Reactive Melt Transport in the Mantle and Geochemical Signatures of Mantle-derived Magmas

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Modeling of equilibrium reactive melt transport in the mantle, including the effects of mineralogic reactions and changes in porosity in the solid matrix, provides a series of robust predictions of the consequences of reactive melt transport on magma trace element compositions. The composition of the leading melt batch through a column of reactive mantle (the melt front) will be shifted towards that of an incipient partial melt of the mantle matrix. Successive melt batches migrating through and emerging from the column will show a temporal-compositional trend reflecting exhaustion of the reactive capacity of the mantle, and will eventually return to the original input melt composition. In cases where the melt source and column matrix are similar in composition, the melt front will be enriched in incompatible elements, and the temporal-compositional trend will be one of decreasing incompatible elements in erupted melt batches with time. Cogenetic melt batches should show some type of chromatographic decoupling in trace element and/or isotopic variations. However, mineralogic reaction in the mantle column, in the form of changing matrix mode, can smooth or mask chromatographic effects on trace element abundances, though not on isotopic compositions. Thus lack of chromatographic decoupling in magma trace element abundances alone does not preclude significant melt-mantle reaction. Mineralogic reactions within the column may also impart distinctive trace element variations to melts. In particular, lherzolite-to-dunite reaction in the matrix produces large variations in heavy rare earth elements in emerging melts, whereas lherzolite-to-pyroxenite reaction produces a series of subparallel rare earth element patterns with decreasing overall abundances with time. Although these models assume end-member conditions and maximum extents of melt-mantle reaction, if reactive melt transport is an important petrogenetic process that strongly influences magma trace element compositions these chemical effects should be observed to some extent in carefully chosen sample suites. Certain magma types show chemical characteristics that are broadly similar to these predicted effects, but more complete sample suites yielding detailed temporal-compositional variations of clearly cogenetic lavas are needed to test the petrogenetic significance of reactive melt transport on erupted magmas.

KEY WORDS: melt migration; trace elements; melt-mantle reaction

INTRODUCTION AND BACKGROUND

Basaltic magmas provide some of the best constraints on the composition of the Earth’s mantle and the heterogeneities within it by providing chemical information about their mantle sources (e.g. Weaver, 1991; Hart et al., 1992; Hofmann, 1997). But geochemical compositions of basaltic magmas reflect the compositions of their mantle sources only to the extent that they have not been modified by reaction with the mantle during melt migration and ascent. The problem of melt-mantle reaction is particularly important in ocean-island magmatism, where typically primitive magmas, erupted far from continental crust, are thought to provide the best evidence of oceanic mantle composition. Such inferences require accurate knowledge of processes that could potentially modify magma compositions from melting to eruption, but poorly constrained magma transport velocities and migration path geometries in any given magmatic system prevent confident constraints on probable extents of melt-mantle reaction. Many studies have

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demonstrated the theoretical potential for significant modification of magma geochemical signatures by reactive melt transport (McKenzie, 1984; Richter & McKenzie, 1984; Kelemen, 1986; Richter, 1986; Navon & Stolper, 1987; McKenzie & O’Nions, 1991; Iwamori, 1993a, 1993b; Spiegelman & Elliott, 1993; Kelemen et al., 1995a, 1995b; Lundstrom et al., 1995; Spiegelman, 1996), which could dramatically affect petrogenetic interpretations of mantle source regions and/or melting processes.

Mantle xenoliths and massifs world-wide show clear evidence that migration of melt strongly modifies both major and trace element compositions of solid mantle (Sen, 1988; Bodinier et al., 1990; Sen & Leeman, 1991; Vasseur et al., 1991; Sen et al., 1993; Hauri & Hart, 1994; Godard et al., 1995; Kelemen et al., 1995a; Van der Wal & Bodinier, 1996). In ophiolites and mantle massifs, dunite and harzburgite zones and veins can clearly be shown to be former melt migration channels resulting from dissolution of pyroxenes and precipitation of olivine (Kelemen & Dick, 1995; Kelemen et al., 1995a, 1995b).

Other evidence of melt–mantle reaction comes from both modal and trace element modification of mantle adjacent to dikes and veins of minerals precipitated directly from migrating melts (Irving, 1980; Sen, 1988; Bodinier et al., 1990; Sen & Leeman, 1991). But despite clear evidence that the composition of solid mantle is strongly modified by reaction with migrating melts, it is difficult to relate the compositions of erupted melts to such processes. The question of whether magma compositions are significantly affected by reactive melt transport is a separate and more difficult problem (e.g. Navon et al., 1996; Nelson & Wilsire, 1996).

Primitive, oceanic alkalic basalts provide one clear example of the difficulty in distinguishing between the geochemical effects of mantle source composition and melt–mantle reaction. In general, oceanic alkalic basalts are distinguished from oceanic tholeiites by large enrichments in incompatible elements, a feature that has led many studies to conclude that the source regions for alkalic basalts are correspondingly enriched in incompatible elements relative to the source regions of tholeiites (Gast, 1968; Kay & Gast, 1973; Sun & Hanson, 1975). Radiogenic isotope studies of most alkalic basalts also further constrain this source enrichment to be relatively recent, from 400 my old to just prior to melting (Roden et al., 1984). Thus the source regions of alkalic basalts are commonly thought to be distinct, and have histories that are distinct, from the source regions of typical tholeiitic magmas. Another hypothesis, however, first put forward some decades ago and essentially untested, is that alkalic basalts react with large volumes of solid mantle during melt migration and ascent, essentially leaching incompatible elements from surrounding mantle (Harris, 1957; Green & Ringwood, 1967; Alibert et al., 1983).

The modeling in this paper addresses the problem of reactive melt transport in the mantle from an end-member perspective, seeking robust predictions of the geochemical effects on melt compositions if melt remains in local equilibrium with surrounding mantle, and trace element exchange between the two is highly efficient. These end-member models predict a number of spatial–temporal–compositional patterns that should be evident to some extent in certain types of magmas if reactive transport through the mantle affects melt compositions significantly. These predictions can be used to guide sampling and analytical programs to look for the effects of reactive melt transport on basaltic magmas and thus evaluate its significance in modifying or contributing to magma geochemical signatures.

**MODELING REACTIVE MELT TRANSPORT**

**Mechanisms of trace element exchange**

A complete model of geochemical exchange between migrating melt and solid mantle would need to include the effects of a long list of complex factors. Among these would be variable mechanisms of elemental exchange including dissolution and precipitation of minerals in the solid, diffusion of elements into and out of solid grains, within the melt phase, and along grain boundaries, volatile transfer between melt and solid, and propagation of veins of reacting and differentiating melt. The physical characteristics of the melt–solid system, such as the nature of melt movement (e.g. porous flow vs hydrofracture), melt velocity and distribution (e.g. films vs tubes), solid compaction, and surface area and grain size of reacting solids, are undoubtedly critical to the efficiency and style of element exchange. Kinetic effects, such as rates of elemental diffusion in both the solid and melt, and dissolution and precipitation rates of minerals, bring important temporal considerations to the reaction. Although some models have focused on various aspects of these parameters (Navon & Stolper, 1987; Vasseur et al., 1991; Iwamori, 1993a, 1993b), many of these considerations are difficult to address in a geochemical model of reactive melt transport, and including all of them in a single model would be prohibitively difficult. For these reasons, instead of seeking a detailed model of melt–mantle reaction including as many physical, chemical, and kinetic parameters and variables as possible, it is necessary to adopt simplified end-member approaches to the problem.

The models presented here assume local trace element equilibrium between migrating melt and solid mantle. In this context, melt–solid trace element exchange can be
considered to occur either by diffusion of elements into and out of solid grains (diffusive exchange) or by dissolution and reprecipitation of solid grains (reactive exchange). Mantle xenoliths and massifs show evidence for both mechanisms (Irving, 1980; Bodinier et al., 1990; Hauri & Hart, 1994; Godard et al., 1995), but the modeling presented here makes no assumption about which mechanism generates local melt–solid equilibrium. Nevertheless, it is important to distinguish these two potential mechanisms of exchange. First, they probably occur at different rates. Typical diffusion rates for trace elements in mantle minerals at near-solidus temperatures range from approximately $10^{-11}$ to $10^{-15}$ cm$^2$/s (Hofmann & Hart, 1978; Sneeringer et al., 1984; Hart, 1993). In contrast, dissolution and precipitation rates for typical mantle minerals near equilibrium with melt range from approximately $10^{-7}$ to $10^{-10}$ cm$^2$/s (Brearley & Scarfe, 1986; Edwards & Russell, 1996). Trace element exchange via dissolution and precipitation is generally expected to occur faster than via solid diffusion (Navon & Stolper, 1987; Lundstrom et al., 1995). This is important because reactive exchange may cause melting, crystallization, or mineralogical changes in the mantle matrix, and thus the approach to trace element equilibrium may be accompanied by local modal and porosity changes that can have large effects on compositions of migrating melts.

It should also be recognized that the assumption of local equilibrium in the reactive column implies that melt is flowing through the solid matrix at a velocity that is small relative to the rate of elemental exchange via either diffusive or reactive exchange. This assumption is not intended to imply that melt flows through solid mantle slowly enough to maintain local equilibrium under all circumstances, but it allows considerable simplification while providing important end-member predictions of the effects of melt–mantle reaction. The scenarios modeled here are not intended to capture the full range of possible conditions of melt–mantle reaction, such as might occur under different melt–mantle geometries or as a result of partial diffusive or reactive equilibration relative to melt movement. Nor are these models designed to address whether reactive melt transport is likely to occur in the mantle, given specific melt velocities or geometries (which probably vary significantly with depth and tectonic environment). Rather, the intent is to predict chemical consequences of ideal equilibrium reactive melt transport that may be comparable with actual magma compositions.

