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## The requirements for chemical disequilibrium during magma migration

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### ABSTRACT

Recent geochemical studies of MORB genesis suggest that at least some degree of chemical disequilibrium occurs during the transport of magma to the surface. If disequilibrium transport does occur in the mantle, it would seem to preclude melt being distributed in a porous network on grain boundaries that could rapidly re-equilibrate with the solid. The questions remain however, as to how big a melt “channel” is required to produce disequilibrium and whether flow in such channels would violate assumptions inherent in the equations of magma migration. Using a series of simple physical scaling arguments, we quantify the requirements for chemical disequilibrium and lay out the conditions for which the melt migration equations are valid. These arguments show that a vein network with veins  $\sim 10$  cm apart is sufficient to cause significant disequilibrium. More precisely, these arguments show that to maintain equilibrium, the solid-state diffusion coefficient would need to increase by 2–4 orders of magnitude for every order of magnitude increase in channel spacing. Nevertheless, because the equations of magma migration are a macroscopic description of melt flow, they can readily describe even large scale networks of melt channels. By demonstrating the fundamental scalings governing the chemistry and motion of partial melts, these simple arguments show that, while the chemistry may be extremely sensitive to the microscopic distribution of melt, our physical understanding of magma migration is robust.

### 1. Introduction

The chemical consequences of the separation of magma from its solid residue is one of the least understood processes in the generation and extraction of partial melts. In particular, one of the more surprising results of recent models of MORB genesis [1,2] is that these models work quite well without actually including the physics of melt transport. Even with the unrealistic assumption that the melt and matrix do not separate as melting proceeds, these parameterizations still can reproduce the volume and chemistry of MORB to within measurement error by simply mixing melts produced at all depths. Nevertheless, it seems reasonable that melts must separate

rather efficiently to produce the oceanic crust. These conflicting results suggest that either the changes in composition and temperature due to melt migration do not affect the thermodynamics of melting—or that the melt separates in a manner such that it does not interact with the solid mantle it must pass through. This second suggestion, that melt migration occurs in a state of at least partial chemical disequilibrium, is also supported by trace element studies [3–5].

If disequilibrium transport does occur in the mantle, it would seem to preclude melt being distributed in a porous network on grain boundaries that could rapidly re-equilibrate with the solid. The questions remain, however, as to how big a melt “channel” is required to produce disequilibrium and whether flow in such channels would violate assumptions inherent in the equations for flow in deformable “porous media” used by many workers [6–11] to study magma migration.

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The purpose of this paper is to develop a better understanding of the fundamental scaling relations that control the chemistry and flow of partial melts. Through a series of simple scaling arguments, we show that the presence of chemical equilibrium is extremely sensitive to the microscopic distribution of melt (a network of 1 mm wide veins spaced only  $\sim 10$  cm apart is sufficient to produce strong disequilibrium transport over 10–100 km). However, because the equations of magma migration are a macroscopic description of melt flow, they can readily describe even large scale networks of melt channels and remain valid over a wide range of parameters.

## 2. A simple scaling argument

Rather than solve the full set of non-linear equations for coupled flow and diffusion (for this see Kenyon [12]), it is often equally instructive to develop a simple approximate solution that demonstrates the fundamental scalings in the problem. In the problem of transport and equilibration, the two competing processes are the transport of chemistry by the melt and the diffusion of chemical species in the solid. To maintain equilibrium, the time it takes for a species to diffuse through the solid between melt channels must be short compared with the time required for it to be carried out of the system by the melt. Figure 1 shows a layer of depth  $L$  of an idealized permeable medium of tubular melt channels each separated by a distance  $d$ . As with all diffusion problems, the characteristic time for a species to diffuse between channels is of the order:

$$t_{\text{diff}} \approx \frac{d^2}{D_s} \quad (1)$$

where  $D_s$  is the solid state diffusion coefficient. Similarly, the time it takes to advect across the entire layer is approximately:

$$t_{\text{adv}} \approx \frac{L}{w_0} \quad (2)$$

with  $w_0$  being the melt velocity. The ratio of these two times is the Peclet number:

$$Pe = \frac{w_0 d^2}{D_s L} \quad (3)$$

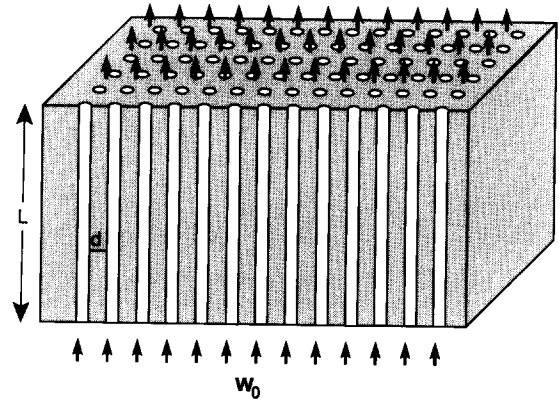


Fig. 1. Schematic diagram of a layer of depth  $L$  of an ideal permeable medium consisting of a uniform network of tubes spaced  $d$  apart. The basic requirement for chemical equilibrium is that the time it takes to diffuse through the solid between the melt channels is small compared with the time it takes to advect across the layer at melt velocity  $w_0$ .

the dimensionless number that describes the relative contributions of diffusion and advection.

