Magma transport and metasomatism in the mantle: A critical review of current geochemical models—Discussion

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ABSTRACT

Nielson and Wilshire (1993) promised a review of geochemically based models for magma transport and metasomatism in the mantle. However, they focused on discrediting the chromatographic model of Navon and Stolper (1987). Nielson and Wilshire concluded that the process operating during melt percolation in the mantle “resembles ion-exchange chromatography for H2O purification, rather than the model of chromatographic species separation proposed by Navon and Stolper (1987).” Our objective here is to show that Nielson and Wilshire (1993) did not offer any new theoretical or modeling advances. We demonstrate that the “water-purification model” (based on the finite-plate model of Helfferich 1962) is controlled by the same physics and mathematics as the frontal chromatography model discussed by Navon and Stolper (1987). Thus, the distinction made by Nielson and Wilshire between the two models has no basis. Moreover, we show that with appropriate boundary conditions, the model of Navon and Stolper (1987) produces an excellent fit to the data that Nielson et al. (1993) fitted using the “water-purification model.” We emphasize that the model of Navon and Stolper can be used to model both small- and large-scale processes and that it allows the recovery of temporal information, which cannot be retrieved using the finite-plate model. The usefulness of these models for understanding the geochemistry of mantle rocks is a subject of active research and beyond the scope of this discussion.

INTRODUCTION

To interpret properly the geochemical characteristics of basalts, it is necessary to know the mechanisms and consequences of melt transport from their mantle source to the eruption site. Two end-member processes are melt migration by percolation along grain boundaries of solid matrix (i.e., porous flow) and melt transport in fractures forming veins and dikes. Both processes must occur in the mantle. Porous flow must be important, at least during the early stage of melt segregation, and field observations of lithospheric rocks clearly indicate the importance of melt transport in fractures. The relative importance of these two end-member processes is a subject of active study (e.g., Bodinier et al. 1990; McKenzie and O’Nions 1991; Hart 1993; Iwamori 1994; Stolper and Newman 1994; Hauri et al. 1994; Kelemen et al. 1994). Nielson and Wilshire (1993) summarized experimental, theoretical, and field observations pertaining to fluid flow in a porous medium and through fractures. They emphasized examples of mantle xenoliths that reflect infiltration of melts from dikes into wall rocks and concluded that the geochemical effects of porous flow are typically limited to scale lengths of a few centimeters. Because fracturing is a necessary condition for entrainment of xenoliths, which are typically <0.5 m in diameter, it is likely that examples of large-scale porous flow cannot be sampled by xenoliths. Large, kilometer-scale peridotites are more suitable for evaluations of the scale of porous flow, but they have added complexities, such as metamorphic reactions, resulting from their transport into the crust.

Following the pioneering work of McKenzie (1984), Navon and Stolper (1987) examined the geochemical consequences of melt percolation. Their approach was general and can be applied to any scale, as long as the percolation distance is large relative to the grain size of the matrix. They concluded that when a percolating melt is not in equilibrium with the host matrix, the interaction between melt and matrix must lead to the development of chromatographic effects. Navon and Stolper (1987) noted that such effects are expected if a melt percolates from a dike into the wall rock and suggested simple chemical criteria for identifying this process, e.g., their Figure 5. We agree with Nielson and Wilshire (1993) that it is important to assess how well chromatographic processes explain geochemical data for mantle rocks. This is an important objective because chromatographic processes can create compositional effects in melts and solids, such as changes in abundance ratios of incompatible elements that are much larger than those created by partial melting or fractional crystallization. Some aspects of
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give a quantitative description of the HrO-purification model, and the reader is referred to Helfferich (1962),

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atics of all chromatographic models are similar. As expected, a close examination of the equations used by Helf-

ferich (1962, p. 450, Eq. 9-3),

and Navon and Stolper (1987, p. 287, Eq. 1a),

reveal that they are identical. The interested reader need

only set the matrix velocity, \( V_r \), in Equation 2 to zero,

neglect the third term in Equation 1, which is justified

when the percolation distance is large in comparison with

the grain size, and make the necessary transformations

between the parameters used in the two references: \( x_i = C_i \rho_f + C_i \rho_m \), \( U = \phi \), \( v_r = V_r \phi_f \), \( D = D_f \sqrt{\frac{2}{\pi}} \), and \( C_i = C_i \rho_m \), where \( q \) is the column cross section; \( z \) is the distance from the bottom of the column; \( \Delta z = 1.64a \) is the thickness of a layer of close-packed spherical grains of radius \( a \); \( x_i \) is amount of species \( i \) (in the melt and the matrix) per unit volume of column; \( U \) is melt volume that passed through distance \( z \) during time \( t \), since operation started; \( v_r \) is the melt volume per unit cross section per unit time; \( C_i \) and \( C_f \) are the concentration of the species of interest in the melt in weight per unit volume and weight per unit weight of melt, respectively; \( C_r \) is the concentration in the matrix (weight species / weight of matrix); \( t \) is time; \( \phi_f \) is porosity; \( \rho_f \) and \( \rho_m \) are the densities of the melt and matrix, respectively; \( V_r \) and \( V_r \) are their respective velocities; and \( D_f \) is the diffusivity of the melt in the melt.

