). As is discussed further below, these simple elemental indices of enrichment are also reflected in more robust element and radiogenic isotopic ratio tracers.

Slab components

In order to assess slab additions in detail it is more instructive to look at incompatible element ratios. As an important first step, the notion of a single "slab component" should be laid to rest. A three component arc model (i.e. mantle plus two slab components) has been long proposed (e.g. Kay 1980) and often advocated but the spectre of a single slab component, much beloved for its simplicity, has frequently muddied issues. Fig 3 shows a plot to illustrate the inadequacy

of attempting to explain arc geochemistry as a single slab flux. Neither in the global data set, nor within in individual arcs can either end of the data array be pinned at a deplete mantle composition. There is an enriched endmember (i.e. high La/Sm) and depleted endmember which nevertheless shows the most marked relative enrichment of some elements such as Ba (but also Pb and Sr).

Sediment component

The 'enriched' endmember is typically associated with a range of features characteristic of subducting sediment, such as less radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$, Pb isotope ratios that closely approach local sediment compositions (see Woodhead 1989) and larger negative Nb anomalies (e.g. higher Th/Nb, Fig 3b). It might be hoped that this component would also clearly correspond to high $^{10}\text{Be}/^9\text{Be}$ ratios, which have been invaluable in unequivocally implicating subducted sediment in arc volcanics (Morris and Tera 1989). This does not appear to necessarily be the case from existing data (e.g, Sigmanson et al 1990). Nevertheless it might be expected that linking an isotopic label present only in the very uppermost sediment (and therefore susceptible to minor off-scraping) with trace element signatures presumably reflecting a larger fraction of the sediment column is not straight forward. Further work is in progress to address this key issue more thoroughly. Nevertheless the geochemical characteristics of the enriched endmember are highly indicative of sediment. In a different but complementary approach, the correlation of sedimentary input and lavas output budgets of incompatible elements in arcs globally implicated the importance of sediment in controlling the budgets of these elements in arc lavas (Plank and Langmuir 1993)

A major question is how sediment is transferred from subducting slab to arc lava source. Important clues are to be gleaned in the signatures of arc lavas in comparison to subducting sediment. This requires good control on sediment input in addition to magmatic output. This requirement is well met at the Marianas, where it is clear that the bulk subducting sediment package, whilst similar, is not exactly appropriate for the enriched component. Notably the latter needed to have more extreme negative Nb anomaly, e.g. higher Th/Nb and La/Nb. This may be readily explained if the sediment melts in the presence of residual rutile (Elliott et al 1997). This is an important constraint, given the implications for temperature of the slab to allow melting.

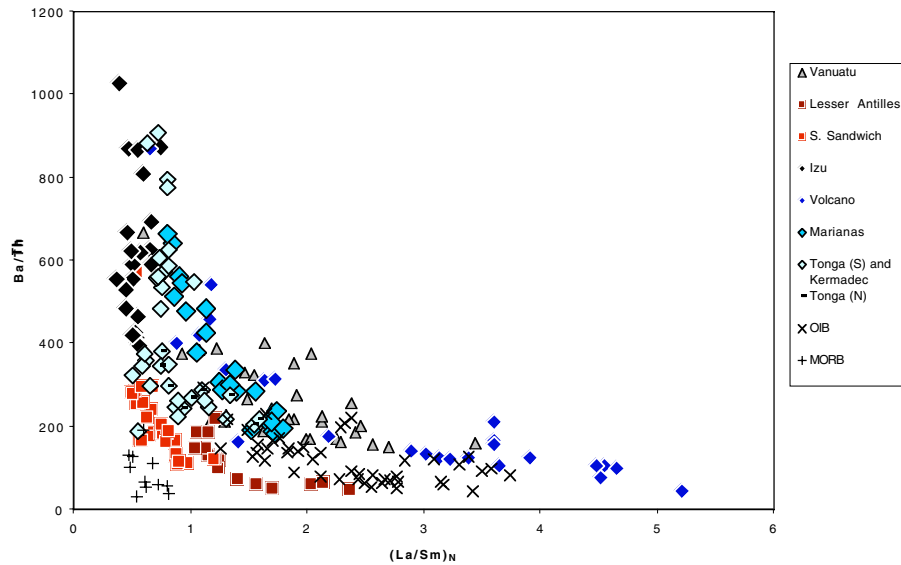


Fig. 3a Plot of Ba/Th vs chondrite normalised La/Sm for oceanic island arcs, with MORB and OIB datasets for comparison. Neither end of the island arc array represents a composition approaching depleted MORB. Thus two slab derived components need to be added to the upper mantle for this array; one component to dramatically increase Ba/Th and one to increase La/Sm. La/Sm is unlikely to be fractionated relative to the arc lava source for the large degrees of melting inferred (and unlike the situation for most OIB)