As long as the diffusion time is small compared with the advection time, equilibrium can be maintained. More complete analysis of advective-diffusive problems (e.g. [12,13]) shows that if  $Pe \ll 10$ , diffusion dominates and the melt can rapidly equilibrate. If  $Pe \gg 10$ , disequilibrium results. If the Peclet number of the system of interest can be estimated, it becomes straightforward to determine whether equilibrium is likely. This sort of scaling argument is not particularly new; however, combining this result with the basic understanding of melt migration yields additional interesting results.

The principal unknown quantity in eq. 3 is the appropriate value for the melt velocity. If the medium is permeable and the flow of melt can be described by Darcy's law, then a reasonable approximation for the melt velocity is the percolation velocity:

$$w_0 \approx \frac{k_\phi \Delta \rho g}{\phi \mu} \quad (4)$$

where  $k_\phi$  is the permeability,  $\Delta \rho = \rho_s - \rho_f$  is the density difference between solid and liquid,  $g$  is the acceleration due to gravity,  $\phi$  is the volume fraction of melt present or porosity, and  $\mu$  is the melt viscosity. Moreover, for a permeable system

of interconnected melt channels, the permeability takes the general form:

$$k_{\phi} \approx \frac{d^2 \phi^n}{b} \quad (5)$$

This equation shows that the permeability depends on the spacing of the channels, the volume fraction of melt to some power  $n$  and a constant  $b$ . Both  $n$  and  $b$  are affected by changing the geometry of the permeable network. It should be noted that eq. 5 does not assume *a priori* that the channel spacing is equivalent to the grain diameter (i.e. that  $d \equiv a$ ). Section 5 shows that the equations for “porous flow” are quite general and make no assumptions about the microscopic geometry of melt distribution.

Substituting eqs. 4 and 5 into eq. 3 gives the Peclet number appropriate for flow in a permeable medium:

$$Pe = \frac{\phi^{n-1} \Delta \rho g d^4}{b \mu L D_s} \quad (6)$$

For a more intuitive understanding of this expression, we can assume marginal equilibrium ( $Pe = 10$ ) and rearrange eq. 6 to show that the solid state diffusivity must scale as:

$$D_s^{eq} > A d^4 \quad (7)$$

for the melt to remain in equilibrium with the matrix. Here:

$$A = \frac{\phi^{n-1} \Delta \rho q}{10 b \mu L}$$

Inspection of eq. 7 shows immediately the extreme sensitivity of chemical equilibrium to the channel spacing. This equation states that to maintain marginal equilibrium, the solid state diffusivity must increase by *four* orders of magnitude for every order of magnitude increase in the channel spacing. Assuming a layer depth of  $L = 50$  km (i.e. roughly the depth of the partially molten region at ridges) and using the parameters given in Table 1, eq. 7 suggests that even a melt network with 1 mm wide veins spaced 10 cm apart requires  $D_s^{eq} \gg 10^{-12} \text{ m}^2 \text{ s}^{-1}$  to maintain equilibrium. This value should be compared to estimates for the diffusion coefficient  $D_s \sim 10^{-14} - 10^{-19} \text{ m}^2 \text{ s}^{-1}$  for cations such as Sr, Sm, and Ca in olivine and clinopyroxene [14–16]. Of

TABLE 1

Parameters used to calculate  $D_s^{eq}$  as a function of vein spacing  $d$

Variable	Meaning	Value used	Dimension
$b$	constant in permeability	1000	none
$g$	acceleration due to gravity	9.81	$\text{m s}^{-2}$
$L$	layer depth	$5 \times 10^4$	m
$n$	exponent in permeability	2	none
$\mu$	melt shear viscosity	10	Pa s
$\rho_f$	density of melt	2800	$\text{kg m}^{-3}$
$\rho_s$	density of solid	3300	$\text{kg m}^{-3}$
$\Delta \rho$	$= \rho_s - \rho_f$	500	$\text{kg m}^{-3}$
$\phi$	porosity	0.01	none

course, the actual value of  $D_s^{eq}$  will change with different assumed parameters. Nevertheless, because of the strongly non-linear scaling of  $D_s^{eq}$  (or  $Pe$ ) with  $d$ , even order of magnitude changes in the value of  $A$  require only small changes in the channel spacing to compensate.