As shown by Navon and Stolper, the effect of diffusion in the melt can be neglected in columns that are on the order of 100 m or longer. Then, if local equilibrium between melt and matrix is assumed (i.e., \( C_i = K_\rho C_f \), at any point, and diffusion in the solid is not an important constraint), a mass balance for a trace element in the porous matrix (Eq. 4 of Navon and Stolper 1987) leads to a simple analytical solution for the position of the concentration fronts of the various elements (see Eq. 5 of Navon and Stolper 1987). These equations are valid for any initial matrix concentration, \( C_r \). In the simple case where \( C_r = 0 \), Equation 4 of Navon and Stolper (1987) reduces to

\[
\frac{z}{C_r} \left[ \phi_f + (1 - \phi) \rho_f K_\rho \right] = z C_r \phi_f
\]

where \( z \) and \( Z \) are the locations of the concentration front of the element of interest and of the melt, respectively, and \( C_r \) is the concentration of this element in the input melt. In Equation 3 the right side represents the total mass of the trace element that was introduced into the column by the input melt, and the left side describes the distribution of this element between the melt and equilibrated matrix behind the concentration front at \( z \). Between \( z \) and \( Z \) in the column, the melt concentration, \( C_r \), was reduced to zero as the input melt equilibrated with the matrix in the interval from the base of the column to \( z \). The mass-balance equation is the basis for all chromatographic models and is responsible for the well-known effect of incompatible elements migrating through the column faster than more compatible elements. The effects of diffusion in the melt are to broaden concentration fronts, but their relative positions are not changed.

If local equilibrium is not attained because of slow solid-state diffusion in the grains, the only difference between the Helfferich (1962) and Navon and Stolper (1987) approaches is in the mathematical method used for solving the mass-balance equations; the same input parameters, diffusion coefficients, porosity, and melt velocities are required by Equations 1 and 2. Helfferich (1962) estimated the time it takes to approach equilibrium and the distance, \( l \), traveled by the melt during that time. He then
used the approximation that a chromatographic column can be considered as a series of segments or discrete plates with thickness / where complete equilibrium is achieved. After equilibration the melt is transferred to the next plate and so on until it reaches the top of the column. This simple scheme was used by Farmer and DePaolo (1987) and by Nielson et al. (1993). Navon and Stolper (1987) demonstrated that the major impediment to achieving local equilibrium is the slowness of volume diffusion in solids. They used a numerical model and formulated an analytical approximation (Appendix A of Navon and Stolper 1987) to evaluate the effects of solid-state diffusion on concentration gradients in the melt and matrix. We emphasize that the solutions of Helfferich (1962) and Navon and Stolper are identical when local equilibrium is achieved. If slow diffusion in the solid prevents such equilibrium, the only difference is in the method used to solve the differential equation. Nielson and Wilshire (1993) used the simplified approximation given in Helfferich (1962), but this approximation and the solutions given by Navon and Stolper lead to similar results.

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In summary, there are no fundamental physical or mathematical differences between the chromatographic models discussed by Navon and Stolper (1987) and that favored by Nielson and Wilshire (1993). Their assertion that the chromatographic process in the mantle "resembles ion-exchange chromatography for H2O purification, rather than the model of chromatographic species separation proposed by Navon and Stolper (1987)" has no basis.

In the following discussion we answer the questions put forward by Nielson and Wilshire (1993, p. 1123) as "Important questions ... unanswered by Navon and Stolper (1987)."

(1) "What region of the mantle constitutes the top of a reacting column?" Chromatographic reaction ceases when melt stops migrating by porous flow. Therefore, a simple answer is that the top may be defined by the level at which melt migration is dominantly in veins and dikes, but this transition may be gradational (Hart 1993). In the case of melt migrating away from a dikes, the top of the column may be placed at the melt front. In mathematical terms, the real answer is that there are no boundary conditions pertaining to the top of the column, and so the location of the top is not important. The only constraint is that the whole column must be uniform on a scale that is large in comparison with the grain size.

(2) "Why does the migrating melt react in this region if the matrix is the same as that within the column?" Because this question directly follows Question 1, we infer that by "this region" Nielson and Wilshire are referring to the top of the reacting column. Our answer is that the melt reacts with the matrix as long as they are not in equilibrium. The very first melt emerging from the column has equilibrated with the column matrix (it is ahead of all the concentration fronts and does not react with the matrix). Later, concentration fronts of the various elements reach the column top, and the matrix there reacts and equilibrates with the original melt composition, first with the incompatible elements and then with the more compatible elements.

