ON DIFFUSION IN HETEROGENEOUS MEDIA

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ABSTRACT.   Diffusion in heterogeneous solid media has been investigated for over forty years. However, the derived equations for bulk (or effective) diffusivity used similarity argument between diffusion and other physical properties such as electrical and thermal conductivity, and hence either implicitly or explicitly assumed that the concentrations are continuous across phase boundaries. That is, these derived relations, which have permeated through the literature and textbooks, can only be applied when the partition coefficients of the component between every pair of phases in the medium is 1, which is rarely the case. In this work, we include the effect of partitioning between different phases and present the method to derive the equations to relate bulk diffusivity to individual-phase diffusivities in heterogeneous media.

Key words: Diffusion, heterogeneous media, multi-mineral rocks, multi-phase media, composite materials, kinetics, porous rocks

INTRODUCTION

One of the frontiers in geochemical kinetics is to understand diffusion in heterogeneous media (Watson and Baxter, 2007), including multi-phase solids (such as rocks, multi-phase metals, and composite materials), multi-grain single-phase solid in which grain boundary diffusion may contribute significantly to bulk diffusion, and porous materials (such as plants, soil, rock with partial melt or fluid, sediment with fluid). Diffusion and transport in heterogeneous media are encountered in geology, chemistry, cosmochemistry, engineering, manufacturing, and daily life, in processes such as volatile diffusion in mantle rocks, elemental diffusion in a slowly cooled planetary core with two-phase Widmanstatten texture, diffusion in composite thin films (Sankur and Gunning, 1989), diffusion in a mixture of two immiscible melts, elemental diffusion during mantle partial melting and in melt mush, drying and dyeing of textiles, transport of air and moisture in soils, drying of paint, wood, and concrete, diffusion of gases in rubber, movement of sap in plants, and transport in other high and low-temperature porous media. The focus in this work is the effective or bulk diffusivity in a heterogeneous medium, not diffusion profiles in the individual phases. In a heterogeneous medium, when the diffusion distance is less than the grain size, the diffusion cannot be treated as bulk diffusion, and bulk diffusivity cannot be defined. When the diffusion distance in the medium is much larger than grain sizes, which means that the time scale under consideration is much longer than the maximum of all x_i^2/D_i where x_i is the radius of phase i and D_i is diffusivity in phase i, diffusion in a heterogeneous medium can be treated as bulk diffusion. Hence, bulk diffusivity approach applies best to components that diffuse rapidly in all phases involved. For example, for diffusion in mantle rocks, the approach works best for neutral species (light noble gases, molecular water, *et cetera*) and univalent ions with small radius (Shannon, 1976; Zhang and Xu, 1995; Baxter, 2010; Farver, 2010; Zhang and others, 2010) and some divalent ions (Brady and Cherniak, 2010). When diffusion in some phases can be ignored completely, bulk diffusion treatment can also be applied.

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Barrer (1968) used the similarity between diffusion and other properties such as electrical and thermal conduction to derive the relations between the bulk (or effective) diffusivity of multi-phase materials (heterogeneous media) and individual-phase diffusivities using analogous solutions for conductivity, elasticity, *et cetera* available in numerous classical works (for example, Maxwell, 1873, p. 365; Hashin, 1962; Hashin and Shtrikman, 1962a, 1962b, 1962c, 1963a; Hill, 1963; and many references cited in Barrer, 1968). Unfortunately, as will be shown in this report, the similarity approach by Barrer (1968) only applies to the special case when the partition coefficient between every pair of phases is 1. In some sections of Barrer (1968), partition of elements is considered but the derived relations contained undetermined coefficients so that they are not directly useful. The similarity approach of Barrer (1968) has permeated through the literature and textbooks for treating diffusion in solid multi-phase materials, with unity partition coefficients either implicitly or explicitly (for example, Bell and Crank, 1974; Crank, 1975; Brady, 1983; Cussler, 1997, section 6.5.2). In his well-known book *Mathematics of Diffusion,* Crank (1975, Chapter 12) summarized relations between bulk diffusivity of composite materials (multi-phase media) and individual-phase diffusivities, following the approach of Barrer (1968). In the geologic literature, Brady (1983) introduced the various relations between bulk diffusivity and individual-phase diffusivities using a similar approach. When Torquato and others (1999) formulated sophisticated algorithm to calculate the effective electrical/thermal conductivity and diffusivity of composite materials using digitized representations, they adopted the same analogy for diffusivity. These diffusivity relations have often been applied by later workers in geology and in other branches of sciences (for example, Care and Herve, 2004; Sun and others, 2011; Youssef and others, 2011).

A key difference between mass diffusion of an element and heat diffusion, which renders the previous similarity approach non-general, is as follows. Even though heat conduction and mass diffusion are characterized by a similar flux equation ($\mathbf{J}_{\text{heat}} = -k\nabla T$ for heat conduction and $\mathbf{J}_{\text{mass}} = -D\nabla C$ for diffusion), in heat conduction, T (temperature) is continuous across phase boundaries, whereas in diffusion, C (concentration of a component) is usually not continuous across phase boundaries. The concentration of a component in one phase could be much larger or smaller than that in another phase, and the ratio of the concentration in one phase to that in the other phase at equilibrium is the partition coefficient, which can be orders of magnitude different from 1. The concentration in each phase plays a major role in controlling the contribution by the phase to the bulk diffusive flux and hence the bulk diffusivity. For example, even if the diffusivity of a component is high in a phase, if the concentration of the component in the phase is negligibly small, diffusion in that phase is not expected to contribute significantly to the bulk diffusion flux, meaning that it does not contribute much to the bulk diffusivity. Hence, previous models for diffusivity in composite materials or multi-mineral rocks, no matter how sophisticated, are not general, and can only be applied to the rare case when the partition coefficient is 1 between every pair of phases. On the other hand, authors who discuss diffusion in porous media or the contribution of grain boundary diffusion to the bulk diffusivity often derive the relations directly without resorting to the similarity approach, and hence often obtained more realistic equations. These relations will also be discussed in this work. In addition, Kalnin and others (2002) incorporated the effect of partitioning for diffusion in a matrix with inclusions.

Realizing that the "potential" (the property inside the grad, such as T in grad T) must be continuous, the correct similarity relation can be obtained if the diffusive flux is expressed as the gradient of the chemical potential μ, or equivalently $μ/(RT)$ (dimensionless) at a constant temperature (DeGroot and Mazur, 1962; Kirkaldy and Young, 1987; Zhang, 2008; Lesher, 2010):

$$\mathbf{J}_{\text{bulk}} = -M\nabla \frac{\mu}{RT}, \qquad (1)$$

where M (referred to as either mobility or phenomenological coefficient, which depends on concentration, as will be clear later) with a unit of $\text{kg}/(\text{m}\cdot\text{s})$ or $\text{mol}/(\text{m}\cdot\text{s})$ is a scalar for an isotropic medium and second order tensor for an anisotropic medium, T is temperature, and R is the universal gas constant. M in equation (1) is not ionic velocity per unit electrical field (for example, Zhang, 2008), but is similar to that defined in Kirkaldy and Young (1987) except for the constant RT, which is introduced for simplicity in subsequent treatment since we focus on isothermal diffusion. Because chemical potential is continuous across phase boundaries assuming interface equilibrium, the relation between the bulk (or effective) mobility of a multi-phase medium and individual-phase mobilities can be written down by analogy to other properties such as electrical conductivity, thermal conductivity, *et cetera*. Because mobility and diffusivity are related, the corresponding equations for bulk diffusivity of a multi-phase medium can also be derived. To emphasize, *bulk mobility of a heterogeneous medium can be generally related to individual-phase mobilities using analogy to conductivity, but bulk diffusivity cannot*. In this report, we derive the equations for bulk diffusivity in various heterogeneous media using the similarity between mobility and conductivity. For some geometry, the bulk diffusivity is also directly derived (Appendices 1 and 2), to verify our approach using similarity between mobility and conductivity.

In this work, individual-phase diffusivity means tracer or effective binary diffusivity (Zhang, 2010) of a given component in an isotropic phase, not diffusivity matrix for multi-component diffusion, nor diffusivity tensor in an anisotropic diffusion medium. Obtaining the isotropic diffusivity of randomly oriented grains of an anisotropic material will be summarized in the last section. For a heterogeneous medium, bulk (or effective) diffusivity is used to describe overall diffusion. When grain boundaries are present, one way to include the contribution of diffusion through grain boundaries is to treat all types of grain boundaries on average as a single separate "phase," or different types of interface boundaries as separate "phases."