### 3. A more refined calculation: constant flux

The strong  $d^4$  scaling of the previous problem has been noted before [17] and arises from the  $d^2$  dependence of the diffusion time (as noted by [12]) and the  $d^2$  dependence in the melt velocity. This calculation, however, assumes implicitly that the porosity remains constant as the channel spacing changes. If this is the case, inspection of eqs. 4 and 5 shows that the melt flux  $\phi w_0$  will also increase at constant porosity. Appendix A, however, shows that for steady state melt extraction from the mantle, a more reasonable condition is that the local *melt flux* should remain constant as the spacing changes. In steady state, the melt flux at any point must equal the total amount of melt produced up to that point, regardless of the permeability structure. Figure 2 illustrates the difference between a simple permeable network that conserves porosity and one that conserves flux.

If the flux  $q = \phi w_0$  is held constant, eqs. 4 and 5 can be rearranged to show that the porosity must change with  $d$  as:

$$\phi = \left[ \frac{q \mu b}{\Delta \rho g d^2} \right]^{1/n} \quad (8)$$

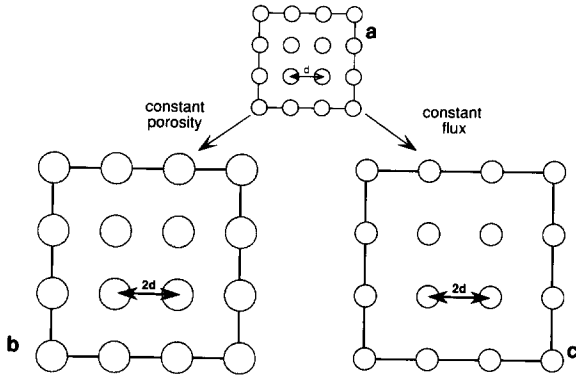


Fig. 2. Schematic diagram showing the difference between a porous network that conserves porosity and one that conserves melt flux. (a) Initial porous network with channel spacing  $d$ . (b) Network with spacing  $2d$  and the same porosity (volume fraction of melt) as (a). (c) Network with spacing  $2d$  and the same flux as (a). For a series of parallel tubes, the melt flux is proportional to  $\phi^2$ .

Substituting into eq. 6 yields the new equilibrium requirement:

$$D_s^{eq} > B d^{\frac{2(n+1)}{n}} \quad (9)$$

with

$$B = \frac{q^{(n-1)/n}}{10L} \left[ \frac{\Delta \rho g}{b\mu} \right]^{1/n}$$

For the constant flux problem, the scaling relations of  $D_s^{eq}$  with channel spacing now depend on the form of the permeability, in particular with  $n$ , the degree of non-linearity between porosity and permeability.

Estimates of  $n$  range from  $\sim 1-5$  with more usual estimates between  $n = 2-3$  [18,19]. For  $n = 1$  [20], the problem reduces to the previous case as the melt velocity becomes independent of porosity. However, a value of  $n = 1$  also means that the velocity of a trace element is independent of how much melt is present. For this, and other, reasons  $n = 1$  is a somewhat controversial value. For a simple system of tubes,  $n = 2$  [21] and  $D_s^{eq} \propto d^3$ . A series of planar channels or veins gives  $n = 3$  ( $D_s^{eq} \propto d^{2.7}$ ) and as  $n \rightarrow \infty$ ,  $D_s^{eq} \rightarrow d^2$ . While changing the value of the exponent  $n$  changes the scaling relations, the effect of changing the channel spacing is still strongly non-linear. For  $n \sim 2-3$ , one order of magnitude change in spacing still requires approximately 3 orders of

magnitude change in diffusivity to maintain equilibrium.

To evaluate eq. 9 for the mantle requires a reasonable estimate of the melt flux  $q$ . Appendix A gives a simple scaling argument for  $q$  based on 1-D steady state adiabatic melting and extraction at ridges. This argument shows that a useful estimate of the maximum steady state melt flux beneath a ridge is:

$$q_{max} \approx \frac{\rho_s F_{max} W_0}{\rho_f} \quad (10)$$

where  $W_0$  is the upwelling rate of the mantle beneath a ridge, and  $F_{max}$  is the maximum degree of partial melting on the ridge axis.  $F_{max}$  should not be confused with the maximum melt fraction  $\phi_{max}$ . These are the same only if the melt does