Model scenario

The physical scenario envisioned in these models is a one-dimensional column of reactive mantle through which melt flows, from bottom to top. As progressively more melt flows through the column and reacts with the finite volume of solid mantle in it, the solid begins to reach trace element (and mineralogic, in some cases) equilibrium with the incoming melt. As this occurs, the extent of melt–solid reaction and compositional modification of any individual batch of melt flowing through the column decreases. This should generate a sequence of melt compositions emerging from the top of the column that show a progressive decrease in the compositional effects of melt–mantle reaction. The temporal–compositional trend of melt compositions both within and emerging from the top of the column are of the greatest interest, as these could potentially be compared with temporal–compositional trends of actual cogenetic lavas.

To model compositional changes to the melt front (the first melt to emerge from the column) as it reacts with progressively larger volumes of mantle, and to allow for spatial variations in composition, mineralogy, and porosity in the column as a function of integrated melt flux through that portion of the column, two different modeling approaches are used here: a mass-balance incremental method, and a continuum method. The incremental mass-balance method calculates melt and solid compositions during initial melt infiltration into the column up to the time the melt front reaches the top of the column. Resulting (and spatially varying) melt and solid compositions, and matrix mineralogy and porosity, are then used as initial conditions in the continuum method, which calculates melt and solid compositions during continued melt flow and reaction. Although the modeling presented here uses both methods, either method could be used independently to model scenarios constrained to movement of melt one cell per timestep (incremental mass-balance method), or to homogeneous or known initial concentration, mode, and porosity conditions (continuum method).

Mass-balance incremental method

This method assumes an initially solid column of mantle with density $\rho$, and trace element concentration $C_i$, infiltrated with melt from below with density $\rho_f$ and concentration $C_f$. As the melt propagates upwards into the column it establishes porosity $\varphi$ in the column in a way that could be imagined as either melt pushing open voids in the rock or shouldering aside portions of the solid rock on either side; these models make no assumptions about geometry of melt flow or its spatial distribution. In reality, the development of finite porosity that allows for initial melt migration through previously solid mantle is undoubtedly more complicated, and this scenario may be oversimplified. The important point, however, is that the melt encounters some volume of fresh, unreacted solid
as it begins to move through the mantle. As the melt moves, it remains in local trace element equilibrium with the solid so that
\[ C_i = DC_j \]  
(1)

at every point and time in the column, where \( D \) is the bulk solid–melt distribution coefficient. The column is divided up into a series of \( i \) one-dimensional cells, and in each of the \( j \) timesteps melt advances one cell whereas the solid remains stationary. The concentration of an element in the melt in cell \( i \) and timestep \( j \) is (Appendix A)
\[ C_j = \frac{\rho \phi C_{i-1} + \rho (1 - \phi) C_{i+1}}{\rho \phi^j + \rho (1 - \phi)^j D_i}. \]  
(2)

Similar approaches were taken by Vollmer (1987) and Liang & Elthon (1990) in modeling metasomatic processes. This method allows for temporally and spatially varying \( \phi \) and \( D \) in the reactive column to simulate changing porosity and mode via dissolution and re-precipitation.

Continuum method

The continuum method requires the assumption of a column of solid mantle with pre-existing porosity \( \phi \), and ratio of solid to melt densities \( \rho \), that is filled with melt in local equilibrium with the solid with bulk distribution coefficient \( D \) (although \( D \), \( \phi \), and composition can vary within the column). Melt flows through the column, and new melt enters the column from the bottom, with a velocity \( v_f \). The concentration of a trace element in the melt \( C_i \) at any point and timestep in the column is (Appendix B)
\[ \frac{\partial C_i}{\partial t} + \frac{\partial j}{\partial x} \frac{\partial C_i}{\partial t} = \rho C_j. \]  
(3)

This equation was used by Godard et al. (1995) and Van der Wal & Bodinier (1996) for modeling trace element effects of recrystallization fronts on residual solid in mantle masses. The first term on the left side accounts for diffusive exchange of the trace element between the solid and melt, the second term for advection of the trace element through the column, and the right side accounts for reactive exchange of the element caused by dissolution and precipitation (changes in \( \phi \) and \( D \)). If \( \phi \) and \( D \) do not change during melt flow then the right side of equation (3) becomes zero, and this equation is equivalent to equation (1b) of Navon & Stolper (1987).

Model procedure and parameters

These models are designed to avoid most assumptions implying particular melt–solid geometries or time- and length-scales. Important parameters that must be specified include the initial melt composition (determined by composition, mineralogy, and degree of melting of the melt source), and matrix composition, porosity \( (\phi) \), and mineralogy (which determines \( D \)). In addition, the type and rate of mineralogic reactions occurring in the column matrix must be imposed, and the number of cells in the column specified. The examples shown here can be divided into two groups that are distinguished by the relative concentrations of incompatible elements in the initial melt source and column matrix.

In the first set of models, the melt source has incompatible element concentrations identical to those of the column matrix, and both are assumed to be garnet lherzolite (Table 1). The initial melt, a 5% non-modal batch melt of the source, migrates through and reacts with matrix with an initial \( \phi \) of 0.05. Parameters for the second set of models are identical except that the initial melt is highly incompatible element enriched (0.1% melt of source) and the column matrix is highly incompatible element depleted (assumed to be a 2% non-modal fractional melting residue of the same melt source composition) (Table 1).

In all models, the column matrix has an initial porosity of 0.05, and a total length of 30 cells \( [i = 1–30 \text{ in equation (2)}] \). Because local equilibrium between melt and solid is assumed, these choices determine the total volume of solid mantle with which the melt reacts, relative to the melt volume (the volume ratio of solid to melt is \( n / (1 - \phi) \), where \( n \) is the number of cells). The procedure models make no assumptions about the absolute dimensions of the column, however. Porosity was specified as 0.05, and the column was divided into 30 cells simply because these values serve to illustrate the main features of the model with reasonable computational expense. Either larger porosity or a smaller number of cells (shorter column length) results in smaller compositional changes to the melt front, as discussed below, but these specific values are not critical to the overall results.

The actual length of the column and the melt velocity could be a range of values, as long as the melt moves one cell per timestep in both the incremental mass-balance method and the finite-difference method used to solve equation (3) (i.e., \( \nu Dt / \Delta x = 1 \)). As an example, one could specify that \( \nu = 5 \text{ m/yr} \), \( Dt = 20 \text{ years} \), and \( \Delta x = 100 \text{ m} \), which would yield a total column length of 3 km in a 30-cell calculation. As long as \( \nu Dt / \Delta x = 1 \), and local equilibrium between the melt and solid is assumed, the chemical consequences of reactive melt transport are not sensitive to the absolute scale of the
### Table 1: Parameters used in reactive transport modeling

#### Modal proportions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Melt source</th>
<th>Source melting mode</th>
<th>Lherzolite matrix</th>
<th>Pyroxenite</th>
<th>Dunite</th>
<th>Densities (kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>olivine</td>
<td>0.65</td>
<td>0.10</td>
<td>0.65</td>
<td>0.10</td>
<td>1.00</td>
<td>2800</td>
</tr>
<tr>
<td>orthopyroxene</td>
<td>0.24</td>
<td>0.10</td>
<td>0.24</td>
<td>0.00</td>
<td>0.00</td>
<td>solid</td>
</tr>
<tr>
<td>clinopyroxene</td>
<td>0.06</td>
<td>0.40</td>
<td>0.06</td>
<td>0.75</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>garnet</td>
<td>0.05</td>
<td>0.40</td>
<td>0.05</td>
<td>0.15</td>
<td>0.00</td>
<td>3300</td>
</tr>
</tbody>
</table>