DEFINITION OF BULK MOBILITY AND BULK DIFFUSIVITY, AND RELATIONS BETWEEN THEM

In this work, interface equilibrium between adjacent grains is assumed so that μ is continuous. Hence, the concentration ratio of an element in two contacting phases at the boundary is treated as a constant (partition coefficient).

The bulk mobility (M_{bulk}) and bulk diffusivity (D_{bulk}) are defined by the following equations:

$$\mathbf{J}_{\text{bulk}} = -M_{\text{bulk}}\nabla \frac{\mu_{\text{ave}}}{RT}, \qquad (2a)$$

$$\mathbf{J}_{\text{bulk}} = -D_{\text{bulk}}\nabla C_{\text{ave}}, \qquad (2b)$$

where μ_{ave} and C_{ave} are the average chemical potential and concentration at a "point" (meaning a representative volume element containing hundreds or more individual grains, so that meaningful C_{ave} can be obtained), $C_{\text{ave}} = \Sigma\phi_i C_i$ with ϕ being the volume fraction and subscript i meaning phase i, and $\mathbf{J}_{\text{bulk}}$ is the bulk diffusive mass flux (mass per unit area per unit time). Because μ is continuous, $\mu_{\text{ave}} = \mu_i$ for every phase i at the given point in a heterogeneous medium. The values of μ_{ave} and C_{ave} depend on the position (x, y, z). For simplicity of the equations, the unit of C is kg/m^3 or mol/m^3. If mass fraction w is used (as often in literature), then density of each phase will appear, that is, C_i in each equation would be replaced by $\rho_i w_i$ where ρ_i is density of phase i and w_i is mass fraction of the given component in phase i.

It is necessary to relate the mobility and diffusivity. From $\mathbf{J}_i = -M_i\nabla[\mu_i/(RT)] = -D_i\nabla C_i$, the general relation between M and D inside any phase i can be obtained as follows (following, for example, Kirkaldy and Young, 1987, p.14):

$$D_i = M_i\frac{d\mu_i/(RT)}{dC_i}. \tag{3}$$

The chemical potential at any point (representative volume element) can be written as:

$$\mu_i = \mu_i^0(T, P) + RT\ln(\gamma_i C_i), \tag{4}$$

where T and P are temperature and pressure, μ_i^0 is the chemical potential of the component at the standard state (that is, when $\gamma_i C_i = 1$), and γ_i is the activity coefficient. Note that subscript i means phases, not components. Combining equations (3) and (4), the following can be obtained:

$$D_i = \frac{M_i}{C_i}\left[1 + \frac{d(\ln \gamma_i)}{d\ln(C_i)}\right]. \tag{5}$$

Because the diffusion flux equation (that is, Fick's law) $\mathbf{J} = -D\nabla C$ only applies to roughly ideal solutions (for highly non-ideal solutions, it is necessary to include the effect of γ in the flux equation, for example, Zhang, 1993, 2008, 2010; Lesher, 2010), equation (5) is also simplified for roughly ideal solutions with γ being roughly constant, leading to the following equation for every phase i:

$$M_i = D_i C_i. \tag{6}$$

In addition to the above equation relating M and D in each phase, the relation between M_{bulk} and D_{bulk} is also required. From equations (2a) and (2b), because $\mu_{\text{ave}} = \mu_A$, we have:

$$\mathbf{J}_{\text{bulk}} = -M_{\text{bulk}}\nabla\frac{\mu_{\text{ave}}}{RT} = -M_{\text{bulk}}\nabla\frac{\mu_A}{RT}, \tag{7}$$

$$\mathbf{J}_{\text{bulk}} = -D_{\text{bulk}}\nabla C_{\text{ave}} = -D_{\text{bulk}}\nabla[C_A(\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots)], \tag{8}$$

where subscripts A, B, and C mean phases, and $K_{B/A} = C_B/C_A$ is the partition coefficient. Assuming constant ϕ_i and $K_{i/A}$, equation (8) becomes:

$$\mathbf{J}_{\text{bulk}} \approx -D_{\text{bulk}}(\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots)\nabla C_A. \tag{9}$$

Comparing equations (7) and (9) leads to:

$$M_{\text{bulk}} = D_{\text{bulk}}(\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots)\frac{1}{d\dfrac{\mu_A}{RT}\bigg/dC_A}. \tag{10}$$

Carrying out the differentiation assuming roughly ideal solutions leads to:

$$M_{\text{bulk}} = D_{\text{bulk}}(\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots)C_A = D_{\text{bulk}}\sum\phi_i C_i. \tag{11}$$

That is, for constant ϕ_i and K_i and assuming roughly ideal solutions for each phase, we have:

$$M_{\text{bulk}} \approx D_{\text{bulk}}C_{\text{ave}}. \tag{12}$$

Using equations (6) and (12), if M_{bulk} can be related to M_i, then D_{bulk} can also be related to D_i.
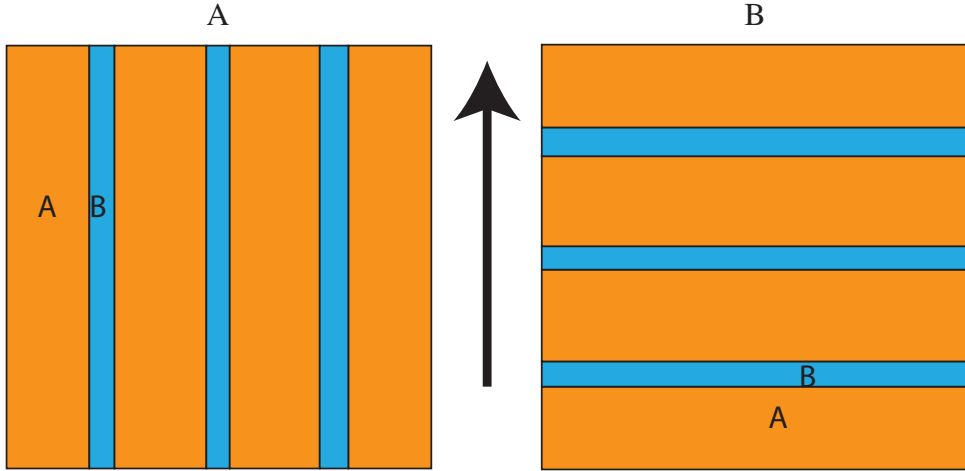
Fig. 1. Two cases of phase alignment. The arrow in the middle indicates the diffusion direction. The first case (left-hand side) is referred to as parallel alignment and the second (right-hand side) is referred to as series alignment. From Brady (1983).

On the other hand, if the phase proportions vary along the diffusion path (such as variable degree of partial melting) but the partition coefficient does not vary, then equation (8) in a two-phase medium becomes

$$\mathbf{J}_{\text{bulk}} = -D_{\text{bulk}}(\phi_A + \phi_B K_{B/A})\nabla C_A + D_{\text{bulk}}C_A(K_{B/A} - 1)\nabla\phi_A. \tag{13}$$

The relation between M_{bulk} and D_{bulk} for roughly ideal solutions becomes:

$$M_{\text{bulk}} \approx D_{\text{bulk}}\left[C_{\text{ave}} - (C_B - C_A)\frac{\text{d}\phi_A}{\text{d}(\ln C_A)}\right], \tag{14}$$

where $\text{d}\phi_A/\text{d}(\ln C_A)$ is taken along the direction of diffusion. It can be seen that the relevant relations are complicated when phase proportions vary.

DIFFUSION IN A MULTIPHASE MEDIUM MADE OF DIFFUSIONALLY ISOTROPIC PHASES

As shown by previous workers (for example, Brady, 1983), the bulk mobility of a multiphase medium depends on the alignment of the individual grains. Two special and simple cases are shown in figures 1A and 1B, referred to as parallel and series alignments, respectively.

Bulk Diffusivity for Parallel Alignment

For parallel alignment (fig. 1A), the bulk mobility of a two-phase medium can be found using the solution in Hill (1963) and the similarity:

$$M_{\text{bulk}}^{\text{parallel}} = M_{AB}^{\text{parallel}} = \phi_A M_A + \phi_B M_B. \tag{15}$$

Replacing equations (6) and (12) into equation (15), we get:

$$D_{\text{bulk}}^{\text{parallel}} = \frac{\phi_A C_A D_A + \phi_B C_B D_B}{\phi_A C_A + \phi_B C_B} = \frac{\phi_A D_A + \phi_B K_{B/A}D_B}{\phi_A + \phi_B K_{B/A}}. \tag{16}$$

This equation differs significantly from $D_{\text{bulk}}^{\text{parallel}} = \phi_A D_A + \phi_B D_B$ in Barrer (1968), Crank (1975), and Brady (1983), and the differences increase when the difference

between C_A and C_B increases. Only when $C_A = C_B$, would equation (16) be the same as that in the earlier works.