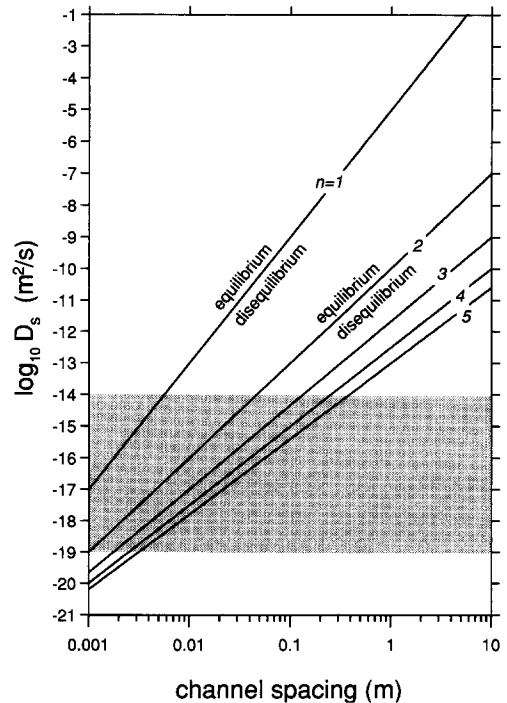


Fig. 3. Constant flux calculation of diffusion coefficient required for marginal equilibrium ( $Pe = 10$ ) as a function of channel spacing and permeability exponent  $n$ . For this plot,  $W_0 = 5$  cm/yr,  $F_{max} = 0.25$ . Other parameters are given in Table 1. For a given exponent and actual diffusion coefficient,  $D_s$ , the system will be in equilibrium if  $D_s > D_s^{eq}$ . If  $D_s$  plots below the curve, disequilibrium is likely. The shaded area shows the estimated range of diffusion coefficients for various cations (Sr, Sm, Ca, Al) in olivine and clinopyroxene at temperatures near 1300°C.

not separate from the solid (i.e. batch melting). Figure 3 shows the boundary between equilibrium and disequilibrium transport ( $D_s^{\text{eq}}$ ) for a system upwelling at 5 cm/yr with  $F_{\text{max}} \sim 0.25$  and  $n = 1-5$ . For  $n = 2$  and  $D_s = 10^{-15} \text{ m}^2 \text{ s}^{-1}$ , marginal equilibrium is attained for a spacing of only  $\sim 3$  cm, i.e. even a porous system with 1 cm between veins (or a 1 cm grain size) may show some signs of disequilibrium.

While the Peclet number is clearly most sensitive to the channel spacing, this solution can also

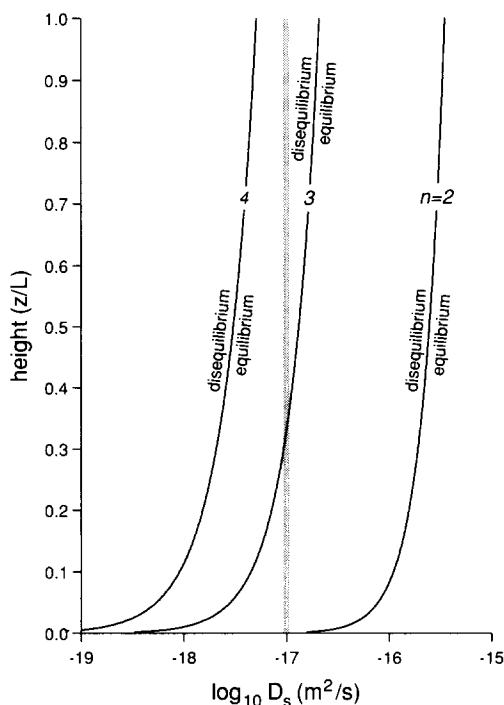


Fig. 4. Calculation of diffusion coefficient required for marginal equilibrium ( $Pe = 10$ ) as a function of  $n$  and the height above the base of the melting region, conserved flux solution. For this problem  $W_0 = 1$  cm/yr,  $d = 2$  cm,  $F_{\text{max}} = 0.25$  and  $n = 2-4$ . This problem uses the result of Appendix A that the melt flux,  $q(z)$  increases linearly with height. For a fixed value of  $n$ , larger values of the diffusion coefficient are required to maintain chemical equilibrium as the flux increases. Note also, that if melting is initially confined to tubular channels on grain boundaries, but evolves to larger spaced vein networks, then the actual profile of  $D_s^{\text{eq}}(z)$  would evolve from  $n = 2$ ,  $d \sim 1$  mm–1 cm, to perhaps  $n = 3$ ,  $d \sim 1-10$  cm. Thus, the increase in channel spacing would be offset by the change in channel geometry. To understand this quantitatively, however, requires a proper physical mechanism to explain the growth of channels.