#### Distribution coefficients*

<table>
<thead>
<tr>
<th>Element</th>
<th>olivine/liq</th>
<th>opx/liq</th>
<th>cpx/liq</th>
<th>garnet/liq</th>
<th>Lherzolite bulk</th>
<th>Pyroxenite bulk</th>
<th>Dunite bulk</th>
<th>Melt source bulk D</th>
<th>Melt source bulk P</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.00046</td>
<td>0.00125</td>
<td>0.0370</td>
<td>0.0070</td>
<td>0.0032</td>
<td>0.0288</td>
<td>0.0005</td>
<td>0.0032</td>
<td>0.0178</td>
</tr>
<tr>
<td>Ce</td>
<td>0.00066</td>
<td>0.00195</td>
<td>0.0690</td>
<td>0.0210</td>
<td>0.0061</td>
<td>0.0590</td>
<td>0.0007</td>
<td>0.0061</td>
<td>0.0363</td>
</tr>
<tr>
<td>Nd</td>
<td>0.00115</td>
<td>0.00435</td>
<td>0.0150</td>
<td>0.0087</td>
<td>0.0151</td>
<td>0.1257</td>
<td>0.0012</td>
<td>0.151</td>
<td>0.0954</td>
</tr>
<tr>
<td>Sm</td>
<td>0.00180</td>
<td>0.00640</td>
<td>0.0200</td>
<td>0.0170</td>
<td>0.0054</td>
<td>0.1827</td>
<td>0.0016</td>
<td>0.0254</td>
<td>0.1676</td>
</tr>
<tr>
<td>Eu</td>
<td>0.00175</td>
<td>0.00830</td>
<td>0.0250</td>
<td>0.0232</td>
<td>0.0044</td>
<td>0.2244</td>
<td>0.0018</td>
<td>0.0332</td>
<td>0.2230</td>
</tr>
<tr>
<td>Tb</td>
<td>0.00170</td>
<td>0.01245</td>
<td>0.0250</td>
<td>0.0725</td>
<td>0.0653</td>
<td>0.2964</td>
<td>0.0017</td>
<td>0.0553</td>
<td>0.3914</td>
</tr>
<tr>
<td>Ho</td>
<td>0.00180</td>
<td>0.01745</td>
<td>0.0252</td>
<td>1.4650</td>
<td>0.0938</td>
<td>0.4093</td>
<td>0.0018</td>
<td>0.0938</td>
<td>0.6889</td>
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<tr>
<td>Yb</td>
<td>0.00275</td>
<td>0.03880</td>
<td>0.2400</td>
<td>4.0300</td>
<td>0.2270</td>
<td>0.7848</td>
<td>0.0028</td>
<td>0.2270</td>
<td>1.7122</td>
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<tr>
<td>Lu</td>
<td>0.00315</td>
<td>0.04000</td>
<td>0.2350</td>
<td>5.6000</td>
<td>0.3079</td>
<td>1.0166</td>
<td>0.0032</td>
<td>0.3079</td>
<td>2.3392</td>
</tr>
<tr>
<td>Ba</td>
<td>0.00030</td>
<td>0.00015</td>
<td>0.0007</td>
<td>0.0001</td>
<td>0.0003</td>
<td>0.0006</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.0004</td>
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<tr>
<td>Zr</td>
<td>0.00100</td>
<td>0.00100</td>
<td>0.2000</td>
<td>0.3000</td>
<td>0.0301</td>
<td>0.1951</td>
<td>0.0010</td>
<td>0.0301</td>
<td>0.2011</td>
</tr>
<tr>
<td>Sc</td>
<td>0.02500</td>
<td>1.1000</td>
<td>3.1000</td>
<td>6.5000</td>
<td>0.9375</td>
<td>3.3250</td>
<td>0.2500</td>
<td>0.9375</td>
<td>3.9750</td>
</tr>
</tbody>
</table>

#### Compositions (ppm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Chondrite#</th>
<th>Melt source±</th>
<th>5% source melt</th>
<th>0-1% source melt</th>
<th>Matrix a†</th>
<th>Matrix b§</th>
<th>C_i/D, lherzolite (matrix a)</th>
<th>C_i/D, lherzolite (matrix b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.370</td>
<td>0.206</td>
<td>3.94</td>
<td>49.70</td>
<td>0.206</td>
<td>0.0026</td>
<td>65.14</td>
<td>0.08</td>
</tr>
<tr>
<td>Ce</td>
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<td>0.722</td>
<td>13.30</td>
<td>102.50</td>
<td>0.722</td>
<td>0.022</td>
<td>118.74</td>
<td>3.65</td>
</tr>
<tr>
<td>Nd</td>
<td>0.720</td>
<td>0.815</td>
<td>13.50</td>
<td>50.79</td>
<td>0.815</td>
<td>0.203</td>
<td>53.83</td>
<td>13.39</td>
</tr>
<tr>
<td>Sm</td>
<td>0.230</td>
<td>0.299</td>
<td>4.46</td>
<td>11.39</td>
<td>0.299</td>
<td>0.131</td>
<td>11.76</td>
<td>5.16</td>
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<tr>
<td>Eu</td>
<td>0.087</td>
<td>0.115</td>
<td>1.60</td>
<td>3.38</td>
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<td>Tb</td>
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<td>0.077</td>
<td>0.90</td>
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<td>0.053</td>
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<tr>
<td>Ho</td>
<td>0.087</td>
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<td>1.42</td>
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<tr>
<td>Lu</td>
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<td>0.054</td>
<td>0.22</td>
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<td>0.054</td>
<td>0.051</td>
<td>0.18</td>
<td>0.17</td>
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<tr>
<td>Ba</td>
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<td>4.0</td>
<td>79.59</td>
<td>n/a</td>
<td>4.0</td>
<td>n/a</td>
<td>14386.49</td>
<td>n/a</td>
</tr>
<tr>
<td>Zr</td>
<td>n/a</td>
<td>7.0</td>
<td>100.01</td>
<td>n/a</td>
<td>7.0</td>
<td>n/a</td>
<td>232.95</td>
<td>n/a</td>
</tr>
<tr>
<td>Sc</td>
<td>n/a</td>
<td>16.9</td>
<td>21.43</td>
<td>n/a</td>
<td>16.9</td>
<td>n/a</td>
<td>18.03</td>
<td>n/a</td>
</tr>
</tbody>
</table>

*REE: average of McKenzie & O’Nions (1991) and Frey et al. (1977, set 3); others: Green (1994).
§Depleted matrix (residue of 2% fractional melting matrix a).
problem, and the time- and length-scales could take on any specific values that might be appropriate.

Mineralogic reaction
Models that involve mineralogic reaction in the mantle matrix employ two different end-member reactions, guided by evidence from mantle massifs and xenoliths, and by thermodynamic simulations using the MELTS thermodynamic software package (Ghiorso & Sack, 1995). All the simulations use garnet lherzolite as the initial mineralogy of the solid mantle (Table 1), with a progressive change in modal proportions to one of two end-member product mineral assemblages as melt continues to flow through the matrix.

One of the mineralogic reactions used here is melt + lherzolite → melt + dunite. Studies of ophiolites indicate that mid-ocean ridge basalts (MORB) are in equilibrium with dunite (Kelemen et al., 1995a, 1995b), and several studies have shown that this is because melts under mid-ocean ridges migrate upwards through lherzolite and harzburgite by dissolving pyroxene and crystallizing olivine. This results in formation of porous dunite channels through which subsequent melts migrate (Kelemen & Dick, 1993; Kelemen et al., 1995a, 1995b). Thus, under some conditions, reaction of migrating basaltic melt with a lherzolite matrix results in a residual matrix that is depleted in pyroxenes and enriched in olivine relative to the initial matrix mode. Thermodynamic studies and evidence from ophiolites suggest that this reaction is often accompanied by an increase in the melt mass, especially under conditions of adiabatic upwelling, because more pyroxene is dissolved by the melt than olivine is precipitated (Kelemen et al., 1995a, 1995b). This can be simulated in a simplified way by imposing an increase in porosity accompanying the lherzolite-to-dunite reaction (although in reality compaction and permeability factors probably also control porosity, so this is somewhat of an oversimplification).

A second mineralogic reaction used here is that of melt + lherzolite → melt + pyroxenite. Two primary lines of evidence suggest that under some conditions melt–mantle reaction results in precipitation of a residue with greater modal proportion of pyroxene than the initial mantle matrix. Composite xenoliths, which most commonly contain veins and dikes of pyroxenite enclosed by lherzolite, indicate that alkalic magmas flow through the mantle they react with surrounding lherzolite and precipitate primarily clinopyroxene ± garnet or spinel (Irving, 1980; Sen, 1988; Sen & Leeman, 1991; Sen et al., 1993). Mantle massifs also suggest similar relations (Bodinier et al., 1990; Pearson et al., 1993; Kelemen & Dick, 1995; Kelemen et al., 1995b). Thermodynamic modeling using MELTS also shows that because of the increased stability of pyroxenes and decreased stability of olivine at higher mantle pressures, higher pressures of melt–mantle reaction increase the proportion of pyroxene in the residual mantle matrix. Decreasing magma mass, caused by cooling during this reaction, also increases the amount of pyroxene precipitated during reaction with mantle, and can be simulated in a simplified way by decreasing porosity during the modal change (although again, in reality porosity changes attending a specific mineralogic reaction are probably also a strong function of compaction and permeability issues).

Models presented here that include changes in matrix mode using a changing bulk distribution coefficient of the matrix, from an initial mineralogic assemblage with \( D_a \), to a final assemblage, with \( D_f \) to represent the effects of changing mineralogy on trace element evolution. This modal change in any cell of the column is assumed to be proportional to the total melt flux through it; as more melt flows through a particular cell, the greater the cumulative modal change in that cell. For these models, the matrix \( D \) in each cell is a function of a reaction rate factor \( r \) and the difference between the \( D \) in the same cell in the previous timestep and \( D_j \):

\[
D^t = D^{t-1} + r(D_j - D^{t-1})
\]

where \( D^t \) and \( D^{t-1} \) are \( D \) in the same cell in the current and previous timesteps, respectively. For the purposes of generalizing mineralogic reaction effects on reactive melt transport, \( r \) has been imposed as 0.05 in the models presented here (Fig. 1). The translation of this \( r \) value to an absolute rate of dissolution or precipitation depends on the absolute length- and time-scales chosen for the model. For example, if the timestep is assumed to be 20 years (as in above example with \( v_\ell = 5 \) m/yr, \( \Delta t = 20 \) years, and \( \Delta x = 100 \) m), then this would correspond to a modal change of 5% (and progressively less as the integrated melt flux increases), in each cell every 20 years. Assuming this means 5% dissolution or growth of a grain ~1 cm in diameter, this would imply dissolution and precipitation rates of about \( 10^{-10} \) cm/s, in the range of typical measured values (Brearley & Scarfe, 1986; Edwards & Russell, 1996). A slightly different scenario is used for changes in \( \phi \) (relative masses of solid and melt) resulting from melt–solid reaction. To conserve mass within the column in simulations involving \( \phi \) change, it changes at a uniform rate in all cells of the column [replace \( D \) with \( \phi \) in equation (4)].