(3) "Why does the matrix pattern so accurately reproduce that in the melt if Kd values remain constant?" In this context, matrix pattern refers to relative abundances of elements such as the REE. If equilibrium is achieved, then the concentration in the solid matrix is $C_s = K_d C_m$, and the matrix pattern reflects the melt through the partition-coefficient operator. In general, because $K_d \neq 1$ and values of $K_d$ are not similar for all trace elements, the melt and matrix never have the same relative abundance of trace elements. If equilibrium is not achieved, because of slow solid-state diffusion, it is also evident that relative abundances of trace elements are very different in the melt and solid, as is clearly illustrated in Figure 4 of Navon and Stolper (1987). It is not clear to us why such a question would be asked. A possible motivation is the superficial similarity of chondrite-normalized REE patterns (on a logarithmic scale) in an amphibole selvage and the adjacent amphibole-peridotite wall rock in a Dish Hill xenolith (Figs. 3 and 5 of Nielson et al. 1993). This similarity may reflect trapped melt in the peridotite or the assumption that amphibole in the selvage represents the REE abundances in a metasomatic agent rather than REE abundances of amphibole crystallized from a melt (Nielson et al. 1993, p. 111).

(4) "What is the likely proportion of melt relative to matrix that can percolate far enough to produce the transient fractionation patterns?" Transient fractionation patterns or, in other words, large variations in the abundance ratios of two elements, i and j, with different compatibility, e.g., $K_{bi} < K_{bj}$, occur in the volume between the concentration fronts of these elements (e.g., Fig. 1a, of Navon and Stolper 1987). The melt-matrix ratio required to generate this region can be determined from Equation 5 of Navon and Stolper (1987). The mass of melt between the concentration fronts for $i$ and $j$ is

$$q(z_i - z_j) \phi_{P_i} = qZ \phi_P(X_i - X_j)$$

(4)

where $q$ is the column cross section and $X_i = z_i/Z = \phi_P/\{\phi_{P_i} + (1 - \phi) P_iK_{bi}\}$. The mass of the matrix that interacted with the melt is the matrix mass behind the melt front. That is,

$$qZ(1 - \phi) \rho_s$$

(5)

Therefore, the melt-matrix ratio is

$$\frac{\phi_P(X_i - X_j)/(1 - \phi) \rho_s}{\phi_{P_i} X_i}$$

(6)

Alternatively, we can consider only the matrix behind the front of the more incompatible element $i$. In this case the melt-matrix ratio is

$$\frac{\phi_P(X_i - X_j)/(1 - \phi) \rho_s}{\phi_{P_i} X_i}$$

(7)

In both cases the melt-matrix ratio depends only on the melt fraction, $\phi$, the densities, $\rho_i$ and $\rho_s$, and the partition coefficient of the two elements, $K_{bi}$ and $K_{bj}$. The
calculation is more complex for the nonequilibrium case, but all the required information is in Appendix A of Navon and Stolper (1987).

These questions of Nielson and Wilshire (1993) lead us to infer that they did not have a thorough understanding of the chromatographic process modeled by Navon and Stolper (1987). This inference is reinforced by their repeated statement that the Navon and Stolper approach is based on the supposition of large-scale percolative processes (see Abstract and p. 1129 of Nielson and Wilshire 1993). Navon and Stolper emphasized applications of the model to problems of large scale, but the model is equally applicable to small-scale problems when the concentrations in matrix and melt vary on a length scale that is large in comparison with the matrix grain size. Another significant erroneous statement by Nielson and Wilshire is that in their discussion of the Dish Hill xenolith they state (p. 1130): "... contrary to Navon and Stolper (1987), the most elevated LREE contents and fractionated patterns of LREE vs. HREE occur within 2 cm of the dike contact." As discussed below these observations are exactly those predicted by the Navon and Stolper model.

**The Dish Hill xenolith**

The compositional variations in a xenolith from Dish Hill, California (Nielson et al. 1993), are the basis for the water-purification model that Nielson and Wilshire (1993) proposed as appropriate for describing chromatographic processes in the mantle. The xenolith is a lherzolite (17 x 16 x 9.5 cm) with a selvage of amphibolite at one end. On the basis of modes inferred from mineral and whole-rock compositions, Nielson and Wilshire found that the amphibole mode in the peridotite decreases from 1.9 to 0.6% with increasing distance from the amphibolite. Major and trace element concentrations and isotopic ratios also vary systematically as a function of distance from the amphibolite selvage; the concentration profiles resemble those produced by chromatographic processes.

