Available online at www.sciencedirect.com

ScienceDirect

Earth and Planetary Science Letters 253 (2007) 307 – 327

EPSL Frontiers

www.elsevier.com/locate/epsl

Frontiers

Diffusion in solid-Earth systems

E. Bruce Watson [a,*], Ethan F. Baxter [b]

[a] Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, Troy, NY 12180, USA
[b] Department of Earth Sciences, Boston University, Boston, MA 02215, USA

Received 28 July 2006; received in revised form 24 October 2006; accepted 9 November 2006
Available online 19 December 2006
Editor: A.N. Halliday

Abstract

Recent years have seen a rapid expansion in the acquisition and use of information on diffusive transport in phases relevant to the solid Earth (crystals, melts and fluids). Although far from complete, the data base on diffusion coefficients is now sufficiently large that broad constraints can be placed upon the length- and time scales of many natural transport phenomena in which diffusion plays a role. Conversely, observations of diffusion progress in specific natural samples can be used to extract time–temperature information for a variety of geologic and geochemical processes, ranging from sediment burial and crustal erosion to fluid-mediated reactions and biosignature retention.

Despite this undeniable progress, several major challenges remain that largely define the frontiers of research in solid-Earth diffusion. Perhaps foremost among these is the need to address and understand the multi-scale, multi-path aspects of diffusion in many systems—a complication that is not limited to polyphase materials (individual mineral grains can exhibit clear indications of multi-path behavior even when visible evidence of such paths is lacking). Many other diffusion frontiers are linked in one way or another to this multi-scale issue; they include: diffusion of molecular H_2O and the effect of H species on diffusion in minerals and rocks; diffusive fractionation of multiple isotopes of a single element; diffusion at the extreme conditions of the deep Earth; reconciliation of observations from natural samples and laboratory studies; and development of theoretical approaches to 'predict' diffusion behavior in regions inaccessible to observation.

Keywords: diffusion; solid Earth; chemical transport; thermochronology; geochronology; diffusive closure

1. Introduction

This contribution is not intended as a comprehensive review of diffusion theory, a compendium of geologically relevant diffusion data, or a 'how-to' guide to diffusion measurements. Rather, it is a broad characterization of the state of understanding of diffusion in geological systems emphasizing both what we already know and what we need to know. It is a perspective that we hope will be of interest to the broader community of scientists concerned in some way and at some level with mass transport and atomic mobility in the Earth. In keeping with the spirit and intent of *Frontiers* articles, we are writing for non-specialists with the objective, first, of building a basic knowledge base. We then proceed to a discussion of the substance, goals and challenges of current research activities.

The phenomenon of diffusion is important in all of Earth's systems (atmosphere, hydrosphere, cryosphere,

---

* Corresponding author.
E-mail addresses: watsoe@rpi.edu (E.B. Watson), efb@bu.edu (E.F. Baxter).

0012-821X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2006.11.015

soils, sediments, and deep subsurface), but for practical reasons we restrict the scope of this paper to the solid Earth. In this realm, diffusion contributes to chemical transport and exchange at scales ranging from nanometers to kilometers. Even when diffusion by itself does not result in long-range mass transport, it may augment or control the effects of advective mass transfer. It could be said that at some finite length scale, diffusion becomes a rate limiting process in any dynamic system. The multiplicity of scales at which diffusion is important will be a recurring theme of this article.

The relevant length scales of the vast majority of geochemical applications of diffusion fall in between the two extremes noted above; these include: geo- and thermochronology; geospeedometry; reaction rates; solid-state grain growth and microstructure development; homogenization of mineral grains; coarsening of grains and pores; growth of bubbles from liquids; dissolution and growth of crystals; rheological properties of solids and magmatic liquids; magma mixing; and bulk diffusion through rock. We will touch on some but not all of these topics, emphasizing areas of current excitement in solid-Earth geochemistry where further research is especially needed.