RESULTS: EXAMPLES OF REACTIVE MELT TRANSPORT EFFECTS ON MELT COMPOSITIONS
The effects of reactive melt transport on melt compositions are sensitive to the initial compositional contrast
between the melt and the column matrix; specifically, the relative magnitudes of \( C_f \) and \( C_s^0/D \) (the concentration of an element in the initial melt, and the concentration in the column matrix divided by its bulk distribution coefficient). Because of this, the results of these models have been divided into two groups: (1) those in which the melt source and column matrix have the same composition (for which \( C_f \) will always be less than \( C_s^0/D \)), and (2) those in which the melt is a very small-degree melt of a source enriched in incompatible elements relative to the column matrix (\( C_f > C_s^0/D \)).

**Results for \( C_f < C_s^0/D \)**

**Temporal-compositional trends**

Figure 2 shows the evolution of Zr concentration in the melt in reactive mantle columns under varying conditions, for identical melt source and column matrix compositions (melt source and matrix a, Table 1), so that \( C_f < C_s^0/D \). Figure 2a shows Zr concentrations in the leading batch of melt (melt front) and throughout the column (\( z/Z \) is position in column normalized to the total column length) at various time intervals for conditions of constant mineralogy (garnet lherzolite, \( D = 0.03005 \)) and porosity (\( \varphi = 0.05 \)). As the melt front (bold line) infiltrates the column and reacts with progressively more mantle, Zr concentrations in the melt front increase by more than a factor of two. The increase slows with time because Zr concentrations approach a limiting, or steady-state value, \( C_s^0/D \), which is purely a characteristic of the solid matrix. \( C_s^0/D \) is also equivalent to the concentration in an incipient partial melt of the matrix. Another important feature of Fig. 2a is that Zr concentrations are high near the melt front, but low and essentially equal to those of the initial input melt just behind it. A steep Zr concentration gradient forms in the column, ahead of which melt is in equilibrium with the initial solid matrix (Zr concentration = \( C_s^0/D \)), and behind which melt has the original input concentration. This chromatographic effect (e.g. Hofmann, 1972; McKenzie, 1984; Navon & Stolper, 1987) causes the concentration front to propagate through the column at a velocity less than that of the melt. Navon & Stolper (1987) showed that in the case of constant \( \varphi \) and \( D \), concentration front (or any point of constant concentration in the column) velocity is given by

\[
\left( \frac{\partial z}{\partial t} \right)_o = \frac{\varphi \rho_p}{\varphi \rho_p + (1 - \varphi) \rho \bar{D}}
\]

Thus the velocity of a trace element concentration front, and the average velocity of the trace element, is inversely proportional to its bulk distribution coefficient.

It should be noted that analytic solutions to a continuum approach to the simple case of constant \( \varphi \) and...
D would result in a series of sharp concentration fronts with infinite width in Fig. 2a [e.g. fig. 1 of Navon & Stolper (1987)]. The finite widths of the smoothed concentration fronts in these examples (Fig. 2a, b) are an inevitable result of the finite approximations inherent to both the incremental mass-balance method and the finite-difference solution used in the continuum method to solve equation (3), but they do not affect the overall results of the calculations (i.e. the finite method solutions shown here adequately approximate and reproduce the important features of the analytic solutions for the constant φ and D case, and they allow solution to the cases of varying φ and D).

Figure 2b shows Zr concentration in melt emerging from the column with time (t/tc is time normalized to time required for melt to flow through the entire column). Melt batches emerging from the column before t/tc ~1.5 have high Zr concentrations, near the limiting Cs/D.
value. Between $t/t_c \sim 1.5$ and 2, the steep Zr concentration front emerges from the column, and Zr in emerging melt batches decreases. Zr in all successive melt batches is essentially at the concentration of the original source melt (100 ppm). After this time, the capacity of the mantle matrix to exchange Zr with the melt is exhausted and the column matrix has come into equilibrium with the input melt.

Figure 2c–f shows the effects of reactive transport with mineralogic reaction from lherzolite to dunite and lherzolite to pyroxenite ($r = 0.05$), at constant porosity. As before, because $C_s < C_s^0/D$, Zr concentrations in the melt front increase to $C_s^0/D$. Behind the melt front, however, Zr concentrations either increase or decrease, as $D$ changes as a result of mineralogic reaction ($D_{Dunite}^Zr = 0.001$, $D_{Pyroxenite}^Zr = 0.1951$), and Zr is partitioned from solid to melt, or melt to solid. Continued influx of fresh input melt at the entrance of the column brings Zr concentrations back to the initial input concentrations. The combination of these effects is the propagation of hump- or trough-shaped concentration fronts, for lherzolite-to-dunite and lherzolite-to-pyroxenite reactions, respectively (Fig. 2c–f). Emerging melts in the case of the lherzolite-to-dunite reaction show a transient rise in Zr concentration, reflecting partitioning of Zr from solid to melt (Fig. 2d), whereas in the case of the lherzolite-to-pyroxenite reaction they show a transient drop (even below those of the input melt), reflecting crystallization of pyroxene and garnet in the column matrix (Fig. 2f). In the pyroxenite case, Zr concentrations in emerging melts do not reach input melt concentration until $t/t_c \sim 8$ because of the increased compatibility of Zr and resulting decrease in velocity of the Zr concentration fronts.

Figure 2g–j shows that relative to mineralogic changes, porosity changes in the column have little effect on melt compositions. Increasing $q$ in the column has the effect of diluting concentrations of incompatible elements behind the melt front, opposing the effect of increasing Zr caused by the lherzolite-to-dunite reaction, whereas decreasing $q$ results in increased Zr concentrations behind the melt front, opposing the effect of decreased Zr caused by the lherzolite-to-pyroxenite reaction. In both cases, however, the modal change in the column dominates the spatial-temporal-compositional patterns observed.

**Rare earth element patterns**

Figure 3 shows rare earth element (REE) patterns (normalized to chondrites; Table 1) of melts emerging from reactive columns for the same examples as shown in Fig. 2. In the case of constant mineralogy and porosity (Fig. 3a), the first melt to emerge from the column (the melt front) is strongly enriched in the light rare earth elements (LREE) and slightly depleted in the heavy rare earth elements (HREE), relative to the original input melt, and is closest to the limiting $(C_s^0/D)$ composition. Successive batches of melt to emerge from the column have decreasing LREE as the reactive capacity of the solid is exhausted and emerging melts return to the original input composition. However, it is the most incompatible elements (those with lowest $D$—the lightest REE) that return to their concentrations in the original melt first, followed by progressively less incompatible elements (heavier REE). This results in the transient LREE-depleted patterns of melts that emerge before the melt compositions finally return to the input melt pattern (Navon & Stolper, 1987).

Figure 3b shows REE concentrations of melts emerging from the column in the case of the lherzolite-to-dunite reaction at constant porosity. As in the constant mode case, the first melt to emerge from the column is strongly LREE enriched, and successive melt batches have lower REE concentrations. But the middle REE (MREE) and HREE show a different behavior. These elements are enriched in the melt behind the melt front as a result of the mineralogic reaction, and, as in the case of Zr, develop hump-shaped concentration fronts that propagate at velocities that are progressively lower from the LREE to HREE. These hump-shaped concentration fronts emerge in succession, producing distinctive MREE-enriched, followed by HREE-enriched patterns, before all REE concentrations finally return to those of the input melt.

Figure 3c shows REE concentrations of melts emerging from the column in the case of the lherzolite-to-pyroxenite reaction at constant porosity. Conversion of lherzolite to pyroxenite increases the modal abundance of pyroxenes and garnet in the column, removing MREE and HREE from the melt. This results in LREE-enriched patterns of all the emerging melts, and a sequence of mostly parallel patterns with decreasing overall abundances. This magnitude of this effect is somewhat sensitive to the modal fraction of garnet in the pyroxenite mode (here 15%; Table 1), although the same general effect is observed for pure clinopyroxenite mode, and even a small fraction of garnet causes a rapid depletion in MREE and HREE. REE concentrations decrease with time to values below those of the initial input melt, reflecting the removal of REE into the matrix, until $t/t_c \sim 1.3$, when concentrations of progressively heavier REE begin to increase again to those of the initial input melt. Because of the decreased velocity of the concentration fronts as a result of decreased $D$, the MREE and HREE do not recover initial input melt concentrations until fairly high $t/t_c (>8)$. One noteworthy feature of the REE patterns of the lherzolite-to-pyroxenite reaction model is the La depletions observed in melts emerging after $t/t_c \sim 1.1$, caused...
Fig. 3. REE evolution of model melts (concentrations normalized to chondrites; Table 1) emerging from reactive mantle columns under conditions of equilibrium exchange with different types of mineralogic reactions. Here the melt source and the column matrix have the same composition (matrix a in Table 1), so $C_0 = C_0/D$. The initial input melt [middle bold line in (a)] is a 5\% batch, non-modal melt of the melt source [lower bold line in (a)]. The first melt to emerge in all cases is strongly LREE enriched relative to the initial input melt, and melts emerging at later times show generally decreasing REE concentrations (back to the input melt composition), although in the cases of the lherzolite-to-dunite reactions MREE and HREE show transient increases, and in the cases of lherzolite-to-pyroxenite reactions all REE decrease to values below those of the input melt before returning to the initial input concentrations. REE patterns are shown for melts emerging at $t/t_c = 1.0$ (melt front), 1.1, 1.17, 1.23, 1.3, 1.5, 1.7, 1.8, 2.0, 2.3, 2.7, 3.0, and 4.0. Distribution coefficients for the REE are shown in Table 1. REE not explicitly modeled here are Pr, Gd, Dy, and Er, and are shown as weighted averages of surrounding elements, so as to represent smoothed patterns. (a) Simple equilibrium exchange, no change in column mode or $\phi$. (b) Equilibrium exchange with reaction from lherzolite to dunite, with constant $\phi$. (c) Equilibrium exchange with reaction from lherzolite to pyroxenite, with constant $\phi$. (d) Equilibrium exchange with reaction from lherzolite to dunite, with increasing $\phi$ (0.05 to 0.1). (e) Equilibrium exchange with reaction from lherzolite to pyroxenite, with decreasing $\phi$ (0.05 to 0.01). The unusual, crossing LREE patterns in the lherzolite to pyroxenite models (c and e) in the latest timesteps (near $t/t_c = 4.0$) patterns with lowest overall REE concentrations) are caused by La and Ce increasing to the concentrations of the initial input melt before other, more compatible elements.
by the significantly higher velocity of the La concentration front (and lower \( D \)) compared with other REE.