To confirm our approach, we show in Appendix 1 that equation (16) can be directly derived. The independent derivation verifies our mobility approach.

It is straightforward to extend equation (16) to an N-phase medium as:

$$D_{\text{bulk}}^{\text{parallel}} = \frac{\sum \phi_i C_i D_i}{\sum \phi_i C_i} = \frac{\phi_A D_A + \phi_B K_{B/A} D_B + \phi_C K_{C/A} D_C + \cdots}{\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots}, \tag{17}$$

where summation is over all phases.

If mass fractions are used as concentrations, then C_i is replaced by $\rho_i w_i$ (where ρ_i is density of phase i) in equation (17), leading to:

$$D_{\text{bulk}}^{\text{parallel}} = \frac{\sum \phi_A \rho_i w_i D_i}{\sum \phi_i \rho_i w_i} = \frac{\phi_A \rho_A D_A + \phi_B \rho_B K'_{B/A} D_B + \phi_C \rho_C K'_{C/A} D_C + \cdots}{\phi_A \rho_A + \phi_B \rho_B K'_{B/A} + \phi_C \rho_C K'_{C/A} + \cdots}, \tag{18}$$

where $K'_{B/A} = w_B / w_A$ (partition coefficient expressed as ratio of mass fractions). If mole fractions rather than mass fractions are used as concentrations, the density ρ_i would be molar density (mol/m^3, or the inverse of the molar volume) of each phase, and the partition coefficient would be the mole fraction ratio in a pair of phases.

Bulk Diffusivity for Series Alignment

For series alignment (fig. 1B), the bulk mobility of the two-phase rock can be expressed as follows (Hill, 1963):

$$\frac{1}{M_{\text{bulk}}^{\text{series}}} = \frac{\phi_A}{M_A} + \frac{\phi_B}{M_B}. \tag{19}$$

Replacing equations (6) and (12) into the above equation leads to:

$$\frac{1}{D_{\text{bulk}}^{\text{series}}} = (\phi_A C_A + \phi_B C_B)\left(\frac{\phi_A}{C_A D_A} + \frac{\phi_B}{C_B D_B}\right), \tag{20}$$

which may also be derived directly for the case of steady-state diffusion (Appendix 2), verifying our mobility approach again.

Bulk diffusivity values obtained from equation (20) can differ from those from Barrer (1968), Crank (1975), and Brady (1983) by many orders of magnitude. For example, for a hypothetical case of a two-phase medium with $C_B = 2.5 \times 10^{-4} \, C_A$, $D_A = D_B$, and $\phi_A = \phi_B$, equation (20) leads to $D_{\text{bulk}}^{\text{series}} = 10^{-3} D_A$, whereas the old expressions would give $D_{\text{bulk}}^{\text{series}} = D_A$, three orders of magnitude different from the correct value.

Equation (20) can be readily extended to multi-phase media:

$$\frac{1}{D_{\text{bulk}}^{\text{series}}} = (\sum \phi_i C_i)\left(\sum \frac{\phi_i}{C_i D_i}\right), \tag{21}$$

which can also be written in terms of partition coefficients:

$$\frac{1}{D_{\text{bulk}}^{\text{series}}} = (\phi_A + \phi_B K_{B/A} + \phi_C K_{C/A} + \cdots)\left(\frac{\phi_A}{D_A} + \frac{\phi_B}{K_{B/A} D_B} + \frac{\phi_C}{K_{C/A} D_C} + \cdots\right), \tag{22}$$

or expressed using mass fractions as concentrations:

$$\frac{1}{D_{\text{bulk}}^{\text{series}}} = (\sum \phi_i \rho_i w_i)\left(\sum \frac{\phi_i}{\rho_i w_i D_i}\right) = (\phi_A \rho_A + \phi_B \rho_B K'_{\text{B/A}} + \cdots)\left(\frac{\phi_A}{\rho_A D_A} + \frac{\phi_B}{K'_{\text{B/A}} \rho_B D_B} + \cdots\right).$$

(23)

Hashin-Shtrikman Bounds and Summary

In addition to parallel and series alignments discussed above, there are other rigorous estimates on the bulk mobility, including Maxwell (1873) and the well-known Hashin-Shtrikman upper and lower bounds (Hashin, 1962; Hashin and Shtrikman, 1962a, 1962b, 1962c, 1963a). Our approach above can be used to derive diffusivity relations corresponding to these and all other conductivity and permeability relations (for example, Tsao, 1961; Cheng and Vachon, 1969; Tinga and others, 1973; Landauer, 1978). For example, the relations derived by Kalnin and others (2002; their eqs 24 and 28) can be readily obtained. Below, we specifically provide the upper and lower bounds of bulk diffusivity corresponding to the Hashin-Shtrikman bounds for permeability or conductivity.

For a heterogeneous medium of N phases with mobilities $M_1 > M_2 > \cdots > M_N$, the value of M_{bulk} satisfies:

$$M_{\text{HS}}^{\text{upper}} \geq M_{\text{bulk}} \geq M_{\text{HS}}^{\text{lower}},$$

(24)

where $M_{\text{HS}}^{\text{upper}}$ and $M_{\text{HS}}^{\text{lower}}$ are the Hashin-Shtrikman upper and lower bounds, and are given by (Milton, 2002, p.458; Liu 2010):

$$M_{\text{HS}}^{\text{upper}} = M_1 + \frac{d}{\dfrac{1}{\displaystyle\sum_{i=2}^{N} \dfrac{\phi_i}{\dfrac{d}{M_i - M_1} + \dfrac{1}{M_1}}} - \dfrac{1}{M_1}},$$

(25)

$$M_{\text{HS}}^{\text{lower}} = M_N + \frac{d}{\dfrac{1}{\displaystyle\sum_{i=1}^{N-1} \dfrac{\phi_i}{\dfrac{d}{M_i - M_N} + \dfrac{1}{M_N}}} - \dfrac{1}{M_N}},$$

(26)

where $d = 3$ is the dimension of the space. Combining the above two equations with equations (6) and (12), the upper and lower bounds of D_{bulk} can be written as:

$$D_{\text{HS}}^{\text{upper}} = \frac{D_1 C_1}{\displaystyle\sum_{i=1}^{N} \phi_i C_i} + \frac{d}{\left[\dfrac{1}{\displaystyle\sum_{i=2}^{N} \dfrac{\phi_i}{\dfrac{d}{D_i C_i - D_1 C_1} + \dfrac{1}{D_1 C_1}}} - \dfrac{1}{D_1 C_1}\right] \displaystyle\sum_{i=1}^{N} \phi_i C_i},$$

(27)

TABLE 1

Comparison of bulk mobility and diffusivity relations in two-phase media

Geometry	Mobility M	Diffusivity D
Parallel (fig. 1A)	$M_{\text{bulk}}^{\text{parallel}} = \phi_A M_A + \phi_B M_B$	$D_{\text{bulk}}^{\text{parallel}} = \dfrac{\phi_A C_A D_A + \phi_B C_B D_B}{\phi_A C_A + \phi_B C_B}$
Series (fig.1B)	$\dfrac{1}{M_{\text{bulk}}^{\text{series}}} = \dfrac{\phi_A}{M_A} + \dfrac{\phi_B}{M_B}$	$\dfrac{1}{D_{\text{bulk}}^{\text{series}}} = (\phi_A C_A + \phi_B C_B)\left(\dfrac{\phi_A}{C_A D_A} + \dfrac{\phi_B}{C_B D_B}\right)$
Hashin-Shtrikman lower bound	$M_{\text{HS}}^{\text{lower}} = M_B + \dfrac{\phi_A}{\dfrac{1}{M_A - M_B} + \dfrac{\phi_B}{3 M_B}}$	$D_{\text{HS}}^{\text{lower}} = \dfrac{C_A D_A + 2(\phi_A C_A D_A + \phi_B C_B D_B)}{(\phi_A C_A + \phi_B C_B)\left(2 + \phi_A + \phi_B \dfrac{C_A D_A}{C_B D_B}\right)}$
Hashin-Shtrikman upper bound	$M_{\text{bulk}}^{\text{upper}} = M_A + \dfrac{\phi_B}{\dfrac{1}{M_B - M_A} + \dfrac{\phi_A}{3 M_A}}$	$D_{\text{HS}}^{\text{upper}} = \dfrac{C_B D_B + 2(\phi_A C_A D_A + \phi_B C_B D_B)}{(\phi_A C_A + \phi_B C_B)\left(2 + \phi_B + \phi_A \dfrac{C_B D_B}{C_A D_A}\right)}$
Maxwell (1873, p. 365)	$M_{\text{bulk}}^{\text{Maxwell}} = M_A + \dfrac{\phi_B}{\dfrac{1}{M_B - M_A} + \dfrac{2\phi_A}{3 M_A}}$	$D_{\text{bulk}}^{\text{Maxwell}} = \dfrac{\phi_A C_A D_A + (2 + \phi_B) C_B D_B}{\left(1 + 2\phi_B + 2\phi_A \dfrac{C_B D_B}{C_A D_A}\right)(\phi_A C_A + \phi_B C_B)}$

