

SUPPLEMENTAL FILE 2

Schema for Ba/Nb Monte Carlo Simulations

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Supplementary file 2, for manuscript *Linking global trace element systematics in arc rocks to subducted slab dehydration models*. Text here refers to analyses going into making Figure S7.

Introduction

Equations used in this document are primarily derived from Dennis Shaw's 2006 book *Trace elements in magmas: a theoretical treatment* [8]. This document briefly explains the rationale and approach for the geochemical modeling found in our paper. The goal of our modeling is to show what [Ba] and [Nb] behavior would be expected in arc magmas experiencing simple fractional melting and fractional crystallization. This modeling assumes a typical enriched mantle source (e.g., KLB-1), and a moderate degree of both melting ($F = 0.3$) and crystallization ($F = 0.3$). First, this guide will explain the mathematics employed in the geochemical modeling. Then the sources of the main modeling variables and a sketch of the Monte Carlo approach will be offered. Finally, the results of this model will be summarized.

Trace Element Modeling - Theory

Trace element modeling follows simple thermodynamic and chemical rules first described in Rayleigh 1902, and summarized in [8]. See Shaw for more details. Symbols used in this section[8]:

W_0 initial mass of unmelted rock

L mass of liquid or melt

$F = L/W_0$ or fraction of liquid to total mass

X_i mass fraction of mineral i in solid
 p_i mass fraction of mineral i in liquid
 c_o concentration of trace element in whole system i.e. at the start
 c^L or c^L concentration of trace element in liquid
 c^s total concentration of trace element in solids
 c_i concentration of trace element in mineral i
 $\bar{c}$ concentration of trace element in accumulated liquid fractions
 D^{i-m} partition coefficient for an element between mineral i & liquid m
 D weighted or whole rock partition coefficient
 D_0 weighted partition coefficient of whole system i.e. bulk D at start
 P mass fraction of minerals in liquid

Batch Melting

Batch or *modal* melting occurs where $X_i^0 = p_i$, and where $D_0 = P = D$:

$$c^s = \frac{D \cdot c_0}{D + F - DF} \quad (1)$$

and:

$$c^L = \frac{c_0}{D + F - DF} \quad (2)$$

Unlike fractional melting (below), batch melting assumes that melts formed remain "in contact" with the resultant solid residue. This means that chemical equilibrium is a necessary assumption to apply these equations. Furthermore, modal batch melting assumes that every mineral in the original starting solid melts equally as readily; in real physical systems this is rarely the case. Thus, in applying these equations to our models, we are making generalizations about bulk chemical properties that, while applicable to our very narrowly defined scope i.e. theoretical model of basic subduction zone petrology, would not be applicable to more specific systems. While batch melting will be initially employed in our models, I include a discussion of fractional melting below should the need for such a model arise.

Fractional Melting

In the physically unrealistic case of *modal* fractional melting i.e. where all minerals melt in equal proportions and at the same time:

$$c^s = c_0 \cdot (1 - F)^{\frac{1}{D} - 1} \quad (3)$$

and

$$c^L = \frac{c^s}{D} \quad (4)$$

While physically unrealistic, some argue that model melt modeling can approximate pooled fractional non-modal melting [7]. In our case, we are simply trying to create the most analytically straightforward model with as few assumptions as possible, thus we will begin our modeling by only considering modal melting processes. If this approach changes, I have also outlined the non-modal approach here. Following Section 7.5 in Shaw[8], if $D_0 = \sum_i X_i^0 D^{i-m}$ and $P = \sum_i p_i^0 D^{i-m}$:

$$D = \frac{D_0 - PF}{1 - F} \quad (5)$$

See Shaw's text for details on this derivation. The key is that D changes depending on the proportion of melting haven taken place, and which minerals have contributed to that melting. For my model, I only consider fractional melting, as this most likely represents the style of melting occurring in subduction zones as a consequence of slab dehydration. In non-modal fractional melting, $p_i \neq X_i$ for all i . This means that we can use the expression for D following Equation 1 above. Melting is governed by the following equations:

$$c^s = \frac{c_0}{1 - F} \cdot \left(1 - \frac{PF}{D_0}\right)^{\frac{1}{D}} \quad (6)$$

and

$$c^L = \frac{c_0}{D_0} \cdot \left(1 - \frac{PF}{D_0}\right)^{\frac{1}{D} - 1} \quad (7)$$

These equations represent instantaneous or stepwise concentrations of a particular trace element in both the solid and the melt. To obtain a concentration averaged across all melt produced so far in the fractional melting event, the expression would be:

$$\bar{c} = \frac{c_0}{F} \cdot \left(1 - \frac{PF}{D_0}\right)^{\frac{1}{D} - 1} \quad (8)$$