2. Basic concepts

2.1. Definition and overview

In common scientific usage, the term "diffusion" refers to the translational motion of atoms or molecules dissolved in a phase. In general, the reference frame for gauging motion of the atoms of interest is the lattice (in the case of a crystal) or structure of the host phase. Diffusion theory is typically put forth in separate but complementary approaches: *atomistics* (deductions based upon consideration of the random motion of individual atoms) and *phenomenology* (the empirical equations governing diffusion in a continuum). These are described only in the most general terms here; for comprehensive, readable treatments with varying emphasis, the reader is referred to Shewmon [1], Manning [2], Cussler [3] and Glicksman [4].

2.2. Atomistic and molecular-scale considerations

Classical atomistic treatments of diffusion usually begin by considering a simple, rigid lattice characterized by atoms in a specific coordination with their neighbors. This framework is fairly realistic for some Earth materials (e.g., simple oxides), less so for complex silicates, and ill-suited in varying degrees for melts and fluids. Some of the basic concepts of the 'lattice-bound atom' approach are nevertheless readily transferred to structurally complex materials. The essential idea is that a constituent atom or ion oscillating in a fixed position has the potential to vacate this position and 'relocate' a short distance away. This displacement constitutes a diffusive 'jump', and amounts to a net migration of the atom. Several mechanisms allow or facilitate the diffusive jump (see Fig. 1).

The basic concept of a jump frequency is relevant to diffusion in all materials having a more-or-less rigid atomic structure, but it is not a suitable conceptualization for diffusion in gases and supercritical fluids, where much of the kinetic energy of individual molecules is contained in their continuous translational motion. In supercritical C–O–H fluids, for example, it may be more accurate to think in terms of solute molecules or ions migrating through an inviscid

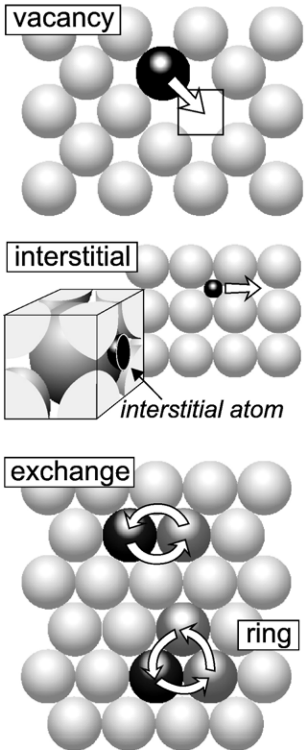


Fig. 1. Schematic representation of selected diffusion mechanisms for crystalline solids. The vacancy and interstitial mechanisms are common and well documented; the others are largely hypothetical and have not been confirmed in minerals. See Manning [2] for a detailed treatment.

continuum. The ‘rigid lattice’ and ‘inviscid continuum’ ideas represent the end-member ways of thinking about diffusion in the full the range of (condensed) geologic media (see Text Box 1). Interestingly, silicate melts could be regarded as falling between the two end-member models, depending upon the composition (hence the degree of polymerization) of the melt and the identity of the diffusant.

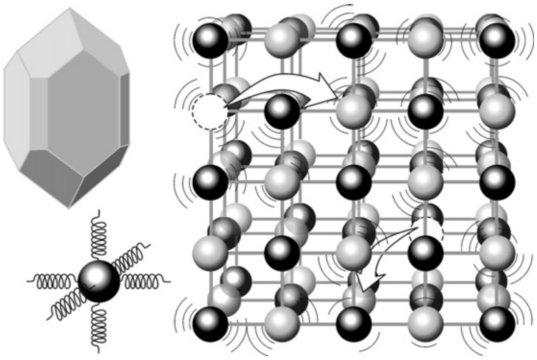
Box 1

Diffusion in geological materials: rigid lattice or inviscid continuum?

Diffusion involves the random motions of individual atoms within the large collections of atoms we call phases. The inherent diversity of Earth materials – liquid, crystal,supercritical fluid – requires several atom-scale conceptualizations of diffusion. Which of these is most accurate in a given case depends mainly upon the dominant form of the kinetic energy of the constituent atoms or molecules: translational, vibrational, or both. Two conceptualizations of diffusion are illustrated below.