The Hashin-Shtrikman bounds are given under the condition of $M_A > M_B$, or $D_A C_A > D_B C_B$. The Maxwell (1873) relation is for dilute dispersion of spherical B in matrix A.

$$D_{\text{HS}}^{\text{lower}} = \frac{D_N C_N}{\sum\limits_{i=1}^{N} \phi_i C_i} + \frac{d}{\left[\dfrac{1}{\sum\limits_{i=1}^{N-1} \dfrac{\phi_i}{D_i C_i - D_N C_N} + \dfrac{1}{D_N C_N}} - \dfrac{1}{D_N C_N}\right] \sum\limits_{i=1}^{N} \phi_i C_i}. \tag{28}$$

If mass fractions are used, the equations are:

$$D_{\text{HS}}^{\text{upper}} = \frac{D_1 \rho_1 w_1}{\sum\limits_{i=1}^{N} \phi_i \rho_i w_i} + \frac{d}{\left[\dfrac{1}{\sum\limits_{i=2}^{N} \dfrac{\phi_i}{D_i \rho_i w_i - D_1 \rho_1 w_1} + \dfrac{1}{D_1 \rho_1 w_1}} - \dfrac{1}{D_1 \rho_1 w_1}\right] \sum\limits_{i=1}^{N} \phi_i \rho_i w_i}, \tag{29}$$

$$D_{\text{HS}}^{\text{lower}} = \frac{D_N \rho_N w_N}{\sum\limits_{i=1}^{N} \phi_i \rho_i w_i} + \frac{d}{\left[\dfrac{1}{\sum\limits_{i=1}^{N-1} \dfrac{\phi_i}{D_i \rho_i w_i - D_N \rho_N w_N} + \dfrac{1}{D_N \rho_N w_N}} - \dfrac{1}{D_N \rho_N w_N}\right] \sum\limits_{i=1}^{N} \phi_i \rho_i w_i}. \tag{30}$$

In equations (27) to (30), the sequence of $D_1, D_2, \cdots$ and D_N is such that $M_1 > M_2 > \cdots > M_N$.

Table 1 summarizes some relations for two-phase media. The Hashin-Shtrikman bounds can be achieved by various microstructures including coated spheres (Hashin,
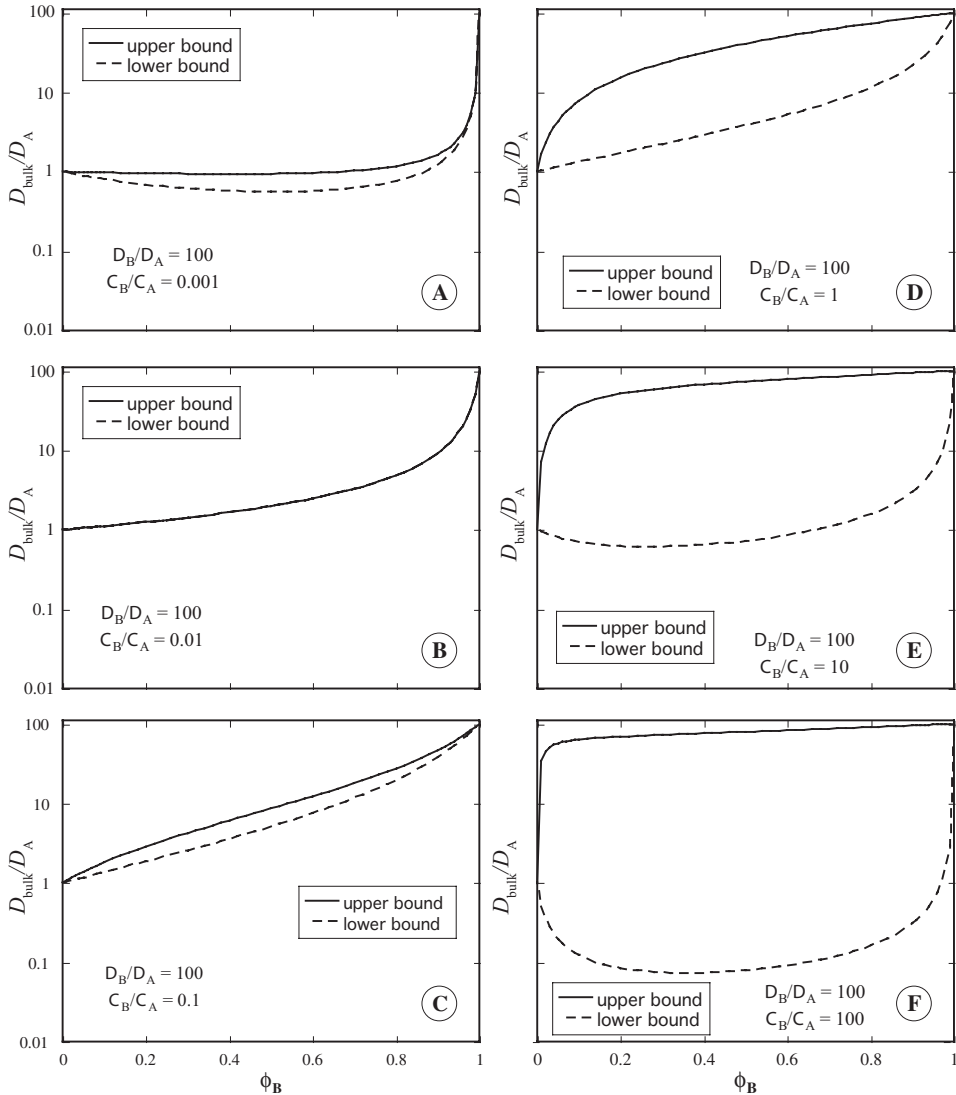
Fig. 2. Hashin-Shtrikman upper and lower bounds of diffusivity in a two-phase medium with $D_B/D_A = 100$ and various C_B/C_A.

1962), multi-rank laminates and periodic E-inclusions (Liu and others, 2007). All these constructions show a noteworthy difference between microstructures attaining the lower bound and those attaining the upper bound. Generally, *for a two-phase medium, if the matrix (the continuous phase) has low mobility, the bulk diffusivity is closer to the lower bound; if the matrix has high mobility, the bulk diffusivity is closer to the upper bound* (Hashin, 1962; Liu, 2010).

Some calculated curves of the Hashin-Shtrikman upper and lower bounds of D_{bulk} versus ϕ_B for $D_B/D_A = 100$ and some specific ratios of C_B/C_A are shown in figure 2. The case for $C_B/C_A = 1$ is shown in figure 2D, in which the dependence of D_{bulk} on ϕ_B is the same as in previous approaches (Barrer, 1968; Crank, 1975; Brady, 1983). Comparing

the results in figures 2A, 2B, 2C, 2E, and 2F ($C_B/C_A \neq 1$) with those in figure 2D shows that the ratio C_B/C_A plays a major role in controlling both the upper and lower limits of the bulk diffusivity. That is, our correction to the literature is a major correction. When $(D_B/D_A) \times (C_B/C_A) = 1$, that is, when $C_A D_A = C_B D_B$, meaning that the mobilities in the two phases are the same, the upper and lower bounds of D_{bulk} become the same. Under other conditions, the upper and lower Hashin-Shtrikman bounds often allow a very large range of the bulk diffusivity. That is, there is a great need to improve these bounds. Another interesting feature in figure 2 is that even though the upper Hashin-Shtrikman bound never exceeds $max(D_A, D_B)$, the lower Hashin-Shtrikman bound can sometimes be smaller than the $min(D_A, D_B)$.