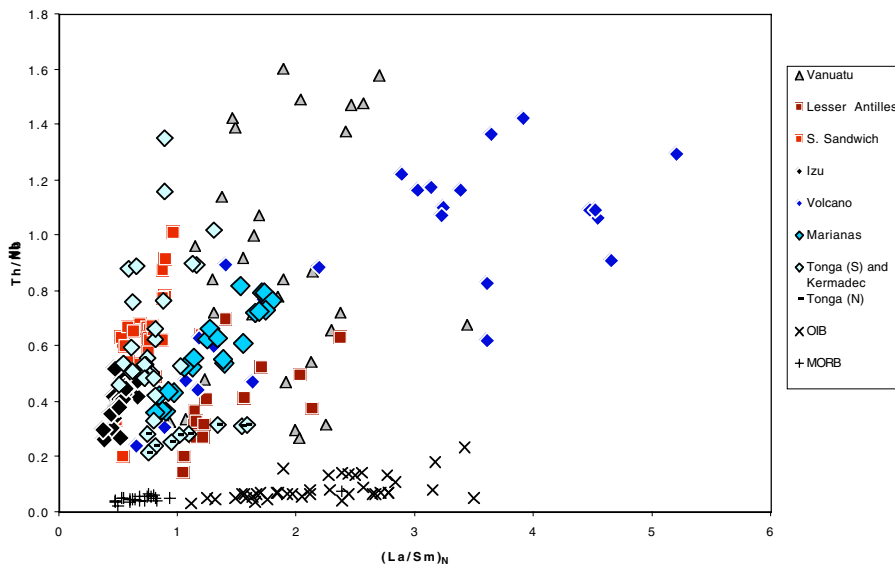


Fig 3b The same datasets as 3a with chondritic normalised La/Sm plotted against Th/Nb. This plot illustrates that using all such "fluid immobile" elements, the arc arrays trend back towards a composition similar to depleted upper mantle. This plot thus focusses on the non-fluid subduction component. Unlike some assertions, this high La/Sm component does not resemble OIB, and for a range of considerations is likely to be sediment (see text). The global dataset does not form a coherent array, although many individual arcs do. The individual arrays appear to radiate away from a field appropriate for depleted mantle towards different enriched endmembers, presumably reflecting different subducting sediment compositions at different arcs (see Plank and Langmuir 1998).

Although the effect of sediment addition is very marked (Fig 1 and 3), due to the highly depleted nature of the mantle wedge, only a very small amount of sediment can result in an most extreme enrichment. For example the most enriched Mariana sample can be modelled by the addition of 0.3% by weight sediment to an appropriate mantle source (Elliott et al 1997). Recent oxygen isotope to data place upper limits on the amount of sediment it is permissible to add (Eiler et al 2000). Many 'normal' island arcs show oxygen isotope ratios within error of the well established mantle values. This allows less than 1% of sediment to be added. Since both sediment and mantle contain similar proportions of oxygen, but very variable amounts of the incompatible elements discussed here, large variations in incompatible element concentrations can be readily explained within this bulk amount of sedimentary mass added. Nevertheless, it should be borne in mind that the subducted sediment is frequently only a 500m layer whereas there is potentially a 100km column of mantle (with higher density). In this scenario, mixing of all the sediment column with the mantle wedge (through equilibrium porous flow for example) would only amount to a by mass mixing proportion of ~0.3%. Thus the small mass mixing proportions are both beguiling in terms of the effect on incompatible element concentrations and also in the consequence for subducted sediment mixed back into the mantle in the subduction zone.