be used to assess the effect of changing other important parameters. For example, Fig. 4 demonstrates how to estimate the potential degree of equilibrium existing in various regions in the melting column. This figure uses the result of Appendix A that the melt flux increases roughly linearly with height above the base of the melting zone and shows the value of  $D_s^{\text{eq}}(z)$  required to maintain equilibrium for a system with upwelling velocity  $W_0 = 1$  cm/yr,  $d = 2$  cm, and  $F_{\text{max}} = 0.25$ . This figure shows that, depending on the parameters, some regions of the mantle may record equilibrium while others would show disequilibrium. This result is consistent with results from uranium series disequilibrium [22]. It is also interesting to note that, for a given channel spacing, a permeable system of tubes ( $n = 2$ ) is more likely to be in disequilibrium than a system of veins ( $n = 3$ ). This may have interesting consequences for chemical signals if the form of the permeability changes with height. Most importantly this figure shows how simplistic scaling arguments can be used to estimate the behaviour of geologically reasonable problems over a wide range of parameters.

#### 4. Evaluating the scaling arguments: disequilibrium transport of trace elements

These simple scaling arguments suggest that small changes in the distribution of melt can have profound effects on the ability of the melt to remain in equilibrium with the solid. These arguments are, of course, no substitute for more complete solutions of the equations governing disequilibrium transport. Fortunately, such a solution has been recently derived for the special case of a series of planar melt channels [12]. To demonstrate that the basic physics underlying the scaling arguments is sound, this section rewrites the results of Kenyon [12] into a more compact form for direct comparison with the scaling arguments. This comparison also illustrates how simplistic arguments can be useful for interpreting the results of more complicated problems.

The disequilibrium transport problem posed in Kenyon [12], is similar to Fig. 1 but with a planar set of melt channels of width  $\delta$  separated by solid walls of width  $d$  (in Kenyon [12],  $h$  is used in

place of  $d$ ). Because of the planar geometry, this solution describes a system with permeability exponent  $n=3$ . A time periodic supply of trace element is input at the base of the layer and trace element concentration is calculated analytically as a function of position and time in both the fluid and the solid. As with the simple scaling argument, the only two processes affecting trace element evolution are horizontal diffusion in the solid and vertical transport by the fluid with the condition that the melt and solid are in local equilibrium ( $c^s = Kc^f$ ) at the boundary between the two phases. The limited interaction with the solid in this solution produces two important effects. First there is a "chromatographic" effect where the velocity of the tracer slows with respect to the melt velocity. Second, there is a damping effect where non-equilibrium interaction with the solid causes the amplitude of the trace element signal to decay.

As shown in Kenyon [12], the principal measures of these two effects are the effective velocity:

$$w_{\text{eff}} = \left[ \frac{\delta\rho_f\omega}{\delta\rho_f\omega + 2A_i D_s \rho_s K} \right] w_0 \quad (11)$$

which is the velocity of the signal with respect to the melt velocity  $w_0$  and the damping length scale (or  $e$ -folding distance):

$$z_e = \frac{\delta w_0 \rho_f}{2A_r D_s \rho_s K} \quad (12)$$

which is the length scale over which the amplitude of the signal is reduced by a factor of  $1/e$  ( $\sim 0.37$ ). Here  $\omega$  is the temporal frequency (radians  $\text{s}^{-1}$ ) of the trace element signal.  $A_i$  and  $A_r$  are functions of  $\omega$ ,  $D_s$  and  $d$  (see Kenyon [12]) with dimensions  $\text{m}^{-1}$ . These functions reflect the degree of solid/fluid interaction.  $K$  is the bulk distribution coefficient.

For direct comparison to the scaling arguments we can rewrite eqs. 11 and 12 as:

$$\frac{w_{\text{eff}}}{w_0} = \frac{1}{1 + K'A_i'(Pe')} \quad (13)$$

$$\frac{z_e}{L} = \frac{1}{K'\omega'A_r'(Pe')} \quad (14)$$

if we define

$$K' = \frac{\rho_s(1-\phi)K}{\rho_f\phi}$$

$$\omega' = \frac{\omega L}{\omega_0}$$

$$Pe' = Pe\omega'$$

and

$$A_i'(Pe')$$

$$= \sqrt{\frac{1}{2Pe'}} \left[ \frac{\sinh(\sqrt{Pe'}/2) + \sin(\sqrt{Pe'}/2)}{\sinh^2(\sqrt{Pe'}/8) + \cos^2(\sqrt{Pe'}/8)} \right]$$

$$A_r'(Pe')$$

$$= \sqrt{\frac{1}{2Pe'}} \left[ \frac{\sinh(\sqrt{Pe'}/2) - \sin(\sqrt{Pe'}/2)}{\sinh^2(\sqrt{Pe'}/8) + \cos^2(\sqrt{Pe'}/8)} \right]$$

$K'$  is the effective distribution coefficient which, for low porosities, is principally the ratio of the bulk distribution coefficient to the porosity  $\phi$ .  $\omega'$  is the signal frequency normalized by the time it takes the melt to cross the layer (i.e.  $t_{\text{adv}}$ , eq. 2). For  $\omega' \ll 1$ , temporal variations occur more slowly than the advection time.  $\omega' \gg 1$  implies very rapid trace element fluctuations. The basic scaling arguments really consider only variations with  $\omega' \sim 1$ .  $Pe'$  is the effective Peclet number for a trace element variation with frequency  $\omega'$ .