A numeric example is shown here to illustrate our approach. Consider H_2O diffusion at 1573 K in a hypothetical mantle rock made of 60 percent olivine and 40 percent clinopyroxene with an average grain diameter of 4 mm. Because the form of H in olivine and clinopyroxene is OH, not molecular H_2O, we use H_2O_t (total H_2O) to denote the component. There is a range of H_2O_t partition coefficient between olivine and clinopyroxene (Kohn and Grant, 2006), and we use an intermediate value 0.04. H_2O_t diffusivity is taken to be 1.4×10^{-9} m^2/s (upper bound) in olivine (Kohlstedt and Mackwell, 1998) and 1.3×10^{-11} m^2/s in clinopyroxene (Hercule and Ingrin, 1999). Mean homogenization time (r^2/D) is 0.8 hours for olivine and 3.6 days for clinopyroxene. For time scales of a year or more, diffusion in the whole rock can be characterized by a bulk H_2O_t diffusivity ($D_{H_2O_t,bulk}$). Using our equations (27) and (28) (or the Hashin-Shtrikman equations for D_{bulk} of 2 phases in table 1), the lower and upper bounds of $D_{H_2O_t,bulk}$ in the rock are 7.29×10^{-11} m^2/s and 8.41×10^{-11} m^2/s. Using previous equations not considering the partitioning of H_2O_t, the lower and upper bounds would be 6.77×10^{-11} m^2/s and 7.08×10^{-10} m^2/s. The difference in the upper bound is large in this case, a factor of 8.4.

For completely random distribution of equidimensional particles of two phases such as olivine and pyroxene, it is expected that there should be only one well-defined bulk diffusivity rather than an upper bound and a lower bound. Such a relation is yet to be discovered. Numerical simulations might be the key toward such progress.

An often-encountered case of multi-phase diffusion is diffusion in porous media. The fluid (either melt or aqueous solution) in a porous media is one phase, and the rest are solid phases. The general relations derived in the preceding section can be applied. Frequently, diffusivities in the solid phases are much smaller than that in the fluid phase so that $\phi_{fluid} C_{fluid} D_{fluid} \gg \phi_{solid} C_{solid} D_{solid}$ for every solid phase, which simplifies the expression of the bulk diffusivity discussed above. Numerous workers have directly derived the relevant diffusion terms in porous media by ignoring diffusion contribution of the solid phases (for example, Dullien, 1979; Berner, 1980; McKenzie, 1984; Bickle and McKenzie, 1987; Bickle, 1992; *et cetera*) rather than using the similarity approach. Hence, elemental partitioning is incorporated, avoiding some of the errors produced due to the use of the similarity argument. Some of these expressions are correct (for example, Berner, 1980), and some are only applicable to parallel alignment (for example, McKenzie, 1984; Bickle and McKenzie, 1987), and some may have minor errors or unclearly defined confusing terms (for example, Dullien, 1979; Bickle, 1992). These expressions were followed by later workers (for example, Baxter and DePaolo, 2000; Watson and Baxter, 2007). Below we derive the relations for porous systems under various simplifications.

High-Temperature Porous Systems Containing Melt

For partial melting with melt as the fluid phase, the temperature is high, and the small diffusivities in solid phases may still be enough for the solid phases to maintain

equilibrium with the adjacent melt. The discussion in this section assumes local equilibrium between the solid phases and melt, whereas the case for the solid phases not participating in the diffusion at all is discussed next (room-temperature sediment). If diffusion in the solid phases is significant in transporting a given component (for example, Li diffusion in plagioclase, Giletti and Shanahan, 1997 and H_2O diffusion in garnet, Wang and others, 1996), then the general equations (for example, eqs 17, 22, 27-30) must be used.

If diffusion in the solid phases does not contribute significantly to the bulk diffusion flux (even though local equilibrium is still maintained), some simplifications can be made as follows. For parallel alignment, the bulk diffusivity can be expressed as (using eq 16 by letting phase A be the melt phase, treating all the solid phases as a combined "phase," and ignoring the terms containing D_{solid}):

$$D_{bulk}^{parallel} = \frac{\phi D_{melt}}{\phi + (1 - \phi)K_{solids/melt}} = \frac{\phi \rho_{melt} D_{melt}}{\phi \rho_{melt} + (1 - \phi)\rho_{solids}K'_{solids/melt}}, \tag{31}$$

where $\phi = V_{melt}/(V_{melt} + V_{solids})$ is the volume fraction of the melt (porosity), ρ_{melt} and ρ_{solids} are melt density and average solid phase density, K is partition coefficient between volume-average solid phases and melt in which the unit of concentration is mol/m^3 or kg/m^3, and K' is partition coefficient between mass-averaged solid phases and melt in which the unit of concentration is mass fraction.

For series alignment with only one mineral phase in addition to the melt, contribution of diffusion in the solid phases to the diffusive flux cannot be ignored, otherwise the bulk diffusivity would be zero. Including the effect of small diffusivity in the solid phases and assuming $\phi D_{solid}/D_{melt} \ll (1 - \phi)/K_{solid/melt}$, using equation (20), the diffusivity can be simplified as:

$$D_{bulk}^{series} = \frac{D_{solid}}{(1 - \phi)\left[(1 - \phi) + \dfrac{\phi}{K_{solid/melt}}\right]} = \frac{D_{solid}}{(1 - \phi)\left[(1 - \phi) + \dfrac{\phi \rho_{melt}}{\rho_{solid}K'_{solid/melt}}\right]} \ll D_{melt}. \tag{32}$$

For estimating the Hashin-Shtrikman upper bound, diffusion in the melt often dominates. On the other hand, for estimating the lower bound, contribution of diffusion in the solid phases (assuming only one solid phase) must be considered. The Hashin-Shtrikman upper and lower bounds are:

$$D_{HS}^{upper} = \frac{2\phi D_{melt}}{[\phi + (1 - \phi)K_{solid/melt}](3 - \phi)} = \frac{2\phi D_{melt}}{\left[\phi + (1 - \phi)\dfrac{\rho_{solid}}{\rho_{melt}}K'_{solid/melt}\right](3 - \phi)}, \tag{33}$$

$$D_{HS}^{lower} = \frac{(1 + 2\phi)D_{solid}}{(1 - \phi)^2 + \dfrac{\phi}{K_{solid/melt}}} = \frac{(1 + 2\phi)D_{solid}}{(1 - \phi)^2 + \dfrac{\phi \rho_{melt}}{\rho_{solid}K_{solid/melt}}} \ll D_{melt}. \tag{34}$$

Equation (31) (for parallel alignment) above is similar to the diffusion part of equation (A42) in McKenzie (1984), as well as equations (6) and (7) in Bickle and McKenzie (1987), except the disappearance of $(1 - \phi)$ in Bickle and McKenzie (1987) (which has only trivial effect for small ϕ). That is, their diffusion models implicitly assumed the maximum diffusivity possible for porous medium diffusion ($\geq$ the Hashin-Shtrikman upper bound) that is only achievable in parallel alignment. If more

accurate handling of diffusion is necessary, one way to improve their treatments is to use the concept of tortuosity (see below).

Room-Temperature Porous Sediment

For processes in sediment, diffusivity in aqueous solutions (often 10^{-9} m^2/s; Cussler, 1997, p.112) is often more than 30 orders of magnitude greater than that in solid phases (for example, Zhang, 2008, p. 583-585). Very rough estimate of diffusion distance in most solid phases at room temperature is typically less than 1 atomic distance in billions of years (for example, Zhang, 2008, p.92). Hence, (i) diffusion in the solid phases is negligible in terms of bulk diffusion, and (ii) diffusion in the solid phases does not change the solid composition, meaning that the solid phases are not in local equilibrium with the pore fluid as fluid composition changes (opposite to the case of high-temperature porous medium with melt) except for newly precipitated solids, which are not considered in our simple treatments because all ϕ_s must be constant. In other words, the solid phases are inert and do not participate in diffusion at all, and the problem of diffusion in porous sediment is essentially diffusion in the fluid phase but with solid particles blocking some of the pathways. Hence, the average concentration in the porous media (in which the solid phases stay the same but are included in the average) is often less interesting than simply the concentration in the fluid phase. Therefore, diffusion treatment often only considers the concentration variation in the pore fluid. As shown in Appendix 3, diffusion in any single phase in a multi-phase medium is also described by the same D_{bulk} that depends on phase alignments. Hence, diffusion in the aqueous solution in porous sediment can be described by the following D_{bulk}:

$$D_{\text{bulk}}^{\text{parallel}} = D_{\text{fluid}}, \qquad (35)$$

$$D_{\text{bulk}}^{\text{series}} = 0, \qquad (36)$$

$$D_{\text{HS}}^{\text{upper}} = \frac{2}{(3-\phi)} D_{\text{fluid}}, \qquad (37)$$

$$D_{\text{HS}}^{\text{lower}} = 0. \qquad (38)$$

It can be seen that the Hashin-Shtrikman lower bound does not provide much constraint. As mentioned earlier, because the matrix phase (the pore fluid) has high diffusivity, the upper bound (eq 37) is closer to the true bulk diffusivity. More accurate treatment can use the empirical tortuosity approach (next section).