Nielson and Wilshire (1993) stated that the reaction gradients in the Dish Hill xenolith can be modeled fairly well by simple finite-plate calculations (Helfferich 1962; Farmer and DePaolo 1987) that are a simplification of Navon and Stolper's (1987) approach. Nevertheless, they claim that the water-purification model can explain observations that cannot be explained by the model of Navon and Stolper (e.g., in the Abstract and p. 1127 and 1130 of Nielson and Wilshire 1993).

How can one model do what the other cannot when they are almost mathematically identical? In particular, Nielson and Wilshire (1993) emphasized that abundances of incompatible elements, such as light REE, are highest in the peridotite wall rocks closest to the amphibolite, and they inferred (p. 1130) that this observation is contrary to the model of Navon and Stolper (1987). In response, we note that when a melt enriched in incompatible elements reacts with a peridotite depleted in such elements, addition of incompatible elements to the peridotite is an expected consequence of the Navon and Stolper (1987) model. Because the length scale is centimeters in the Dish Hill sample, diffusion in the melt should be important (Navon and Stolper 1987, p. 293). Under these boundary conditions, the simple chromatographic model of Navon and Stolper may be used to model trace element profiles and to constrain time-scale and other physical parameters of the process. For example, by using the Navon and Stolper equations with the $K_p$ values ($K_p^{B_{Sr}} = 0.06$ and $K_p^{Nd} = 0.09$) proposed by Nielson and Wilshire (1993), a pore volume of 1%, densities of 2.7 and 3.3 gm/cm$^3$ for melt and matrix, respectively, and a melt percolation distance of 14 cm, we find that the observed Nd abundances and isotopic variations with distance from the contact can be matched by the theoretical profiles (Fig. 1). The observed dispersion of the concentration and isotopic fronts could have been caused by several processes (Navon and Stolper 1987). If this dispersion reflects control by diffusion in the melt and a diffusion
coefficient of $1 \times 10^{-7}$ cm$^2$/s is assumed (Magaritz and Hofmann 1978), the best fit to the data requires a time scale of about eight months, corresponding to a percolation rate of $\sim 21$ cm/yr.

The preferred $K_0$ values for Nd and Sr used by Nielson and Wilshire (1993) are higher than expected from recent measurements of clinopyroxene/melt $K_0$ (e.g., Hart and Dunn 1993). These high $K_0$ values may reflect amphibole formation during the melt-wall-rock reactions. Navon and Stolper (1987) cautioned that their model assumed major element equilibrium between migrating melt and matrix; hence, modal mineralogy and $K_0$ are constant in their model. However, if the H$_2$O content of the metamorphic melt (or fluid) were higher than $\sim 5\%$, then, because the rock now contains $<0.2\%$ H$_2$O, the effective partition coefficient for H$_2$O would be $<0.04$. If so, the H$_2$O front preceded the Sr and Nd concentration fronts, and the Sr and Nd fronts migrated through an amphibole peridotite. Because the amphibole grain size is small, it is logical, in this case, to assume local equilibrium. Bulk solid-melt partition coefficients are functions of mineral $K_0$ and mass fraction of the mineral in the solid. Because clinopyroxene forms 10–20% of the Dish Hill peridotite, clinopyroxene was the major contributor to the bulk solid $K_0$ for Sr and Nd. However, amphibole typically has $K_T$ values higher than clinopyroxene (e.g., Green et al. 1992), and it is possible that during the chromatographic process the creation of amphibole was in part responsible for incorporation of Sr and Nd into the peridotite wall rocks of the amphibolite.

Undoubtedly, the actual process was more complex than this simple model. For example, formation of additional pore volume, the rates of amphibole formation, and the retention of some melt, along with its trace element content, may also have been important. The model preferred by Nielson and Wilshire (1993), however, does not address any of these additional complexities, and it is a less accurate solution that adds nothing to the model proposed by Navon and Stolper (1987).

### Conclusion

Since the early recognition of relative light REE enrichments in dunite and harzburgite (e.g., Varne and Graham 1971; Frey and Green 1974), there have been many proposed explanations for this phenomenon (see review by McDonough and Frey 1989). There is now consensus that chromatographic processes, such as proposed by Navon and Stolper (1987), are important in creating incompatible element enrichments in mantle rocks. An unresolved question is the scale of such a process. We agree with Nielson and Wilshire (1993) that study of well-exposed samples collected from xenoliths and massive peridotites on scales ranging from centimeters to hundreds of meters is the best way to evaluate the scales of porous flow in the mantle.

As for the models used to simulate the geochemical consequences of porous flow, we stress that the model preferred by Nielson and Wilshire (1993) offers no advantage in comparison with the model of Navon and Stolper (1987). The physics of both models are identical, but the preferred approach of Nielson and Wilshire uses a cruder mathematical approximation, disregards the temporal information in the concentration profiles, and does not describe accurately the position of the concentration fronts when slow diffusion into the crystals of the matrix prevents local equilibration of melt and rock.

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### References Cited


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