Fractional Crystallization

The mathematics applied to simple fractional crystallization are much simpler, as explained in Chapter 3 of Shaw[8]. The key assumptions made in using the equation below is (1) that the relationship between c^s and c^L is linear over some range, and (2) the proportion of minerals being crystallized stays the same. If these conditions are met, simple mass balances using Rayleigh’s model lead us to derive the following:

$$c^L = c_0 \cdot F^{D-1} \quad (9)$$

And the concentration in the solid would be:

$$c^s = D \cdot c^L \quad (10)$$

Model Parameters

With this theory in mind, we need to define the six key variable crucial to our model. Our model is testing the null hypothesis that magmatic [Ba] and [Nb], as reflected in the arc magmas in our global database, is only a function of simple trace element partitioning processes as classically understood in silicate melts[8]. These classical processes would include (1) fractional modal melting of a fertile peridotite source, followed by (2) fractional crystallization in the upper crust. This model then assumes that neither the depth of melting (related to but not a direct function of the depth to slab or DTS) nor the major element composition of the melt has any bearing on [Ba] and [Nb] of the final melt. Using a Monte Carlo (MC) approach, which is a deterministic method that uses random sampling to obtain numerical results, we can evaluate the probability that the Ba and Nb distributions we see in the real rock record are a function of purely stochastic melting and fractionation processes. We expect to find that the MC model shows a much more tightly distributed, homogeneous parameter space than is observed in our global dataset, thus falsifying the null hypothesis and showing our Ba/Nb analyses attributed to slab dehydration have statistical validity.

Some of these variables can be assumed to be truly random, while others can only reasonably be generated from physically realistic geological processes:

- the Mg# of the starting melt
- $[Ba]_{final}$ after melting and crystallization

- $[Nb]_{final}$ after melting and crystallization
- F_{melt} i.e. degree of mantle melting
- F_{cryst} i.e. degree of fractional crystallization
- Depth to Slab of melt

Even those variables that we will regard as truly random have defined limits. For instance, Mg# of a peridotite melt will never fall much below 50. By the same logic, both F_{melt} and F_{cryst} should not exceed 30% - such high degrees of either melting or fractionation are physically unrealistic.[7, 6]. Finally, the depth to slab can assumed to be truly random - if the null hypothesis is correct and the location of melting relative to the slab and overlying crust has no bearing on [Ba] or [Nb], then DTS should be normally distributed about the range 30-400 km.

Thus, the two variables this section needs to spend the most time parameterizing are the trace element concentrations in the final "typical" arc magma, which has been extracted as a fractional melt from a peridotite source, and then experienced some degree of fractional crystallization. Both of these processes are regulated by intrinsic factors, like:

- $[Ba]_0$ and $[Nb]_0$ in the primary melt
- D_0^{Ba} and D_0^{Nb}
- Mineral proportions, X_i , in the melting source
- Mineral proportions, p_i in the melting assemblage
- Mineral proportions, X_i in the fractionating assemblage

For simplicity's sake, the proportions of minerals melting and fractionating will be fixed. For our purposes, aimed at understanding 1st order global processes, such a modal simplification is justified. If this approach were to be applied at a specific volcano or in a particular arc, such a simplification would not be warranted and a more complete inventory of the systems mineralogy would need to be made. What will we vary in our models then? The most sensible and straightforward variables to make stochastic are the starting concentrations of both trace elements, and the bulk D partition coefficients for both. So long as we apply these c_0 and D_0 variables to a sufficiently realistic mantle and fractional assemblage, we should approximate how simple petrological processes would drive [Ba] and [Nb] systematics in a slab flux absent system.

To take the c^0 variables first, we follow the approach of models in localities like Kamchatka[7], which use Depleted MORB Mantle (DMM) as the starting reservoir for their subduction zone melting and fractionation; the c^0 and D_0 values in both cases have been taken from classic MORB (Table 3)[9] back-arc basin ([6], and primitive arc[3] sources. Specifically, when using Workman and Harts reservoir, I will be using the Enriched DMM source, of E-DMM source. Workman and Hart also provide a tabulation of estimated mineral proportions in the source DMM mantle (Table 3), which can be used in the event we decide to model fractional melting or non-modal melting. As in [7], we will assume that polybaric melting occurs in the spinel-lherzolite facies consistent with MORB style melting.

For $[Ba]_0$, we will use values falling in the following range: 0.227, 0.563, 1.219 ppm (Depleted DMM, Average DMM, and E-DMM respectively, [9]); 0.0168 (Depleted source, [3]). For $[Nb]_0$: 0.0864, 0.1485, 0.2462 ppm (Depleted DMM, Average DMM, and E-DMM respectively [9]); 0.21 (Depleted NMORB, [6]); 0.0495 (Depleted Source, [3]).

Bulk partition coefficients will be taken from similar sources. For D_0^{Ba} : 0.00012 (DMM, [9]); $2 \cdot 10^{-6}$ (spinel peridotite, [5]). For D_0^{Nb} : 0.0034 (DMM, [9]); 0.003 (Depleted NMORB, [6]); $1.8 \cdot 10^{-3}$ (spinel peridotite, [5]).