Rewriting eqs. 11 and 12 in this manner, makes the parameters that control disequilibrium transport more clear. For example, the effective transport velocity, eq. 13, depends only on  $K'$  and  $Pe'$ . Figure 5 illustrates this relationship and shows that the transition between equilibrium and disequilibrium transport occurs at  $Pe' \approx 10$ , for all  $K'$ , as presumed in the scaling arguments. For  $Pe' \ll 10$ , the tracer velocity approaches the equilibrium transport velocity  $1/(1+K')$  in accordance with previous results [6,17]. Note the velocity actually depends on  $K'$ , not just the distribution coefficient. As disequilibrium becomes more important, the effective velocity approaches the melt velocity  $w_0$ . However, unless  $Pe'$  is very large, some chromatographic effect is expected.

The basic results of the scaling arguments are readily seen in Fig. 5. In general,  $Pe'$  is most sensitive to the channel spacing  $d$ . This solution,

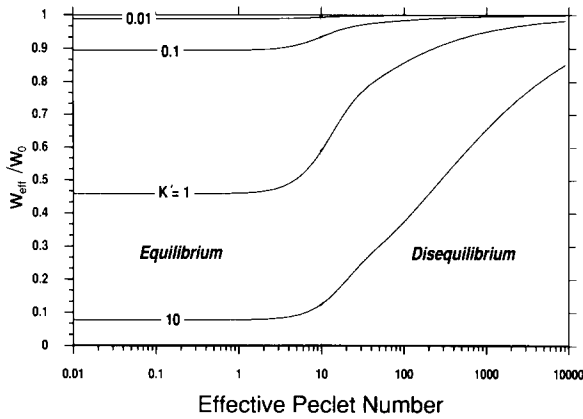


Fig. 5. Effective velocity of a trace element as a function of the effective Peclet number and effective partition coefficient  $K'$  (rescaled from the solution of Kenyon [12]). This figure shows that for  $Pe' \leq 10$ , variations in trace element concentration travel near the equilibrium effective velocity  $1/(1 + K')$  relative to the melt velocity. For  $Pe' \geq 10$ , the effective velocity approaches the melt velocity. For the simple constant porosity solution with fixed  $\omega' = 1$ ,  $Pe' \propto d^4$  and therefore an order of magnitude increase in channel spacing produces a 4 order of magnitude increase in  $Pe'$ .

however, also suggests that the frequency of trace element variation will affect the ability to maintain equilibrium. For the simplest constant porosity scaling argument we implicitly assumed that variations were comparable to the advection time (i.e.  $\omega' \sim 1$ ). For constant porosity and constant  $\omega'$ ,  $K'$  remains constant with channel spacing and  $Pe' \propto d^4$ . This result should be contrasted with the solution presented in Kenyon [12] which assumes constant angular frequency  $\omega$ , rather than constant  $\omega'$ . In this case  $Pe' \propto d^2$ . For the constant flux argument,  $K'$  will generally increase with increasing channel spacing (as  $\phi$  decreases), and overall changes in the transport velocity will be less pronounced. Nevertheless, if for any circumstance  $K'$  and  $Pe'$  can be determined, the velocity and degree of equilibration are readily estimated.

The behaviour of trace element damping is somewhat more complicated than that of the effective velocity. Equation 14 shows that the damping length scale depends on three parameters  $K'$ ,  $\omega'$  and  $Pe'$ . Figure 6 shows contours of  $K'z_e/L$  as a function of frequency and Peclet number. In general, for a constant  $K'$ , strong damping occurs when the damping length scale is

comparable or smaller than the layer depth (i.e.  $z_e/L \leq 1$ ). For  $z_e/L \gg 1$  damping is negligible. Thus for  $K' = 100$ , the contour labeled 100 in Fig. 6 marks the boundary where damping becomes severe. The effect of changing  $\omega'$  and  $Pe'$  on the damping length scale is also apparent but is different in two separate regimes. In the equilibrium transport regime ( $Pe' \ll 10$ ) an increase in either frequency or  $Pe'$  causes increased damping as the non-equilibrium interaction between solid and liquid becomes more pronounced. For  $Pe' \gg 10$ , however, further increases in  $Pe'$  cause a decrease in damping as the tracer in the liquid has a decreasing amount of interaction with the solid. Thus it is possible that very rapid variations in quite incompatible elements can be preserved throughout the transport process, while more compatible element variations can be damped