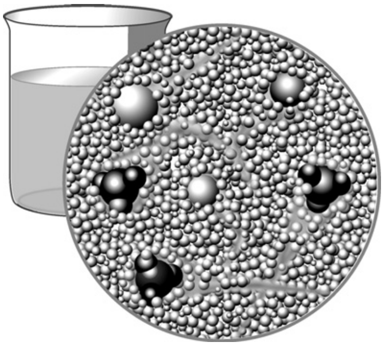
Rigid lattice. Atoms oscillate about a generally fixed position, occasionally jumping to a neighboring site. Here, long-range migration of an atom requires a sequence of discrete jumps whose frequency is given by $\Gamma = v\exp(-E/kT)$, where v is the vibrational frequency of the atom on the site, E is the energy barrier that must be overcome during the jump, k is Boltzmann's constant and T is temperature in Kelvins.

Example: Pb diffusion in zircon.



Inviscid continuum. The momentum of larger atoms or molecules (generally solute) carries them through a ‘sea’ of smaller molecules (solvent) that exert a viscous drag. Here the diffusivity is accurately ‘predicted’ by the Stokes–Einstein equation, $D = kT/(6\pi\eta R_o)$, provided that the radius of the solute species is less than 5X that of the solvent species [155]; η is the fluid viscosity and R_o is the radius of the solute diffusant.

Example: diffusion of SiO_2 solute in supercritical aqueous fluid.



2.3. Phenomenology: the basic equations

2.3.1. Fick's laws

Through random motions of its constituent atoms, an initially heterogeneous phase will eventually reach a state of homogeneity due to fluxes of atoms from regions of high concentration (strictly, chemical potential; see Section 2.3.2) to low concentration. In 1855 Adolph Fick formalized this observation by asserting (and later showing consistency with experiment) that

$$J_i = -D_i \cdot \frac{\partial c_i}{\partial x} \tag{1}$$

where J_i is the flux of species i through the medium of interest (units of J_i are atoms per unit time passing through unit area $\perp x$), $\partial c_i/\partial x$ is the concentration gradient of i in the x direction, and D_i is a constant that we now recognize as the *diffusion coefficient* or *diffusivity* (units = $m^2\ s^{-1}$) for species i in the specific medium of interest. Eq. (1) is a 1-dimensional flux equation, so concentration gradients in directions other than x are implicitly assumed to be zero. As expected, J_i goes to zero as $\partial c_i/\partial x$ goes to zero, but it is important to realize that it is actually the *net* flux in the x direction that goes to zero. This is Fick's first law, also called the steady-state diffusion equation because $\partial c_i/\partial x$ and J_i are not explicitly time-dependent. There are relatively few instances in geochemical systems where the steady state truly holds, but this does not diminish the conceptual and intuitive value of this equation.

Box 2

Multi-dimensional diffusion

The non-steady state diffusion equation for three dimensions is

$$\frac{1}{D_i}\frac{\partial c_i}{\partial t} = \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}$$

but the most common approach to dealing with multi-dimensional diffusion is to approximate the geometry of the object or system of interest by a simple shape such as a cylinder or sphere in which diffusion is assumed to be radially symmetric. For these simple shapes, equations analogous to (2) express c_i as a function only of radial position (r) and time:

$$\frac{\partial c_i}{\partial t} = \frac{D_i}{r}\frac{\partial}{\partial r}\left[r\frac{\partial c_i}{\partial r}\right] \text{ for a cylinder}$$

$$\text{and } \frac{\partial c_i}{\partial t} = D_i\left[\frac{\partial^2 c_i}{\partial r^2} + \frac{2}{r}\frac{\partial c_i}{\partial r}\right] \text{ for a sphere}$$

See chapters 5 and 6 of Crank [5] for analytical solutions to these equations for various boundary conditions. Note also that numerical (finite difference) solutions are readily implemented with these equations, so we have ready escape from the limitations of D_i being independent of both r and t, and from restrictive boundary conditions (e.g., constant surface concentration).