Finally, [4] provides D^{i-m} for each of the four minerals assumed to comprise DMM in Workman & Hart [9]. These values can be found below:

Table 1: Halliday et al. 1995 for Ba

Mineral	D^{i-m*}	X_i^0 (%)**	D_0^{Ba}
Ol	$5x10^{-6}$	58.2	$4.4x10^{-5}$
Opx	$6x10^{-6}$	28.6	
Cpx	$3x10^{-4}$	13.2	
-	-	-	

* All values from [4]

** All values renormalized from 98% to 100% total from [9] to account for lack of spinel partition coefficient in Halliday et al. 1995.

The above values only consider c_0 and D_0 for mantle melting in arcs. Since these models are attempting to provide a simplistic explanation for Ba/Nb variation globally by invoking simple FC following mantle melting, we will assume c_0 at the start of FC is the same as the endpoint for mantle melting. Therefore the only additional data we need are realistic, if synthetic, X_i^0 and D_0 values for a hypothetical arc magma fractionating assemblage.

Table 2: Halliday et al. 1995 for *Nb*

Mineral	D^{i-m*}	X_i^0 (%)**	D_0^{Nb}
Ol	5×10^{-5}	58.2	2.1×10^{-3}
Opx	0.003	28.6	
Cpx	0.0089	13.2	
-	-	-	

* All values from [4]

** All values renormalized from 98% to 100% total from [9] to account for lack of spinel partition coefficient in Halliday et al. 1995.

Table 3: Bulk D in FC Models for *Ba*

Mineral	D^{i-m*}	X_i^0 (%)	D_0^{Ba}
Ol	5×10^{-6}	20	$1.5 \times 10^{-1} \pm 1 \times 10^{-1}$
Cpx	3×10^{-4}	30	
Plag	0.3**	50	
-	-	-	

* All values from [2] and [1]

** Full range $\pm$ given but only 0.3 reported here

If the starting material for this FC simulation is a primitive arc basalt, up to 30% crystallization will maintain a basaltic composition. The most likely mineral assemblage of such a fractionating magma would likely be dominated by plagioclase in the upper crust (<10 km.). This assumption holds generally - specific volcanoes obviously can have much deeper plumbing systems dominated by amphibole. Smaller amounts of clinopyroxene and olivine would also predominate in this upper crustal magma, particularly in the first few fractions of minerals. Let's assume that the relative total plag/cpx/ol proportions are 50/30/20% - if this is the case, we can simply reuse the D_0 's for cpx and ol as used in our mantle melting.

Parameterizing the FC problem in the way outlined above means we only need to add D_{Ba}^{plag} and D_{Nb}^{plag} to our tabulations. While both Ba and Nb are incompatible in ol and cpx, both elements are much more compatible, if technically still incompatible, in plag. For Ba, $D_0 = 0.183-0.661$ [2] - more likely the range 0.277-0.301 holds at low pressure [1]. For Nb, the values are lower: $D_0 = 0.029-0.139$. Taking these new partition coefficients for plag into account with the existing data, we can arrive at the following Bulk D

Table 4: Bulk D in FC Models for *Nb*

Mineral	D^{i-m*}	X_i^0 (%)	D_0^{Nb}
Ol	5×10^{-5}	20	$5 \times 10^{-2} \pm 1 \times 10^{-1}$
Cpx	0.0089	30	
Plag	0.1	50	
-	-	-	

* All values from [2] and [1]

for each element in Table 3 and 4.

Taking all of these resources into account, the following values will be used in our Monte Carlo sampling method. The method will randomly sample these ranges in even increments to conduct an individual simulation - this will be repeated thousands of times to generate a representation of the parameter space.

- Mg#: 50 to 75
- DTS: 30 to 400 km.
- F_{melt} : 0.1 to 30%
- F_{cryst} : 0.1 to 30%
- $[Ba]_0^0$: 0.01 to 1.5 ppm
- $[Nb]_0^0$: 0.05 to 0.25 ppm
- Bulk D_{Ba}^{melt} : 2×10^{-6} to 1×10^{-4}
- Bulk D_{Nb}^{melt} : 4×10^{-3} to 1×10^{-3}
- Bulk D_{Ba}^{cryst} : 5×10^{-2} to 3×10^{-1}
- Bulk D_{Nb}^{cryst} : 2×10^{-2} to 6×10^{-2}

Monte Carlo Modeling In Brief

(From Wikipedia) Monte Carlo methods vary, but tend to follow a particular pattern:

- Define a domain of possible inputs

- Generate inputs randomly from a probability distribution over the domain
- Perform a deterministic computation on the inputs many times
- Aggregate the results

Caution should be applied to using Monte Carlo methods if it is found that either (1) the data is not uniformly distributed and (2) only a few MC data points are generated. Using an MC method, the larger the sample size N the better!

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