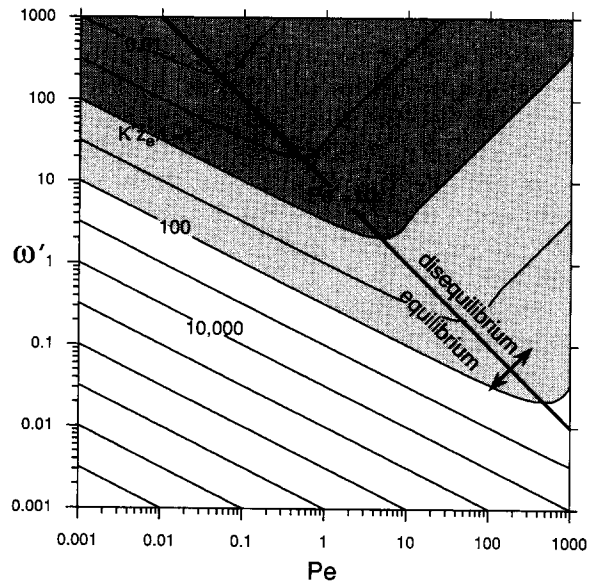


Fig. 6. Contours of the damping length scale (actually  $K'z_e/L$ ) as a function of the Peclet number and scaled frequency  $\omega'$ . Severe damping occurs for  $z_e/L \leq 1$ . Thus the dark shaded region is the region of significant damping for trace elements with effective distribution coefficient  $K' = 1$ . For  $K' = 100$ , the field expands to include the lighter grey region. The line marked  $Pe' = 10$  marks the boundary between equilibrium and disequilibrium transport (see Fig. 5). For  $Pe' \ll 10$  an increase in  $Pe'$  or frequency produces more pronounced damping. For  $Pe' \gg 10$ , however, the damping length is constant for increasing  $Pe'$  (more precisely for constant  $Pe'/\omega'$ ), as the more rapid transport reduces the interaction between solid and liquid.

out. This damping behaviour is not apparent from the simple scaling arguments but may be a significant effect in the mantle.

While the more general behaviour of trace elements is more complicated than suggested by the simplest scaling arguments, the basic physics of the scaling arguments is still valid. The two principal processes governing chemical transport are advection by the melt and diffusional exchange with the solid. The Peclet number is still the most important parameter for determining whether chemical equilibrium is achieved and the Peclet number is extremely sensitive to small changes in the distribution of melt.

### 5. The requirements for Darcy flow

The preceding arguments suggest that the ability to maintain chemical equilibrium depends strongly on the spacing of the melt channels. The question remains however, whether the presence or absence of chemical equilibrium places any strong constraints on the physics of melt transport. This section clarifies the requirements for which the equations governing flow in deformable permeable media are valid, and shows that the assumption that Darcy's law is valid is justified for a large range of geologically reasonable parameters.

The key to understanding the relationship between Darcy flow and chemical equilibrium is to understand that Darcy's law, and in fact the entire system of equations governing flow in deformable permeable media, are macroscopic, continuum equations that describe the flow of melt averaged over many melt channels. Detailed analysis of the governing equations [23,24] shows that the principal assumptions inherent in these equations are that the two-phase medium is viscously deformable and permeable at some scale. Clearly, these two conditions are required for these equations to be consistent with mantle convection and to allow the melt to separate from the solid. These equations, however, make no *a-priori* assumptions about the microscopic distribution of melt channels and it is this feature that allows Darcy's law to be applicable to systems ranging from flow in granular materials to flow in large scale fracture networks.

Considerable work has considered the conditions under which Darcy's law remains valid (e.g. [21,25]). For flow in porous media with an interconnected series of melt channels, the principal requirements are that melt flow within the channels is "laminar" and that variations in melt content occur on a scale much larger than the channel spacing, i.e. that there are a sufficient number of channels in the region of interest so that the averaging process is meaningful.

Laminar flow in porous media requires that the flow of melt within the channels is sufficiently slow to be dominated by viscous forces. The Reynolds number appropriate for porous media:

$$Re = \frac{\rho_f q d}{\mu} \quad (15)$$

is a measure of the ratio of inertial forces to viscous forces. Bear [21] states that "In practically all cases, Darcy's law is valid as long as the Reynolds number based on average grain diameter does not exceed some value between 1 and 10." For  $Re \ll 10$ , the flux increases linearly with pressure gradients. For larger  $Re$  there is a transition from Darcy flow to a non-linear regime where inertial forces become more important. Finally, for  $Re \geq 100-1000$  the flow in the channels actually becomes turbulent.