Tortuosity

An empirical, and probably more practical, way to treat diffusion in porous materials is to use the concept of tortuosity (θ), defined as the ratio of the actual path length (L_{actual}) through the pore fluid, to the shortest straight distance (L_{straight}) along the diffusion direction z, or $\theta = L_{\text{actual}}/L_{\text{straight}}$. For parallel alignment, $\theta = 1$. For all other alignments, $\theta > 1$. Tortuosity is often estimated empirically, not based on the specific phase alignments. Because (i) tortuosity makes the bulk diffusivity through the media smaller than straight fluid diffusivity, and (ii) tortuosity is defined as the ratio of distance, whereas the distance-diffusivity relation is $L^2 \sim Dt$, the general relation between the bulk diffusivity and fluid-phase diffusivity in porous media can be written as:

$$D_{\text{bulk}} = D_{\text{bulk}}^{\text{parallel}}/\theta^2. \qquad (39)$$

If the solid phases can maintain local equilibrium with the fluid but diffusion in the solid phases does not contribute significantly to the overall diffusion flux (high-

temperature porous material containing melt), then combining equations (31) and (39) leads to:

$$D_{\text{bulk}} = \frac{\phi D_{\text{melt}}/\theta^2}{\phi + (1 - \phi)K_{\text{solids/melt}}} = \frac{\phi \rho_{\text{melt}} D_{\text{melt}}/\theta^2}{\phi \rho_{\text{melt}} + (1 - \phi)\rho_{\text{solids}} K'_{\text{solids/melt}}}, \qquad (40)$$

If the composition of solid phases does not change at all (porous sediment), then combining equations (35) and (39) leads to:

$$D_{\text{bulk}} = D_{\text{fluid}}/\theta^2. \qquad (41)$$

There is often confusion in the literature on how θ plays a role in D_{bulk}: some authors used the first power rather than the second power of θ (for example, Smith, 1970, p.465; Dullian, 1979, p. 346, eq 7.3.6; Cussler, 1997, p.173), and some authors placed the first power of tortuosity on the numerator rather than the denominator (for example, Bickle, 1992; Baxter and DePaolo, 2000; Watson and Baxter, 2007). These might be simple typographical errors or different definitions, but they are confusing (some authors did use the tortuosity correctly, for example, eq 3-49 in Berner, 1980). Dullian (1979) further added to the confusion by presenting another (even more erroneous) equation of $D_{\text{bulk}} = \phi D_{\text{fluid}}/\theta$, which he called the relation in steady-state experiments and was sometimes quoted by others (for example, Bickle and McKenzie, 1987). Epstein (1989) published a paper that specifically cleared the confusion in detail.

Li and Gregory (1974) measured that $\theta^2 = 1.8$ for deep-sea sediments. Cussler (1997, p.173) stated (likely from experimental measurements) that the value of "tortuosity" (actually meaning θ^2) is typically between 2 and 6. The simulation results of Scott (2001) showed that the optimal value of "tortuosity" (actually meaning θ^2) is 2.6. Summarizing these results, θ^2 can range from 1 to 6, with typical values of 1.8 to 2.6. On the other hand, the θ^2 value ranges from 1 ($\phi = 1$) to 1.5 ($\phi = 0$) based on the Hashin-Shtrikman upper bound (eq 37) of $\theta^2 = (3 - \phi)/2$, and is infinity based on the lower bound, confirming that for the case of porous medium in which the diffusivity in the matrix is high, the upper bound is much closer to the true bulk diffusivity.

If some of the pores are isolated, then only the connected pores contribute to the bulk diffusion, and equation (39) becomes:

$$D_{\text{bulk}} = (1 - \varepsilon)D_{\text{bulk}}^{\text{parallel}}/\theta^2, \qquad (42)$$

where $(1 - \varepsilon)$ is the volume fraction of connected pores over total pores.

We extend the concept of tortuosity to provide an alternative way to express the bulk diffusivity in a heterogeneous medium by incorporating tortuosity into the parallel alignment equation (eqs 16-18) so that the expression is in closed form. By extending equation (17) including the tortuosity, it becomes

$$D_{\text{bulk}} = \frac{\sum \phi_i C_i D_i/\theta_i^2}{\sum \phi_i C_i}, \qquad (43)$$

where θ_i is tortuosity in terms of phase i. In the above general equation, the concept of θ_i for an interconnected phase is straightforward, especially when there is no exchange between the phases. However, when there is exchange between the phases, and especially for an unconnected phase, the θ_i value is not straightforward as $L_{\text{actual}}/L_{\text{straight}}$, but can be viewed an extension of the tortuosity concept, with values obtainable from models. For example, on the basis of the Maxwell (1873) relation (table 1) for the case of dilute spherical B in matrix A, meaning phase A is intercon-

nected but phase B is not, by comparing the expression of $D_{\text{bulk}}^{\text{Maxwell}}$ and equation (43), we obtain:

$$\theta_{\text{A}}^2 = 1 + 2\phi_{\text{B}} + 2\phi_{\text{A}}\,\frac{C_{\text{B}}D_{\text{B}}}{C_{\text{A}}D_{\text{A}}} > 1,$$

$$\theta_{\text{B}}^2 = \frac{\phi_{\text{B}}\left(1 + 2\phi_{\text{B}} + 2\phi_{\text{A}}\,\dfrac{C_{\text{B}}D_{\text{B}}}{C_{\text{A}}D_{\text{A}}}\right)}{2 + \phi_{\text{B}}}.$$

Hence, in our extended definition, "tortuosity" of a phase may even be smaller than 1.

CONTRIBUTION OF GRAIN BOUNDARY DIFFUSION TO BULK DIFFUSION

A rock (even a single phase rock) is polycrystalline with grain boundaries. Sometimes there could be a minor amount of fluid along the grain boundaries, meaning that they may not be simple grain boundaries. Hence, the term "grain boundaries" has often been replaced by terms like the intergranular region (IGR) (Brady, 1983), or intergranular transporting medium (ITM) (Baxter and DePaolo, 2000; Watson and Baxter, 2007). We follow the latter and use ITM hereafter. Even though diffusivity likely depends on the exact interfaces between two grains (for example, between two similar crystalline faces or different faces), such consideration is too complicated. For simplicity, all kinds of interfaces are averaged to be one ITM and treated as one "phase" in terms of their contribution to the diffusive flux. Assuming ITM and grain interiors are in equilibrium, the equations in table 1 and equation (43) will be applicable. For example, the general expression of D_{bulk} (eq 43) is:

$$D_{\text{bulk}} = \frac{\phi_{\text{ITM}}K_{\text{ITM/interior}}D_{\text{ITM}}/\theta_{\text{ITM}}^2 + (1 - \phi_{\text{ITM}})D_{\text{interior}}/\theta_{\text{interior}}^2}{\phi_{\text{ITM}}K_{\text{ITM/interior}} + (1 - \phi_{\text{ITM}})}, \tag{44}$$

where D_{ITM} means diffusivity in the ITM and D_{interior} means that in the grain interior, θ is the tortuosity factor, and $K_{\text{ITM/interior}}$ is the segregation factor equaling the ratio of the elemental concentration in the ITM to that in the grain interior with concentration in kg/m^3, or in mass fraction if ITM has the same density as the crystalline phase.

In the literature on grain boundary diffusion, some authors did not include the effect of possible segregation (enrichment or depletion) of a given element in ITM (for example, Hart, 1957; Chen and Schuh, 2007), that is, $K_{\text{ITM/interior}}$ was assumed to be 1. Other authors (for example, Mortlock, 1960; Mishin and Herzig, 1995; Baxter and DePaolo, 2000; Watson and Baxter, 2007; Dohmen and Wilke, 2010) included such effect but with various simplifications.