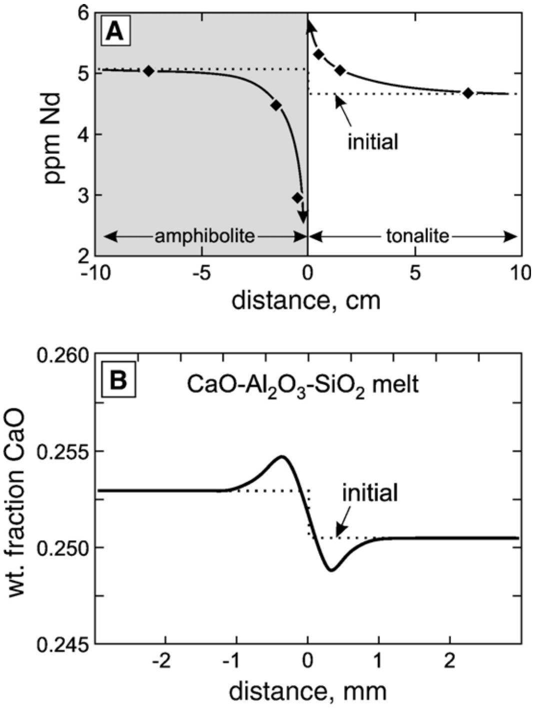


Fig. 2. Two illustrations of 'uphill' diffusion. A: Bulk-rock example in the form of uphill Nd diffusion near the contact of Archean-age tonalite and amphibolite rocks from Greenland. Dashed lines show inferred initial Nd rock concentrations before diffusive exchange. Diffusion appears to have been driven by a chemical potential gradient in Nd that did not correlate with concentration across the lithologic contact (E.F. Baxter and D.J. DePaolo, unpublished data). **B:** Uphill diffusion of Ca during chemical interdiffusion of CaO–Al$_2$O$_3$–SiO$_2$ melts at 1500 °C and 1 GPa for 1 h [8].

Fick's more general mass-conservation equation is (for one-dimensional diffusion with D_i independent of x and c_i)

$$\frac{\partial c_i}{\partial t} = D_i \cdot \frac{\partial^2 c_i}{\partial x^2} \tag{2}$$

Box 3

'Types' of diffusion

Some practical definitions are useful when discussing diffusion in geological materials. These vary somewhat among authorities and disciplines, but there is general agreement on the essential characteristics.

Self diffusion refers to the migration of the constituent atoms of substance in the absence of chemical gradients (the 'random-walk' idea). Geochemists tend to use the term '*isotopic diffusion*' for the same phenomenon, but in geological systems it is probably rare that isotopic heterogeneity with respect to a specific element would exist in the absence of gradients in concentration of that element. Isotopic tracers are generally needed to characterize self diffusion, so the term 'tracer diffusion' is often equated with self diffusion.

Chemical diffusion refers to diffusion in a chemical potential (μ) gradient, for which conditions are widespread in natural systems. Approaches to the study of chemical diffusion range from the practical to the complex. In a binary system, diffusive mixing is generally described by an *interdiffusion coefficient* defined simply in terms of Fick's first law:

$$\widetilde{D}|_x = -J/(\mathrm{d}c/\mathrm{d}x)$$

$\widetilde{D}$ generally varies with concentration (i.e., with distance across the interdiffusion zone), but this can be addressed using the Boltzmann–Matano approach (see Shewmon [1], pp. 34–37). Chemical diffusion in multicomponent systems becomes complicated because interdiffusing species experience 'thermodynamic' effects on top of their intrinsic mobilities (the concentration of one component may affect μ of another). For systems of more than 2 components it may be expedient to use an *effective binary diffusion coefficient* (EBDC; see [156,157]), but rigorous treatment of multicomponent diffusion involves determination of the diffusion coefficient matrix defined by Onsager's [158] extended version of Fick's first law:

$$J_i = -\sum_{j=1}^{n-1} D_{ij} \cdot (\partial c_j/\partial x)$$

where n is the number of components in the system ($n-1$ of the diffusivities are independent). See the textbooks cited in Section 2.1 and [6,10,159–161] for more discussion.