Fluid component

The other endmember causes major enrichments in certain elements, e.g. Ba (Fig 1 and 2) but for some elements the contribution is not readily discernible, Fig 3b (i.e. the arc lavas are equally well accounted for by addition of a single component, albeit different for different arcs, to a depleted mantle source). The array of elements for which the second component is most significant include Ba and other divalent cations (e.g. Sr and Pb), see Figs 1 and 2. Other elemental additions are more subtle, as discussed below, but the sensitivity of U-series disequilibrium to recent disturbance also clearly indicates U and Ra transported in this fluid phase. The array of enriched elements is neither like sediment nor altered oceanic crust, the chief inputs into the subduction. Isotopic arguments (see below) implicate altered oceanic crust as the ultimate source but an elemental fractionation mechanism is also required. The array of elements associated with this component are notably those which a range of experiments predict should be enriched in an aqueous 'fluid' resulting from dehydration of the altered oceanic crust, and so this component can be dubbed the 'fluid' component. Although providing some agreement with the empirical observations (e.g. Tatsumi et al 1986), experiments do not yet provide totally consistent results between themselves (c.f. Brenan 1995 and Stalder et al 1998) and thus independently constrain fluid mobility of all elements

A significant observation is that the fluid component is most evident in the most sediment poor lavas. This is most readily explained by addition of a near constant amount of fluid to sources with a range of added sediment. In sediment rich sources, the fluid contribution is swamped but in sediment poor lavas sources it becomes prominent. That the most depleted samples are relatively more affected than sediment rich samples accounts for the suppression of variability in elements added by the fluid (Fig 2). Near constant fluid but variably sediment enriched sources also accounts for the general inverse global trend observed in Fig 3a. Some individual arcs, e.g. the Marianas, also show an inverse trend on Fig 3a but elsewhere the picture is more complex

and variable amounts of fluid are required in similarly sediment rich sources (e.g. the Izu arc) to account for their systematics on plots such as Fig 3a. It is not unexpected that a component derived from the heterogeneously altered oceanic crust should be variable, and it is perhaps more surprising that this component can in general be modelled as a near constant flux. This is rather significant for modelling of global recycling processes.

The ultimate source of the 'fluid' endmember is rather well constrained by the isotope signature of Pb and Sr. In island arc suites, the high Ba/Th lavas also typically have most MORB-like Pb isotope ratios. Such a signature may either be derived from subducting oceanic crust or mantle wedge. The Sr isotope ratio associated with MORB-like Pb is however more radiogenic than most MORB and compatible with average altered oceanic crust (e.g. Staudigel et al 1995). Furthermore, recent light isotope studies have demonstrated arc lavas have heavier $^7\text{Li}/^6\text{Li}$ and $^{11}\text{B}/^{10}\text{B}$ ratios than mantle values (e.g. Palmer 1991, Moriguti and Nakamura 1998, Ishikawa and Tera 1999, Tomascak et al 2000). B and Li are particularly powerful tracers of slab additions given that light isotope fractionation occur only at low temperatures and variations in light isotope ratios therefore unequivocally implicate contributions from surface material. Moreover, unlike oxygen, for example, both are strongly enriched in the altered oceanic crust. Unfortunately, the isotopic ratios of B and Li in arc rocks are not on their own the smoking gun for altered oceanic crust involvement, as both sediment and altered oceanic crust have heavier values than upper mantle. Nevertheless, within the limited database, more depleted (i.e. sediment poor) lavas have relatively greater relative boron enrichments, and heavier isotopic compositions. In the absence of crustal contamination, this B rich, isotopically heavy source must be derived from the altered oceanic crust. Li is much less depleted in the mantle wedge than B, and so larger amounts of sediment would need to be added to significantly affect the Li isotope ratio. Indeed for the arcs so far studied, impermissible amounts of sediment (from $^{143}\text{Nd}/^{144}\text{Nd}$ constraints, for example) would be required to make the Li isotope ratios as heavy as observed in the arc lavas (Bouman and Elliott 1999). Thus an isotopically heavy source of fluid Li, namely the altered oceanic crust, is also implicated.

A very exciting recent development is the observation that the fluid component, as traced by Ba/Th ratios for example, is well correlated with extreme ($^{226}\text{Ra}/^{230}\text{Th}$) excesses (Turner et al 2000). Previously $^{238}\text{U}-^{230}\text{Th}$ systematics in arc lavas have provided important constraints on the timing of sediment and fluid addition (e.g. Elliott et al 1997). The new Ra, especially in combination with unexpected ($^{231}\text{Pa}/^{235}\text{U}$) excesses observed in arc lavas (e.g. Pickett and Murrell 1997) alarmingly stringent constraints on the timescales (at face value less than 1000a) and processes of fluid component addition and melt transport.

Despite clarification of the nature and source of the slab derived components in arcs globally, the mechanism of the addition represents a major outstanding problem to be explored. This appears a fruitful and exciting prospect in the light of a number of new chemical tracers to hand.

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