For example, if diffusion in the interior of grains does not significantly contribute to the overall diffusion flux, the problem becomes similar to diffusion in a solid-melt porous medium at high temperature and can be treated using the concept of tortuosity as follows (eq 40, or simplified from eq 44):

$$D_{\text{bulk}} = \frac{\phi_{\text{ITM}}D_{\text{ITM}}/\theta^2}{\phi_{\text{ITM}} + (1 - \phi_{\text{ITM}})/K_{\text{ITM/interior}}}. \tag{45}$$

At one extreme, assuming $\phi_{\text{ITM}}K_{\text{ITM/interior}} \gg 1$, meaning the element under consideration is mostly in the ITM rather than in grain interiors, then equation (45) simplifies to

$$D_{\text{bulk}} = D_{\text{ITM}}/\theta^2. \tag{46}$$

The above equation is similar to equation (41), and points out a small error in equation (5) of Watson and Baxter (2007) since ϕ enters their expression (in addition to identifying their "tortuosity" as $1/\theta^2$) as in one of Dullian's equations discussed earlier in this work. The difference is because we incorporated partitioning in deriving the bulk diffusivity for a two-phase medium (different from implicitly assuming $K_{\text{ITM/interior}} = 1$ by Barrer, 1968, Crank, 1975, and Brady, 1983) so that ϕ is canceled.

At the other extreme, assuming $\phi_{\text{ITM}}K_{\text{ITM/interior}} \ll 1$, meaning the element under consideration is mostly in grain interiors rather than in the ITM, then equation (45) simplifies to

$$D_{\text{bulk}} = \frac{\phi_{\text{ITM}}K_{\text{ITM/solid}}D_{\text{ITM}}}{(1 - \phi_{\text{ITM}})\theta^2}. \tag{47}$$

The above equation is similar to equation (2) of Baxter and DePaolo (2000) and equation (6) of Watson and Baxter (2007) if their "tortuosity" is identified to be $1/\theta^2$.

If diffusion in grain interior cannot be ignored, and $\phi_{\text{ITM}}K_{\text{ITM/interior}} \ll 1$ (the element under consideration is mostly in grain interiors rather than in the ITM), and further ignoring tortuosity (that is, assuming parallel alignment, meaning $\theta = 1$), the general equation (44) becomes

$$D_{\text{bulk}}^{\text{parallel}} = \phi_{\text{ITM}}K_{\text{ITM/interior}}D_{\text{ITM}} + (1 - \phi_{\text{ITM}}K_{\text{ITM/interior}})D_{\text{interior}},$$

which is the same as the equation given in Mortlock (1960) and Dohmen and Wilke (2010, eq 13). Because perfect parallel grain boundary alignment is unlikely, we suggest that the tortuosity factor be included in estimating the bulk diffusivity.

EFFECTIVE DIFFUSIVITY OF ONE-PHASE POLYCRYSTALLINE MATERIAL

In a single-phase polycrystalline material, if diffusion through grain boundaries is significant, then an approximate treatment is to treat grain boundaries as a separate "phase" (ITM) and the problem becomes a two-phase problem as discussed earlier. This section treats the case when contribution by ITM diffusion is negligible to bulk diffusion.

Because the bulk mineral is made of one single phase, there is no concentration partitioning, meaning concentration is continuous. Hence, results derived for conductivities (Hashin and Shtrikman, 1963b) can be applied directly to diffusion. To distinguish with bulk diffusivity for multiphase systems, effective diffusivity is used to denote diffusivity in a single-phase system with various grain orientations. For an isotropic mineral, the effective diffusivity in the bulk material is simply the diffusivity in the mineral. For three-dimensional anisotropic minerals, the effective diffusivity (D_{eff}) is bounded between the following (Hashin and Shtrikman, 1963b):

$$D_3\frac{4D_3^2 + 7D_1D_2 + 8D_1D_3 + 8D_2D_3}{16D_3^2 + D_1D_2 + 5D_1D_3 + 5D_2D_3} < D_{\text{eff}} < D_1\frac{4D_1^2 + 8D_1D_2 + 8D_1D_3 + 7D_2D_3}{16D_1^2 + 5D_1D_2 + 5D_1D_3 + D_2D_3}, \tag{48}$$

where $D_1 > D_2 > D_3$ are the principal diffusivities of the mineral considered. When differences in D_1, D_2 and D_3 are large, the upper and lower bounds can be far apart.

For diffusion in a multiphase medium in which some phases are diffusionally anisotropic, the best estimate of diffusivity at present is to use the Hashin-Shtrikman upper and lower bounds, in which each diffusivity can have a range as in equation (48), making the estimated upper and lower bounds even farther apart. Hence, there is a critical need to improve the estimation of bulk diffusivity in heterogeneous media and randomly oriented grains of anisotropic material.

APPENDIX 1

DIRECT DERIVATION OF BULK DIFFUSIVITY FOR PARALLEL ALIGNMENT

Consider the case when phases A and B are aligned along the direction of diffusion as in figure 1A and the diffusion cross section area ratio is the same as the volume ratio of the two phases. Then, for any component i, we have

$$\mathbf{J}_{i,\text{bulk}} = \phi_A \mathbf{J}_{i,A} + \phi_B \mathbf{J}_{i,B} = -\phi_A D_{i,A} \nabla C_{i,A} - \phi_B K_{i,B/A} D_{i,B} \nabla C_{i,A}. \tag{A1-1}$$

$$\mathbf{J}_{i,\text{bulk}} = -(\phi_A D_{i,A} + \phi_B K_{i,B/A} D_{i,B}) \nabla C_{i,A}. \tag{A1-2}$$

Because $C_{i,\text{ave}} = \phi_A C_{i,A} + \phi_B C_{i,B} = (\phi_A + \phi_B K_{i,B/A}) C_{i,A}$, we obtain:

$$\mathbf{J}_{i,\text{bulk}} = -\frac{(\phi_A D_{i,A} + K_{i,B/A} \phi_B D_{i,B})}{(\phi_A + K_{i,B/A} \phi_B)} \nabla C_{i,\text{ave}}. \tag{A1-3}$$

Comparing with the definition of $D_{i,\text{bulk}}$ (eq 2b) we obtain:

$$D_{i,\text{bulk}} = \frac{(\phi_A D_{i,A} + K_{i,B/A} \phi_B D_{i,B})}{(\phi_A + K_{i,B/A} \phi_B)}. \tag{A1-4}$$

The above can also be written into the following form:

$$D_{i,\text{bulk}} = \frac{(\phi_A C_{i,A} D_{i,A} + \phi_B C_{i,B} D_{i,B})}{(\phi_A C_{i,A} + \phi_B C_{i,B})}, \tag{A1-5}$$

which is identical to equation (16), and hence verifies the mobility approach.

APPENDIX 2

DIRECT DERIVATION OF BULK DIFFUSIVITY FOR SERIES ALIGNMENT

Consider the case when phases A and B are aligned along the direction of diffusion as in figure 1B. Assume that the width of A is uniform (d_A) and that of B is also uniform (d_B) throughout. The ratio of the width would be the same as $d_A/d_B = \phi_A/\phi_B$. For the series alignment, for simplicity, we only treat the steady state case to compare with the general solution (eq 20). Although we only consider the steady state here, equation (20) applies more generally as long as the diffusion distance is much larger than individual grain sizes.

If steady state is reached, then concentration profile in each layer is linear with constant flux:

$$\mathbf{J}_{\text{bulk}} = -D_{\text{bulk}} \partial C_{\text{ave}}/\partial z = -D_A \partial C_{A1}/\partial z = -D_B \partial C_{B1}/\partial z = -D_A \partial C_{A2}/\partial z = \cdots \tag{A2-1}$$

where A1 is the first layer of A, B1 is the first layer of B following A1, A2 is the second layer of A following B1, *et cetera*. At the contact of A and B, it is assumed that there is interface equilibrium with the partition coefficient of $K = C_B/C_A$. Let coordinates of the layers be z_0, z_1 (interface from A1 to B1), z_2 (interface from B1 to A2), z_3 (interface from A2 to B2), z_4 (interface from B2 to A3), *et cetera*. For example, if $\phi_A/\phi_B = 0.75/0.25 = 3$, $K = K_{B/A} = C_B/C_A = 2$, and $D_A/D_B = 6$, then we would have a profile as shown in figure A2-1 (black solid points with dashed lines), and the average concentration profile is given by the solid line.