Figure 3d and e shows that porosity changes in the column have a minor effect on REE patterns of emerging melts compared with mineralogic changes. REE patterns of emerging melts are dominated by mineralogic changes within the column, especially the dissolution or precipitation of the major REE-bearing phases clinopyroxene and garnet.

**Results for \( C_f > C^0_r / D \)**

**Temporal–compositional trends**

Figure 4 shows the evolution of melt Zr concentrations for cases involving highly incompatible element enriched melt (0–1% non-modal batch melt of the melt source; Table 1) and highly incompatible element depleted matrix (the solid residue of 2% fractional melting of matrix \( a \); Table 1). In these examples, \( C_f > C^0_r / D \), so Zr concentrations in the melt front decrease, partitioning Zr from the melt to the matrix, as the melt front reacts with progressively larger volumes of mantle. Figures 4a and 4b are essentially mirror images of Figs 2a and 2b, with a series of propagating concentration fronts of opposite sense. Sequences of melts emerging from the column show the opposite trend in Fig. 4b, with increasing Zr as the reactive capacity of the column is exhausted. Figure 4c–f shows that the overall spatial and temporal patterns of melt compositions produced by the mineralogic reactions in the column are not changed by the relative compositions of melt and matrix (compare with Fig. 2c–f). Mineralogic reaction from lherzolite to dunite still results in a series of hump-shaped concentration fronts and a transient rise in Zr concentrations in emerging melts (Fig. 4c and d), and reaction from lherzolite to pyroxenite results in trough-shaped concentration fronts, and a transient decrease in Zr concentrations in emerging melts (Fig. 4e and f).

**REE patterns**

Figure 5 shows REE concentrations of melts emerging from reactive columns for the same examples as shown in Fig. 4 (\( C_f > C^0_r / D \)). In these examples, the melt front has a LREE-depleted pattern, closest to the strongly LREE-depleted \( C^0_r / D \) composition of the matrix. Sequences of emerging melts in the case of constant mode and porosity (Fig. 5a) have increasing REE concentrations, with progressively heavier REE increasing in succession, resulting in overall LREE-enriched patterns. Emerging melts in the case of lherzolite-to-dunite reaction (Fig. 5b) are broadly similar to the \( C_f < C^0_r / D \) case (Fig. 3b), showing large variation in HREE concentrations, but in this case melts emerging after \( /t_f = 1-1 \) are all LREE enriched. Emerging melts in the case of the lherzolite-to-pyroxenite reaction (Fig. 5c) initially show increasing LREE simultaneously with decreasing MREE and HREE, because of crystallization of pyroxene and garnet, but eventually all the REE increase to the original input melt concentrations, in progression from LREE to HREE.

**DISCUSSION: KEY FEATURES OF REACTIVE MELT TRANSPORT**

Identifying key features or predictions of these models that are potentially observable in real lavas is the first step to constraining the actual significance of reactive melt transport in magmatogenesis. Although real magma compositions are complicated by variations in source composition and degree of partial melting, as well as mixing of time-integrated melt batches, if reactive melt transport exerts a significant control on their geochemical signatures, some of these effects should be evident. Three particularly robust effects of reactive melt transport on melt compositions are: (1) enrichment, or under certain conditions depletion, of incompatible elements in the melt as it infiltrates and equilibrates with fresh, unreacted mantle, resulting in a compositional shift towards \( C^0_r / D \) of the matrix, (2) chromatography, by which concentration fronts of elements in the melt propagate at different velocities causing unusual co-variations of trace element abundances and REE patterns, (3) mineralogic reaction effects, by which changing mineralogy in the column matrix adds elements to or removes elements from the melt and imparts characteristic trace element patterns to emerging melts.

**The melt front and zone-refining–AFC**

One of the most robust features of these and previous models is that regardless of initial melt composition, the melt front approaches the composition of an incipient partial melt of the column matrix—\( C_f \) is always shifted towards \( C^0_r / D \) in the first melt to emerge from the column (Navon & Stolper, 1987). In cases in which the melt source and column matrix compositions are the same, this will always result in an increase in incompatible elements in the melt front. This is the zone-refining process (e.g. Pfann, 1952; Harris, 1957; DePaolo, 1981), and has been widely invoked to explain incompatible element enriched magmas (Harris, 1957; Green & Ringwood, 1967; Alibert, 1983; Navon & Stolper, 1987), especially in cases where isotopic compositions do not indicate a long-term enrichment in incompatible elements in the mantle source. In the case of constant mode and porosity, the concentration of an element in a zone-refining process (Pfann, 1952; Harris, 1957; DePaolo, 1981) can be expressed as
Evolution of Zr concentration in 0.1% depleted mantle melt migrating through, and reacting with, a column of highly depleted lherzolite (matrix b in Table 1). In this case $C_f > C_s/D$, and incompatible elements are initially transferred from the melt to the matrix. Porosity ($\phi$) in the column is 0.05. (See text and Table 1 for details.) In each example, the first plot shows Zr concentration in melt front (bold line) and everywhere in the column at various times, and the second plot in each example shows the Zr concentration in melt emerging from the top of the column at various times. Symbols and axes as in Fig. 2. Besides the fact that Zr increases, instead of decreases, from the Cs0/D melt front composition to the input melt composition in (b), the general shapes of concentration fronts and temporal–compositional trends in emerging melts are similar to the cases where $C_f < C_s/D$ (Fig. 2).

$$C_f = C_f^0 \exp\left(-\frac{\rho_f V_f}{\rho_f V_f + \rho_f V_f} D\right) + C_f^0 \left[1 - \exp\left(-\frac{\rho_f V_f}{\rho_f V_f} D\right)\right]$$

where $C_f^0$ is the initial concentration in the original melt and $V_f$ and $V_f$ are the volumes of solid and melt, respectively. Compatible elements (those with larger $D$) approach the limiting $C_s^0/D$ concentration faster than incompatible elements (smaller $D$). Figure 6 shows that this can generate large enrichments in highly incompatible elements (e.g. La, Ba), but large volumes of solid are required to reach this limiting concentration, whereas more compatible elements (e.g. Zr, Sc) reach it at much smaller volumes.

If the melt composition is highly enriched in incompatible elements relative to the column matrix, or the column matrix has a modal mineralogy with a high $D$ ($C_f > C_s^0/D$), this process results in a transfer of incompatible elements from the melt to the solid, depleting the melt, and enriching the solid in incompatible elements. This is how metasomatic effects on xenoliths and massifs are typically envisioned (Navon & Stolper, 1987; Vollmer, 1987; Bodinier et al., 1990; Liang & Elthon, 1990; Hauri & Hart, 1994). It should be emphasized, however, that if the column matrix is typical peridotite, this situation requires both that the melt source has higher incompatible element concentrations than the solid column matrix, and either the melt was derived by a small degree of melting, or incompatible elements were concentrated in the initial melt by some other fractionation mechanism. In general, if the original melt and solid column matrix are similar in composition, then melt–mantle reaction will result in enrichment of the melt, and depletion of the solid, in incompatible elements.

In the case of changing $\phi$, trace element effects on the melt front are not equivalent to those of zone-refining, but assimilation–fractional crystallization (AFC; e.g. DePaolo, 1981). For incompatible elements, reaction (i.e. assimilation) combined with decreasing porosity (i.e. crystallization) drives concentrations to values higher than the limiting $(C_s^0/D)$ concentrations. Reaction combined with increasing porosity (i.e. melting) drives concentrations to values lower than the limiting $(C_s^0/D)$ concentrations.

Chromatographic effects
Although dramatic in their capacity to enrich the melt front in incompatible elements, the trace element effects of zone-refining or AFC on the melt front do not provide
Fig. 5. REE evolution of model melts emerging from reactive mantle columns for cases in which the matrix is highly incompatible element depleted (matrix b—the residue of 2% fractional melting of matrix a) and the melt is highly incompatible element enriched (0.1% melt of source), so that \( C_i > C_{i/D} \) (Table 1). The first melt to emerge in each case (melt front) is strongly LREE depleted relative to the initial input melt (upper bold line), because of reaction with the strongly LREE-depleted matrix [lower bold line in (a)]. La and Ce concentrations in the melt front are not at the limiting \( C_{i/D} \) concentrations, however, because of the larger volumes of mantle required for these most incompatible elements to reach the \( C_{i/D} \) concentrations. Melts emerging subsequent to the melt front generally show increasing REE concentrations, back to the input melt composition, although in the case of the lherzolite-to-duntile reaction MREE and HREE show transient increases (as in the \( C_i < C_{i/D} \) case, Fig. 3), and in the case of lherzolite-to-pyroxenite reaction, the MREE and HREE initially decrease to concentrations lower than those of the input melt as the LREE increase. REE patterns of melts emerging at the same times \( (t/t_c) \) as in Fig. 3 are shown.
patterns of some of the model melts (Figs 2 and 5), another important effect is chromatography, or the decoupling of abundances of trace elements with varying degrees of compatibility in emerging melt batches.