This equation describes the change in local concentration with time (t), and so is referred to as the nonsteady-state diffusion equation (and also as Fick's second law). Solutions have been obtained for many different boundary conditions; a summary can be found in the classic reference work by Crank [5]. Many geologic applications involve chemical gradients in more than one direction, for which a multi-dimensional form of Eq. (2) is needed (see Text Box 2).

2.3.2. Complications

In Eqs. (1) and (2), D_i for a given medium is implicitly constant. However, situations may arise in which $D_i=f(c_i)$ if c_i varies substantially, as in a solid solution or melt. Dependence of D_i upon c_i may be inevitable due to changing thermodynamic influences of other components of the solution. Eq. (1) can be stated in words as "a gradient in concentration will lead to an observable flux"—but a more rigorous wording is required by chemical thermodynamics: "a gradient in *chemical potential* (μ_i) will lead to an observable flux." At low concentrations where Henry's law applies (as for trace elements) diffusion within a *single* phase generally obeys the simple forms of Fick's laws, because μ_i is proportional to c_i. However, when major components are involved, or when considering diffusion across a phase boundary, concentration gradients alone generally are not adequate to describe system behavior. For example, thermodynamic influences can actually lead to 'uphill' diffusion of a given component; that is, cases where the net flux of i occurs *with* the chemical potential gradient, μ_i (as required) but *against* the concentration gradient in i. Geochemical examples may be surprisingly common, and include interdiffusion of silicate melts (e.g., [6–8]), near-surface diffusion phenomena in minerals [9], and chemical diffusion across phase or lithologic boundaries ([10]; see Fig. 2). Use of appropriate boundary conditions taking in to account the difference in the $\mu_i = f(c_i)$ relationship (i.e. the partition coefficient) is frequently sufficient in the modeling of diffusive exchange between phases.

The foregoing considerations necessitate a general classification scheme for 'types' of diffusion that might apply to atom migrations within a single phase such as an individual crystal or a volume of melt (Text Box 3). For the most part, these definitions address the nature of the gradients (if any) that diffusion tends to eliminate. They do not consider diffusion pathways–the subject of the next section–but is worth noting that a particular type of diffusion as described in Text Box 3 could take advantage of any pathway.

2.3.3. Diffusion pathways in geologic media

Classical treatments of diffusion typically recognize several distinct diffusion *paths* in polycrystalline materials: 1) *volume (or lattice) diffusion* refers to atomic migrations occurring within a single crystal; 2) *grain-boundary diffusion* involves migrations along two-dimensional regions between the mismatched lattices of individual grains; 3) *defect diffusion* describes migrations along extended intracrystalline defects such as dislocations; and 4) *surface diffusion* refers to migration along (parallel to) a crystal surface against a vacuum or a fluid medium. In geological systems, the relative importance of these 'classical' paths depends upon the phenomenon or process of interest. In isotopic studies of individual crystals, for example, intragrain diffusion is a primary concern, but may not be controlled entirely by lattice diffusion because extended defects can play a role (see below). Surface diffusion may enter in to nanometer-scale phenomena such as migration to step edges during crystal growth from a fluid [11]. Diffusion along boundaries between mineral grains probably determines the overall effectiveness of bulk transport in rocks (Section 3.2), but there may be complexities not encountered in simple ceramics and metals. Rocks at depth in the Earth can be complicated by the presence of intergranular fluid, and even when a free fluid is lacking, the grain- and interphase boundaries may be laden with incompatible ions – including C–O–H species – which might impart diffusion qualities quite different from those of grain boundaries in relatively pure materials. When fluid is present, the long-range connectivity depends upon the mineral/fluid wetting characteristics, which are affected by the compositions of both phases [12]. If stable grain-scale connectivity is achieved, the fluid geometry is that of a grain-edge network-which does not wet the interfaces between grains (i.e., the grain boundaries) under conditions of chemical and mechanical equilibrium (but see [13]).