Define the concentration slopes in phases A and B to be s_A and s_B. Then, from equation (A2-1), the following can be obtained:

$$D_A s_A = D_B s_B. \tag{A2-2}$$

The concentrations at points z_1, z_2, z_3, and z_4 can be given as:

$$C_A(z_1) = C_A(z_0) + s_A d_A,$$

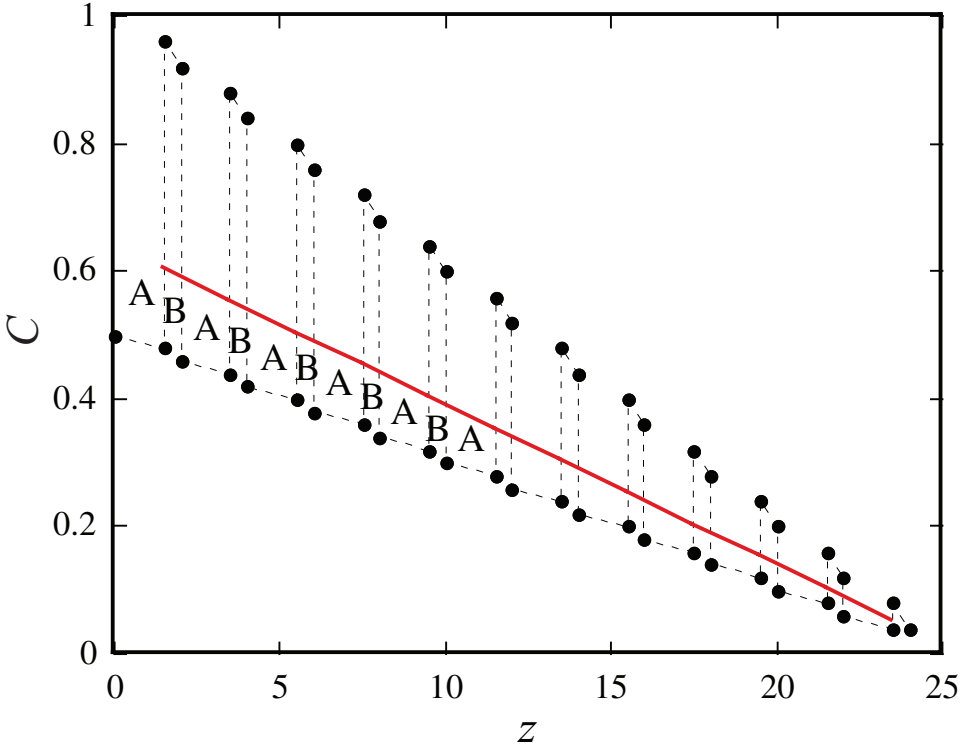$$C_B(z_1) = K C_A(z_1) = K[C_A(z_0) + s_A d_A].$$

Fig. A2-1. Steady state concentration profile due to diffusion and partitioning in a two-phase heterogeneous medium with laminates aligned normal to the diffusion direction and the following parameters: $\phi_A/\phi_B = 3$, $K_{B/A} = 2$, and $D_A/D_B = 6$. The difference in phase proportion ϕ is reflected in the thickness of phase A and B; the partition is reflected in the jump in concentration at the contact of A and B, and the difference in diffusivity D is reflected in the slope of C versus z in each phase. The points above the red line are for concentrations in phase B, and those below the red line are for concentrations in phase A.

$$C_B(z_2) = C_B(z_1) + s_B d_B = K[C_A(z_0) + s_A d_A] + s_B d_B = K[C_A(z_0) + s_A d_A] + D_A s_A d_B/D_B,$$

$$C_A(z_2) = C_B(z_2)/K = C_A(z_0) + s_A d_A + D_A s_A d_B/(K D_B),$$

$$C_A(z_3) = C_A(z_2) + s_A d_A = C_A(z_0) + 2 s_A d_A + D_A s_A d_B/(K D_B),$$

$$C_B(z_3) = K C_A(z_3) = K[C_A(z_0) + 2 s_A d_A] + D_A s_A d_B/(D_B),$$

$$C_B(z_4) = C_B(z_3) + s_B d_B = K[C_A(z_0) + 2 s_A d_A] + 2 D_A s_A d_B/(D_B).$$

Hence, the average concentration of layers A1 + B1 (from z_0 to z_2) as a representative volume element is

$$\begin{aligned} C_{ave1} &= 0.5\phi_A[C_A(z_0) + C_A(z_1)] + 0.5\phi_B[C_B(z_1) + C_B(z_2)] \\ &= \phi_A C_A(z_0) + \phi_B C_B(z_1) + 0.5(\phi_A s_A d_A + \phi_B s_B d_B). \end{aligned}$$

Similarly, the average concentration of layers A2 + B2 (from z_2 to z_4) is

$$\begin{aligned} C_{ave2} &= \text{average of A2 + B2} = 0.5\phi_A[C_A(z_2) + C_A(z_3)] + 0.5\phi_B[C_B(z_3) + C_B(z_4)] \\ &= \phi_A C_A(z_2) + \phi_B C_B(z_3) + 0.5(\phi_A s_A d_A + \phi_B s_B d_B). \end{aligned}$$

Therefore, the slope of the average concentration can be written as:

$$\partial C_{ave}/\partial z = (C_{ave2} - C_{ave1})/(d_A + d_B) = \{\phi_A[C_A(z_2) - C_A(z_0)] + \phi_B[C_B(z_3) - C_B(z_1)]\}/(d_A + d_B)$$
$$= \{\phi_A[s_A\phi_A + D_As_A\phi_B/(KD_B)] + \phi_B[Ks_A\phi_A + D_As_A\phi_B/D_B]\}$$

From A2-1, we have

$$\mathbf{J}_{bulk} = -D_{bulk}\partial C_{ave}/\partial z = -D_As_A.$$

Hence,

$$D_{bulk}\{\phi_A[\phi_A + D_A\phi_B/(KD_B)] + \phi_B[K\phi_A + D_A\phi_B/D_B]\} = D_A, \tag{A2-3}$$

which is equivalent to equation (20) in the text.

Appendix 3

DIFFUSION EQUATION FOR CONCENTRATION IN ANY PHASE IN A MULTI-PHASE SYSTEM

Any phase here does not mean any single grain, but all grains of the same phase. The length scale of consideration here is much larger than individual grains so that D_{bulk} can be defined. Based on the flux equation that defines D_{bulk} (eq 2b), we can write:

$$\frac{\partial C_{ave}}{\partial t} = -\nabla\mathbf{J}_{bulk} = \nabla(D_{bulk}\nabla C_{ave}). \tag{A3-1}$$

Using the local equilibrium condition, C_{ave} can be expressed as:

$$C_{ave} = \sum \phi_i C_i = C_A \sum \phi_i K_{i/A}, \tag{A3-2}$$

where the summation is over all the phases, and $K_{i/A}$ is the partition coefficient of the given component between phase i and phase A. Replacing equation (A3-2) into equation (A3-1) leads to

$$\frac{\partial(C_A \sum \phi_i K_{i/A})}{\partial t} = \nabla[D_{bulk}\nabla(C_A \sum \phi_i K_{i/A})]. \tag{A3-3}$$

If all ϕ_i and $K_{i/A}$ values are independent of space and time (for example, there is no variation in the degree of partial melting), then

$$\frac{\partial C_A}{\partial t} = \nabla[D_{bulk}\nabla C_A]. \tag{A3-4}$$

That is, the effective diffusion of a component in any phase can also be described by the bulk diffusivity if all ϕ_i and $K_{i/A}$ are constant. Note that (i) the diffusivity in equation (A3-4) is the bulk (or effective) diffusivity of the multi-phase medium, not the individual diffusivity in phase A, and (ii) equation (A3-4) does not relate D_{bulk} to diffusivities in individual phases. Equation (A3-4) is similar to that in Berner (1980). A special case is when phase A is fluid and the rest are solid phases whose compositions do not change with time, meaning that the solid phases do not participate in the diffusion at all. Then equation (A3-4) still holds, and D_{bulk} simply becomes D_{fluid}/θ^2 (eq 41).

On the other hand, if ϕ_i values vary (for example, increasing degree of partial melting, or porous media with mineral dissolution) and/or $K_{i/A}$ values vary (for example, changing temperature and/or pressure), then the full equation (A3-3), in which D_{bulk} is a complicated function of ϕ_i and $K_{i/A}$, must be used.

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