In cases of \( C_0 < C_{\text{th}} / D \) and either constant mode and porosity or the lherzolite-to-dunite reaction (Fig. 3a, b), sequences of emerging melts show distinct depletions in LREE relative to MREE and HREE (Navon & Stolper, 1987). Such chromatographic decoupling should be evident in REE patterns or in plots of LREE vs HREE for sequences of erupted magmas, if melt mixing does not obscure them. In cases where \( C_0 > C_{\text{th}} / D \) such decoupling is less pronounced in REE patterns, as LREE return to the original input melt concentrations rapidly (Fig. 5a, b), but chromatographic decoupling should still be evident in plots of LREE vs HREE.

In cases of lherzolite-to-dunite reaction (Figs 3b and 5b), the chromatographic effect is evident in large variations of HREE, regardless of the relative compositions of the input melt and column matrix. This reflects the fact that increases in HREE caused by dissolution of pyroxene and garnet in the matrix take longer than LREE and patterns of some of the model melts (Figs 2 and 5), another important effect is chromatography, or the decoupling of abundances of trace elements with varying degrees of compatibility in emerging melt batches.

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Mineralogic reaction: changes in \( D \) and \( \Phi \)

Mineralogic reaction within the mantle column has several important effects on trace element concentrations of emerging melts. First, reactive exchange of elements caused by either changing \( D \) or \( \Phi \) acts as a source or sink of elements within the column, and produces the characteristic hump- or trough-shaped concentration fronts that are observed as transient increases or decreases in element concentrations in emerging melts (Figs 2 and 4). Second, regardless of relative melt and matrix compositions, reaction from lherzolite to dunite in the column generates a large variation in HREE relative to other REE in emerging melts (Figs 3 and 5). This appears to be a robust and characteristic feature of this particular mineralogic reaction that is not strongly modified by varying other parameters of the model. One of the particularly important feature of the mineralogic reaction models is the strong correlation of incompatible element concentrations in emerging melt batches in the case of the lherzolite-to-pyroxenite reaction and \( C_0 < C_{\text{th}} / D \) (Fig. 3c, e). In these cases, elemental variations in emerging melts are dominated by the mineralogic reaction in the column, not the arrival of propagating concentration fronts. This also appears to be a robust feature of lherzolite-to-pyroxenite models, not strongly affected by variation of other model parameters. Thus the REE
chromatographic effect can be masked by mineralogic reaction. The only REE that does show chromatographic decoupling in these examples is La, which shows depletions relative to the other REE in some of the emerging melt batches; this is discussed further below.

One final note regarding mineralogic reaction is that it imparts a strong geochemical signature of the product mineral assemblage to emerging melts. Even though there was no pyroxenite in the original mantle source of the melt or the initial matrix through which the melt passed, compositions of the melts emerging from such a column show a clear trace elemental signature of equilibration with pyroxene, and might lead to an interpretation (without the context of reactive melt transport) of a pyroxenitic mantle source.

**Inferring mantle source characteristics**

**Trace element compositions of mantle sources**

In general, reactive transport of melt through the mantle will add incompatible elements to regions in which $C_j > C_j^0/D$, and remove them from regions in which $C_j < C_j^0/D$ (this may also be an important mechanism of compositional homogenization in the mantle). This shifting of trace element composition of erupted melt towards the composition of incipient partial melt of the solid mantle through which it migrates could lead to erroneous inferences of mantle source region composition, if typical batch or fractional melting models are used. Figure 7 shows REE concentrations of solid mantle sources inferred from the composition of a melt that has reacted with a volume of depleted mantle sufficiently large so that REE concentrations are at the limiting $C_j^0/D$ concentrations. Any melting model that assumes a degree of melting >0.5% for this melt would yield a mantle source with a LREE-enriched REE pattern when in fact the melt preserves no information of its original source composition, which could have been either LREE depleted or LREE enriched. Because segregation and extraction of melts from extents of melting lower than a few percent have traditionally been considered unlikely, this has led most studies to conclude that the source regions of strongly LREE-enriched magmas are LREE enriched. Because the isotopic compositions of these melts usually require a long-term depletion in LREE, a recent metasomatic enrichment of LREE before melting is also invoked. Only if the extents of melting are extremely small, typically <0.2% (Alibert et al., 1983; Frey & Roden, 1987; Sims et al., 1995), can the isotopic and trace element compositions of these magmas be reconciled without invoking recent, pre-melting metasomatic enrichment. Some recent studies have suggested that extraction of melt from very low-porosity regions of the mantle may not be unreasonable (McKenzie, 1989; Riley & Kohlstedt, 1991; Jin et al., 1994), thus LREE-enriched magmas may not require such special mantle source histories. But the examples of reactive melt transport shown here, and in other studies (e.g. Navon & Stolper, 1987) illustrate that extensive melt-mantle reaction can also generate strong incompatible element enrichments in relatively large-degree melts of typical depleted mantle, in agreement with isotopic constraints, and without the need for extremely low degrees of melting or recent pre-melting metasomatic enrichment.

**Isotopic compositions**

Isotopic compositions of primitive, oceanic basalts are typically considered to reflect the isotopic compositions of their mantle sources. If melt migrates through and reacts with mantle matrix that has a different isotopic composition, however, then the composition of the melt will shift towards that of the solid matrix. The isotopic composition, $\varepsilon_i$, of melt migrating through reactive solid can be approximated in the context of the incremental mass-balance method (Appendix A) as

$$\varepsilon_i = \frac{\varepsilon_{i-1} \rho_i (1 - \psi_i) C_j^{i-1} + \varepsilon_{i-1} \rho_i (1 - \psi_i) C_j^{i-1}}{C_j^i (1 - \rho_i (1 - \psi_i)) C_j^{i-1}}. \quad (7)$$

Because the isotopic signature of a given element propagates through the column at the same rate as the concentration front of the element (and concentration fronts of different elements propagate at different rates), there may be decoupling in isotopic composition variations in melts emerging from reactive mantle columns. Some studies have interpreted apparently decoupled isotopic variations of Hawaiian lavas in terms of chromatographic effects (McKenzie & O’Nions, 1991; DePaolo, 1996), suggesting significant extents of melt-mantle reaction, whereas others have found very little decoupling between isotopic composition variations of elements with greatly differing compatibilities, suggesting the opposite (Cohen et al., 1996; Hauri et al., 1996). Some of this discrepancy may be due to a difference in the time- and length-scales inferred for the chromatographic effects (DePaolo, 1996).

It is also important to note that although mineral reaction in the column can repartition trace elements between solid and melt, dominating the elemental variation observed in melts emerging from the column, this has no effect on isotopic compositions. In other words, although mineralogic reaction may mask chromatographic effects with respect to trace element abundances (e.g. the lherzolite-to-pyroxenite reaction), it cannot mask chromatographic decoupling of isotopic compositions of elements with different compatibilities.

**Source mineralogy**

Changes in matrix mineralogy during reactive melt transport can impart trace element signatures of minerals to
Fig. 7. Inferred REE patterns of a mantle source, from a melt composition reflecting reaction with a sufficient volume of mantle (with REE concentrations of $C_{n}$) so as to achieve limiting $C_{n}/D$ concentrations for all the REE. The inferred melting is assumed to be modal batch melting, with total extents of melting $F$, shown adjacent to each inferred source. Because the $C_{n}/D$ concentrations are those of incipient partial melting of the matrix, any inferred extent of melting $>0.01$ predicts a LREE-enriched source composition. Distribution coefficients for the REE are shown in Table 1. REE not explicitly modeled here are Pr, Gd, Dy, and Er, and are shown here as weighted averages of surrounding elements, so as to represent smoothed patterns.

The melt that were not present in the melt source, confounding efforts to extract source mineralogy characteristics from mantle-derived basalts. One example of this is would be a residual garnet and clinopyroxene trace element signature caused by the lherzolite-to-pyroxenite reaction of the models. Other types of mineralogic reactions could also be important in terms of interpreting mantle source characteristics. Reaction of small-degree mantle melts with peridotite may cause precipitation of phases not initially present in the melt source or the peridotite. It is well known that metasomatic effects on mantle wallrocks, possibly caused by migrating melts, include precipitation of trace phases uncommon in typical depleted mantle rocks such as amphibole, phlogopite, zircon, apatite, and rutile (Menzies et al., 1985; Roden & Murthy, 1985; Bodinier et al., 1990; Sen & Dunn, 1994). Precipitation of such phases as a result of melt–mantle reaction will have a strong effect on the trace element composition of derivative melts. Interpreted in the typical context of single-stage melting and instantaneous extraction, the logical interpretation would be that the original mantle source contained residual amphibole or phlogopite. But the distinction between residual source amphibole and amphibole as a result of melt–mantle reaction is important. Amphibole, phlogopite, or other trace phases in a steady-state solid mantle assemblage suggest a somewhat special history for that mantle region, as they are not particularly common primary mantle minerals in oceanic environments. In contrast, it is reasonable to expect that small-degree melts of typical lherzolitic mantle might be hydrous and could precipitate amphibole as they cool and react with surrounding mantle during migration through the mantle overlying the source region. Simply including this reactive mantle matrix as part of the magma ‘source region’ would be misleading because (1) the reactive mantle matrix may never have contained these phases before melt–mantle reaction, (2) melt movement and open-system reaction are integral parts of the geochemical signature, and (3) the extent of trace phase elemental signatures may be associated with other compositional factors, such as isotopic composition, which would also signify the extent of melt–mantle interaction, not isotopic source heterogeneity.