Using eq. 10 for an estimate of the maximum melt flux beneath ridges with  $F_{\max} = 0.3$ ,  $W_0 = 10$  cm yr<sup>-1</sup> and the values of the other parameters from Table 1 gives  $Re \approx 3 \times 10^{-7} d$  where  $d$  is in metres. Thus even with order of magnitude variations in the channel spacing or melting rate, the melting rates beneath ridges are simply too slow to produce a melt flux large enough for inertial effects to become important. As laminar flow is expected, the only additional way for Darcy's law to break down is for the channel spacing to be comparable to the size of the region of melt extraction. However, from the previous sections, disequilibrium requires only a vein network with channel spacings on the order of 10 cm to 1 m to completely remove the melt from contact with the solid residue. Consequently, even strong chemical disequilibrium does not imply a violation of the requirements for Darcy flow. Put another way, the potential existence of chemical disequilibrium may rule out a grain scale permeability for at



least some regions of the mantle; however, the overall description of how melt moves in a permeable medium remains the same.

## 6. Discussion

The purpose of the simple scaling arguments given here is to clarify the fundamental scalings inherent in the processes governing the chemistry and motion of melts. These arguments show that the presence or absence of chemical equilibrium is extremely sensitive to the microscopic distribution of melt and solid. If disequilibrium transport is responsible for the gross chemical signature of mantle melts, it does not require unusually large melt “channels” or dikes or extremely short extraction times (i.e. weeks to years). Rather, these arguments suggest that even a coarse vein network with melts percolating at metres per year can produce severe disequilibrium. Given the extreme slowness of solid state diffusion, these results should not be that surprising. The second point to stress is that these arguments are self-consistent with the physics of flow in deformable permeable media. Because the governing equations are macroscopic, continuum equations, they are equally valid for vein networks as for a grain scale permeability. If melt flow is dominated by some form of vein network, then the constitutive relationships between permeability and porosity will change as may the matrix rheology. Nevertheless, as long as these constitutive relationships can be formulated, they are readily accommodated by the general form of the governing equations which only require that the two-phase system is permeable and deformable.

Of course, if melt flow is controlled by veins rather than grains, then some mechanism is still required to develop and maintain such channels in the face of the homogenizing processes of mantle convection and textural equilibration. There must also be some mechanism for melt migration from the four phase boundaries where melt is produced to the channels. To date, there has been only one mechanism proposed for developing a channeling instability. Using the equations for flow in deformable porous media, Stevenson [26] suggests that if the mantle is deforming and the crystalline matrix is porosity softening, then high porosity channels can develop

oriented parallel to the principal stress axis. However, this rather intriguing solution has only been demonstrated for initial infinitesimal perturbations within a fairly restricted geometry and it still needs to be shown for the fully deforming, non-linear case.

Finally, while disequilibrium transport is reasonable for the earth, we still have little understanding of the simplest equilibrium transport in physically consistent mantle flows. While most geochemical models assume some degree of equilibration these models do not yet include the physics of melt transport. It is possible, therefore, that at least some of the observed geochemical variations that have been attributed to disequilibrium may actually be explained using proper mass conservative transport solutions. Fortunately, given our better physical understanding of magma migration, including the behaviour of trace elements in equilibrium or complete disequilibrium is straightforward. While there is much work to be done, the tools are now available. Using a robust macroscopic description of the physics of magma migration, coupled with a theory governing both equilibrium and disequilibrium chemistry, we now have the opportunity to develop a more quantitative and testable theory of chemical transport in the mantle.

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## Appendix A: Estimating steady flux beneath ridges

Steady state conservation of mass for the melt flux is governed by:

$$\nabla \cdot \rho_f \phi \mathbf{v} = \Gamma \quad (16)$$

where  $\Gamma$  is the melting rate and  $\mathbf{q} = \phi \mathbf{v}$  is the volume flux of melt. If melting at ridges is approximately adiabatic then the melting rate is roughly proportional to the upwelling rate of the solid mantle. Thus a good approximation to the

melting rate is:

$$\Gamma \sim \frac{\rho_s F_{\max} W_0}{L} \quad (17)$$

where  $W_0$  is the upwelling rate,  $F_{\max}$  is the maximum degree of melting on axis and  $L$  is the depth of the melting zone. Substituting eq. 17 into eq. 16, assuming a roughly 1-D regime directly beneath the ridge axis and integrating yields:

$$q(z) \approx \frac{\rho_s F_{\max} W_0 z}{\rho_f L} \quad (18)$$

i.e. the melt flux increases linearly with height and is independent of the permeability  $k_\phi$ . Clearly, the maximum flux is  $q_{\max} = q(L)$ .

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