Earth materials are complicated still further by the fact that each individual mineral grain may be, in a sense, a microcosm of the host rock, with multiple pathways available for diffusion within the grain itself (Fig. 3). Generally speaking, lattice diffusion by site-to-site jumping of atoms will constitute the slowest intracrystal 'path', but the overall diffusive response of a mineral grain to a disequilibrium condition may depend upon the presence and number of fast paths, which could include 2-D features (e.g., sub-grains; exsolution boundaries), as well as 1-D edge and screw dislocations. These types of features logically constitute the fast diffusion paths in multi-path diffusion models and the domain boundaries in the multi-domain diffusion (MDD) model (Text Box 4). Diffusive fluxes normal to – but within a few nanometers of – a surface or grain boundary may influence the uptake of impurities during crystal growth [9]. In this case the

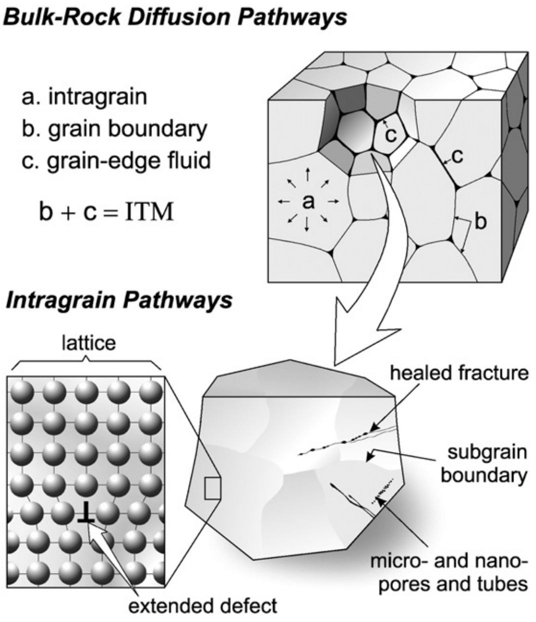


Fig. 3. Schematic representation of diffusion pathways available in rocks (top) and individual mineral grains (bottom). By definition, rocks contain at least two pathways (grains+grain boundaries); the third pathway (grain-edge fluid) may or may not be present. The grain boundaries and grain-edge fluid are 'fast paths' and together represent the ITM (see Baxter and DePaolo [31] and Watson [164]). Mineral grains can be regarded as scaled-down versions of rocks, but here the fast paths are extended defects in the crystal lattice. See text for discussion.

Box 4

"Multiple-path diffusion" jargon

The following terms have been used to describe individual systems characterized by spatially variable diffusion characteristics. All definitions incorporate the idea of discrete 'slow' and 'fast' diffusion pathways (domains) and the diffusion timescales associated with each. In all but the multi-domain diffusion case, the equilibrium partitioning of the diffusant between the slow and fast paths is a fundamental property of the system.

Multi-domain diffusion: frequently abbreviated MDD [47], this concept has been popularized mainly in thermochronologic applications of Ar diffusion in potassium feldspars. The MDD model describes intragrain diffusive loss controlled by multiple intragrain domain sizes (of dimension a_1, a_2, a_3...) each with the same D, and separated from each other by domain boundaries (fast paths) with infinite diffusivity. Net diffusive loss of Ar from a MDD mineral is controlled by a_i^2/D of each domain population (i) and its volumetric fraction in the mineral.

Multi-path diffusion: connotes the presence of multiple intragrain pathways characterized by fundamentally different D, and probably also different characteristic diffusion length scales (a). These intragrain pathways may include the lattice (slowest pathway), as well as "pipes" or planar features consisting of defects or nanopores (see Fig. 3) within and along which diffusion proceeds at a faster rate. Multi-path diffusion has also been referred to as "fast-path", "short circuit", or "pipe" diffusion [162]. Multi-path diffusion differs from the MDD concept only in that the diffusivities of the fast paths are not treated as infinite. Thus diffusive loss from such a mineral is governed by the combined effects of the fast path diffusivity and slow intragrain diffusion providing diffusant to (or accepting it from) the fast paths.