Phases that are commonly invoked as residual mantle source minerals on the basis of magma trace element
compositions include amphibole, phlogopite, apatite, ilmenite, zircon, and sulfides (Sun & Hanson, 1975; Clague & Frey, 1982; Clague & Dalrymple, 1988; Greenough, 1988; Halliday et al., 1995; Spath et al., 1996; Class & Goldstein, 1997). Most studies assume that trace element evidence for residual phases such as these requires their presence in the original, pre-melting, solid mantle source. But little inquiry has been made as to the possibility that these phases are products of melt-mantle reaction and do not require an unusual mantle source with a special enrichment history. This could be especially important in cases where stability of the inferred residual phase is limited to the lithosphere (e.g. phlogopite), whereas other trace element evidence suggests melting at greater depths, in the convecting upper mantle (Class & Goldstein, 1997).

Correlation of the extent of trace element signature of these phases with isotopic composition, or the temporal-compositional variation of these melts, would help address this question of source- vs process-imparted chemical signatures.

The physical characteristics of melt transport

The models of reactive melt transport presented here are end-member models that make a number of assumptions regarding the characteristics of melt flow and reaction with solid mantle. Most importantly, they assume that melt is in local equilibrium with surrounding solid, and is capable of exchanging trace elements via diffusion into and out of solid grains (diffusive exchange) or solid dissolution and precipitation (reactive exchange). Given reasonable dissolution-precipitation and diffusion rates, reactive exchange probably occurs at a significantly faster rate than diffusive exchange. This has several implications. First, if diffusive equilibration is assumed, then potential changes in porosity and matrix mode need to be considered because they occur much faster than diffusive equilibration and they have dramatic effects on melt compositions. Second, if the melt maintains local equilibration with surrounding solid mantle via diffusive exchange, the melt velocity must be sufficiently slow relative to solid diffusion rates (Navon & Stolper, 1987). Assuming an average grain radius of ~0.25 cm, a solid diffusion rate of ~10^{-11} cm^2/s for near-solidus mantle temperatures at ~30-40 kbar (Hofmann & Hart, 1978; Hart, 1993), and an average melt velocity of 1-0 m/yr, a characteristic length-scale of full diffusive equilibration would be ~200 m. Thus a column of reactive mantle must be at least several hundred meters long for significant diffusive exchange to occur, if melt is traveling at this velocity. Increasing melt velocity by an order of magnitude increases the characteristic length-scale of equilibration by an order of magnitude. Thus melt flowing faster than 100 m/yr would require a length-scale of equilibration of ~20 km, and would not likely to maintain equilibrium with its surroundings over length-scales appropriate for mantle extraction.

Studies of xenoliths and U disequilibria in mantle-derived magmas commonly focus on velocity constraints pertinent to those portions of the magma transport path in which the melt has left equilibrium with its surroundings and is no longer reacting with the mantle to a large extent (e.g. Spera, 1984, 1987; McKenzie, 1985; Macdonnald, 1993). Some U-series studies do suggest, however, that the melt maintains equilibrium with its surroundings for some portion of time, moving at velocities on the order of 1 m/yr, in regions of extremely small porosity, <0.5% (Spiegelman & Elliot, 1993; Lundstrom et al., 1995). Trace element and petrologic constraints on the geometry of melt transport regions from mantle massif or xenoliths are difficult to generalize. Some evidence suggests that melt migration, at least close to the source regions of melts, may be accomplished via pervasive porous percolation over long length-scales (Kelemen et al., 1992; Van der Wal & Bodinier, 1996), whereas other evidence suggests efficient channelization and chemical isolation of migrating melts (Nielson & Wilshire, 1993, 1996; Kelemen et al., 1995a). Some of the discrepancy probably arises from the likelihood that melt migrates via different mechanisms in different mantle depths and tectonic environments. But this uncertainty of melt migration mechanisms, and the potential for significant melt-mantle reaction in any regime, provides the impetus for this study. Although melt must react with surrounding solid during transport to some extent, the significance of this reaction in magma geochemical signatures is debatable at this time (e.g. Navon et al., 1996; Nielson & Wilshire, 1996). Our best hope may be to compare predictions of these end-member models with real lava compositions in an attempt to ascertain the significance of reactive melt transport in mantle petrogenesis.

Geochemical predictions and comparisons with real lava sequences

One approach to looking for evidence of reactive melt transport in natural sample suites is to examine the solid residue of melting and melt migration such as ophiolites, massifs, and xenoliths (Irving, 1980; Sen, 1988; Bodinier et al., 1990; Liang & Elthon, 1990; Sen & Leeman, 1991; Sen et al., 1993; Hauri & Hart, 1994; Godard et al., 1995; Kelemen et al., 1995a; Van der Wal & Bodinier, 1996). In one respect this approach has been fairly successful: most of these studies find abundant evidence that the trace element composition of solid mantle is strongly affected by migrating melt. Chromatographic concentration fronts have been well documented in mantle
adjacent to dikes (Bodinier et al., 1990; Liang & Elthon, 1990; Hauri & Hart, 1994) and in some cases, in large-scale regions of pervasive porous percolation (Godard et al., 1995; Van der Waal & Bodinier, 1996). However, demonstrating that solid mantle residue is affected by reactive melt transport does not demonstrate that the complementary melts that have migrated through the mantle have been affected to any significant extent. First, melts are highly enriched in incompatible trace elements relative to solid mantle and thus any small increment of melt–mantle reaction can greatly modify melt rocks with respect to incompatible elements, whereas melt compositions can be little affected. To cause significant incompatible element compositional changes in melts, large volumes of mantle are required to equilibrate with melt (volumes of mantle tens to hundreds of times the melt volume). Second, passage of melt through solid mantle may result in a small amount of residual melt left behind in the solid, which can cause significant mantle trace element modification, whereas melt that passes through could be essentially unreacted. Examination of residual mantle may document metasomatic effects that are important for solid compositions (and perhaps future melting events), but we seek an answer to the question: Does reactive melt transport through the mantle affect the trace element composition of melts erupted as lavas at the surface, and thus our interpretations of mantle source regions?

The task of examining erupted melts for evidence of reactive melt transport is somewhat more difficult because (1) trace element variations in mantle-derived magmas can often be interpreted as resulting from variations in the degree of partial melting of a single source or compositional variation between one or more mantle sources, or both, and (2) mantle trace element signatures can also be modified by shallow-level processes such as fractional crystallization, contamination by assimilation of country-rocks in low-pressure magma storage areas, and mixing and accumulation of time-integrated melt batches. These processes may obscure any chemical variations caused by melt–mantle reaction.

Assuming that shallow-level or melt-mixing processes do not obscure trace element effects of reactive melt transport, several robust features of reactive melt transport can be generalized from these and other models. The two primary and potentially observable predictions of this process are (1) some sort of systematic temporal–compositional trend in sequences of cogenetic magmas, and (2) chromatographic decoupling in variations of trace elements and/or isotopic compositions. Other, more specific symptoms that may be present and provide supporting evidence include (1) an initial enrichment in incompatible element concentrations in the first melt batches to emerge in an individual eruption, and decreasing incompatible element concentrations in subsequent melts; such effects would be expected if reactive melt transport is responsible for incompatible element enriched magma compositions (and if the melt source and column matrix had similar compositions); and (2) REE or other trace element patterns suggesting a particular mineralogic reaction during melt flow and reaction, specifically large variations in the HREE in the case of the lherzolite-to-dunite reaction, or systematically decreasing REE (or MREE and HREE) concentrations and subparallel REE patterns in the case of the lherzolite-to-pyroxenite reaction.

It is important to delineate the conditions under which these effects might be observed in real magmas. If present, systematic temporal–compositional trends and chromatographic variations could only be observed in suites of clearly cogenetic samples, preferably from individual eruptions or eruption sequences for which a time sequence of eruption is known. Magmas should also be primitive, with compositions not significantly affected by shallow-level fractional crystallization. Additionally, to demonstrate potential chromatographic effects and rule out mantle source or partial melting variations, a range of major element, trace element and isotopic analyses are required. Demonstrating chromatographic effects on isotopic compositions also requires isotopic analyses of elements with significantly different degrees of compatibility (e.g. combining Os or O with Sr, Nd, and Pb; Hauri et al., 1996).

Few trace element or isotopic studies of primitive lavas focus on providing detailed stratigraphic control of clearly cogenetic magmas that may show chromatographic variations or temporal–compositional trends. Some recent studies have examined isotopic compositions of tholeiitic lava sequences in Hawaii, and have reached contradictory conclusions regarding the presence or absence of chromatographic variations (Cohen et al., 1996; DePaolo, 1996; Hauri et al., 1996). Considerable HREE variation, broadly similar to the effects of the lherzolite-to-dunite mineralogic reaction in reactive melt transport, is a fairly common feature of some mid-ocean ridge basalts but is typified ascribed to dynamic partial melting processes (e.g. Langmuir et al., 1977; Devey et al., 1994). Some stratigraphic sequences of co-eruptive basalts and related lavas do show temporal–compositional trends of decreasing incompatible elements with time, but these trends have been attributed to variations in degree of partial melting, dynamic melting, or mixing with more primitive magmas during eruptions [Wood (1979) and references therein; Hofmann et al., 1984; West & Leeman, 1994; García et al., 1996].

It is noteworthy that many of the predicted effects of reactive melt transport on REE patterns, such as the
chromatographic LREE-depleted or convex-upward patterns, are not generally observed in typical primitive basalts. This might suggest that most trace element variability is dominated by processes other than reactive melt transport, such as melt mixing. At present, despite evidence from massifs and xenoliths suggesting that reactive melt transport is an important process in generation of trace element variability in solid mantle, there is little evidence from available data to support a significant role for reactive melt transport in generating trace element and isotopic variability in mantle-derived lavas. If we are to critically evaluate the significance of this process on erupted magmas, focused studies providing detailed temporal-compositional constraints on clearly cogenetic lavas are required.

Among the best possible candidates for focused study of sequences of primitive cogenetic magmas (although there may be others) are the primitive alkalic magmas that erupt from monogenetic vents on ocean islands. These lavas also commonly contain garnet peridotite xenoliths carried from fairly high pressures (10–25 kbar) (Sen, 1983, 1987, 1988; Clague, 1987; Sen et al., 1990), evidence that they have migrated through large regions of mantle and not resided in shallow-level magma chambers for long periods of time. These lavas are characteristically enriched in incompatible elements (Clague & Frey, 1982; Clague, 1987; Clague & Dalrymple, 1988; Maaløe et al., 1992), although few or no data from multiple samples from single eruptions are available (however, Maaløe et al. did analyze multiple samples from individual lava flows). Another reason to focus efforts to identify evidence for melt-mantle reaction on primitive alkalic lavas is the characteristic incompatible element enrichments, and usually depleted isotopic compositions, of such lavas. These observations have traditionally forced workers to invoke either an unusual recently metasomatized mantle source (Clague & Frey, 1982), extremely low (<0.2%) degrees of partial melting (Frey & Roden, 1987; Frey & Ringwood, 1967; Alibert et al., 1983). In fact, historically, the trace element compositions of primitive alkalic magmas have been one of the prime motivations for even considering the effects of melt-mantle reaction. The useful extension and potential test of this hypothesis that this study provides is that during a single monogenetic eruption of these types of lavas, the earliest melts should have the highest incompatible element enrichments and successive melt batches should have decreasing concentrations of incompatible elements. Chromatographic effects in trace element concentrations may or may not be present in these temporal-compositional sequences, depending on the mineralogic reaction in the transport region.

Although most primitive alkalic lavas have strongly LREE-enriched REE patterns, some post-erosional lavas of Niihau, Hawaii, do show La depletions, relative to other REE, in samples with overall low REE (Fig. 8; D. A. Clague, unpublished data). The REE patterns of these lavas are similar to the patterns observed in the lherzolite-to-pyroxenite models (Fig. 5c, g). If stratigraphic sequences of post-erosional lavas from individual, monogenetic vents could be obtained, they may allow the crucial comparison of temporal-compositional trends predicted in these models.

CONCLUSIONS

End-member models of reactive melt transport through the mantle, including the effects of mineralogic reaction and porosity changes in the mantle matrix, illustrate several important features of melt-mantle reaction that may be potentially observable in actual erupted melts, and could constrain the significance of melt-mantle reaction in geochemical signatures of mantle-derived magmas. The three most robust effects of reactive melt transport on model magmas are: (1) the composition of the leading melt batch through a column of reactive mantle (the melt front) will be shifted towards the composition of an incipient partial melt of the mantle matrix, (2) successive melt batches migrating through and emerging from the column will show a temporal-compositional trend reflecting exhaustion of the reactive capacity of the mantle, and a return to the original input melt composition, and (3) cogenetic melt batches should show some type of chromatographic decoupling in trace element and/or isotopic variations. In the general case of similar melt source and column matrix compositions, these effects should be manifest as an enrichment of incompatible elements in the melt front, and a temporal-compositional trend of decreasing incompatible elements in erupted melt batches with time, back to the original input melt composition, with element concentrations returning to original input melt concentrations in order of increasing compatibility.

Reactive exchange via dissolution and precipitation is a potentially important mechanism in reactive melt transport not only because it should occur faster than diffusive exchange as suggested by Navon & Stolper (1987), Landström et al. (1995), and others, but also because it can result in mineralogic changes to the column matrix that strongly affect erupted melt compositions in ways that cannot be modeled by purely diffusive exchange. In particular, some mineralogic reactions, such as the lherzolite-to-pyroxenite reaction, may efficiently mask chromatographic decoupling of trace element variations in erupted magmas and produce smoothly varying REE (and other trace element) patterns. Thus lack of chromatographic decoupling in magma trace element abundances alone does not preclude significant
melt-mantle reaction. The lherzolite-to-dunite reaction may also produce distinctively large variations in the HREE and other moderately incompatible elements. Porosity changes arising from mineralogic reactions in the mantle column do not appear to have as large an effect on melt compositions as modal changes.

Constraining the significance of reactive melt transport on geochemical signatures of mantle-derived magmas requires detailed temporal-compositional relationships of clearly cogenetic magmas. Some types of ocean-island lavas show chemical variations that are broadly similar to the predicted effects of reactive melt transport outlined here, such as trends of decreasing incompatible elements in discrete eruptive episodes, and LREE depletion in primitive alkalic basalts, but documentation of chromatographic decoupling of trace element and/or isotopic variations in erupted magmas has proven more elusive. More focused studies using a combination of model predictions and sampling and analytical programs providing detailed trace element and isotopic data on temporally controlled sequences of cogenetic magmas are needed to evaluate the significance of reactive melt transport on magma geochemical signatures.

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APPENDIX A: MASS-BALANCE INCREMENTAL METHOD

An initially solid column of mantle with density $\rho$, and concentration of a trace element $C$, is infiltrated with melt with density $\rho_m$ and element concentration $C_m$ from below, establishing a porosity $\phi$ in the column. The column is divided up into a series of finite cells 0 to $i$, and the melt propagates through these cells in a series of finite timesteps 0 to $j$. In each timestep, melt propagates forward one cell whereas the solid remains stationary, so
\[ \rho \frac{\partial \phi j_{i}^{k}}{\partial z^{k}} + \rho (1 - \phi j_{i}^{k}) C j_{i}^{k-1} = \rho \phi C j_{i} + \rho (1 - \phi j_{i}^{k}) C w_{i}^{k}. \]  

(A1)

If the solid and melt are in trace element equilibrium in each cell, then the trace element concentration in the solid is related to the concentration in the liquid by the solid–melt bulk distribution coefficient \( D \) of the element:

\[ C_{i} = D C_{i}. \]  

(A2)

so after equilibration in cell \( i \), time \( j \), equation (A1) becomes

\[ \rho \phi j_{i}^{k-1} C j_{i}^{k-1} + \rho (1 - \phi j_{i}^{k-1}) C w_{i}^{k-1} = \rho \phi C j_{i} + \rho (1 - \phi j_{i}^{k}) D C_{i}. \]  

(A3)

This equation can be solved for a sequence of cells in a sequence of timesteps to simulate equilibrium transport of melt with an initial concentration \( C_{i} \) through a column with an initial solid concentration \( C_{i} \).

The concentration of the element in the melt in cell \( i \) and timestep \( j \) is

\[ C j_{i} = \frac{\rho \phi j_{i}^{k-1} C j_{i}^{k-1} + \rho (1 - \phi j_{i}^{k-1}) C w_{i}^{k-1}}{\rho \phi + \rho (1 - \phi j_{i}^{k}) D C_{i}}. \]  

(A4)

This equation was used by Vollmer (1987) in modeling crustal metasomatic processes.

**APPENDIX B: CONTINUUM METHOD**

This continuum approach requires the assumption of a column of solid mantle with pre-existing porosity \( \phi \), already filled with melt in equilibrium with the solid with bulk distribution coefficient \( D \). The total masses of melt and solid must be conserved in any representative elementary volume of this reactive column, although melt and solid can be created or destroyed at an equal and opposite rate. Conservation of mass can be written as

\[ \frac{\partial}{\partial t} \left[ \phi \rho j + (1 - \phi) \rho w \right] + \frac{\partial}{\partial z} (\phi \rho w) = 0. \]  

(B1)

Using the equilibrium assumption \( C_{i} = D C_{i} \), and setting \( \rho = \rho j / \rho w \) yields

\[ \frac{\partial}{\partial t} \left[ \phi C j + (1 - \phi) \rho D C_{i} \right] + \frac{\partial}{\partial z} (\phi \rho w) = 0. \]  

(B3)

Using the relation from equation (B1),

\[ \frac{\partial \phi}{\partial t} + \frac{\partial}{\partial z} (\phi \rho w) = 0. \]  

(B4)

Assuming constant densities, and simplifying, yields

\[ \left[ \rho (1 - \phi) D + \phi v_{f} \right] \frac{\partial C_{i}}{\partial t} + \phi \frac{\partial C j}{\partial z} = \rho C_{i} (\phi - 1) \frac{\partial D}{\partial t} + (D - 1) \frac{\partial \phi}{\partial t} \]  

which is solved using a finite difference solution. Variations of this equation were used by Godard et al. (1995) and Van der Wal & Bodinier (1996) in modeling compositional changes in recrystallization fronts in residual mantle. An additional complication arises when porosity changes in a column of reactive mantle, such that

\[ \frac{\partial \phi}{\partial t} \neq 0. \]  

(B6)

In this case the flux \( \phi j \) must vary spatially in a way given by equation (B4). If \( \frac{\partial \phi}{\partial t} = 0 \) (\( \phi \) changes at a single rate in all cells of the column, to maintain mass balance), then equation (B4) simplifies to

\[ \frac{\partial v_{f}}{\partial z} = (\rho - 1) \frac{\partial \phi}{\partial t}, \]  

(B7)

and the velocity in each cell can be calculated by

\[ v_{f} = \rho \partial z + \left( \frac{\rho - 1}{\rho} \right) \]  

(B8)

where

\[ C = \frac{\partial \phi}{\partial t} \]  

for each time and position in the column.