Bulk diffusion: connotes diffusion through a rock or other porous medium where the minerals and the intergranular region (ITM) that surrounds them have fundamentally different properties. It is often the case that the ITM can accommodate much faster diffusion, so the bulk diffusivity of that rock may be governed mainly by the properties and abundance of the ITM. For this to be true, however, the diffusant of interest must be sufficiently concentrated in the ITM, as discussed in Section 3.2. Bulk diffusion in its simplest conceptualization requires that the ITM and the solids maintain equilibrium with respect to the diffusant of interest.

Double-diffusion: essentially a more general term for bulk diffusion where the requirement of equilibrium between mineral grains and ITM is relaxed. Here, the net rate at which a diffusant is transported through a rock system is governed by the diffusion properties of both the ITM and the mineral grains. The ratio of the diffusive timescale for the ITM and the diffusive timescale for equilibration of the solids (called a diffusion-exchange parameter, De) is useful in characterizing net system behavior for the length scales of interest. (Note: Double-diffusion in the present context should not be confused with *double-diffusive convection*, which applies to magma chambers and involves diffusion of heat and matter; see [163])

governing diffusivities may resemble values pertaining to grain boundaries.

2.4. Diffusion at depth in the Earth: general effects of T and P

2.4.1. Temperature dependence

From the discussion in Section 2.2, it follows that diffusion is a temperature-dependent phenomenon: no matter what atomistic model is envisioned to apply in any specific case, the increased kinetic energy associated with higher temperature means greater atom mobility. In the site-jumping model, the diffusivity is proportional to the jump frequency and so is expected to show, qualitatively, the same dependence upon temperature (Text Box 1). The temperature dependence of D 'predicted' by the Stokes–Einstein relation (Text Box 1) is difficult to evaluate because the viscosity (η) of the solvent is itself temperature dependent. In most experimental characterizations of diffusion in geologic media, D varies with T^{-1} in log-linear fashion within the uncertainty of the measurements. In a very broad sense, then, the diffusivity of a given species (i) in a particular medium conforms to the Arrhenius equation

$$D_i = D_{o,i}\exp(-E_a/RT) \tag{3}$$

where D_o and E_a are temperature-independent constants and R is the gas constant. In principle, the pre-exponential constant D_o contains attributes of the diffusion medium such as site type and lattice characteristics, but this has not proven useful in predicting diffusion behavior in complex crystals such as silicates, apart from empirical correlations. The activation energy for diffusion, E_a, varies enormously, the extreme range being from ~40 kJ mol^{-1} for CO_2–H_2O interdiffusion in supercritical fluid [14] to several hundred — e.g., ~700 kJ mol^{-1} for diffusion of C in diamond [15] and ~800 kJ mol^{-1} for diffusion of tetravalent cations in zircon [16]. Both the absolute value of D and its sensitivity to temperature correlate in a broad sense with parameters such as atom packing density ('ionic porosity'), bond strength (as gauged, for example, by ionic charge), and lattice rigidity [17–19].

2.4.2. Pressure dependence

Theories addressing the effect of pressure on D are well developed for simple crystals and van der Waals liquids (see, e.g., [1,20]). In general, it has been shown that

$$D_{T,P} = D_T\exp(-PV_a/RT) \tag{4}$$

where $D_{T,P}$ is the diffusivity at some temperature and pressure, D_T is the 'zero-pressure' diffusivity at the same temperature (given by Eq. (3)) and V_a is a constant characteristic of the diffusant and the medium, having the units of volume. The atomistic significance of V_a (called the activation volume) depends upon the operative diffusion mechanism [1], and it is not in fact always constant over large changes in P or T. The interpretation of V_a in melts and glasses is uncertain, but there are examples in which its value approximates the volume of the diffusing entity [21,22] — which implies that the effects of pressure on diffusion will be most significant for large ions. For $Mg^{2+} \rightleftharpoons Fe^{2+}$ interdiffusion in olivine [23], V_a exceeds the molar volume of the cations (~1.3 cm^3 mol^{-1}), closely approaching that of O^{2-} (~5.5 cm^3 mol^{-1}). Apparently negative values of V_a – i.e., D increasing with increased pressure – have been observed for diffusion in silicate melts (e.g., of Al; [24]), but this behavior is generally attributed to P-dependent aspects of the melt structure.

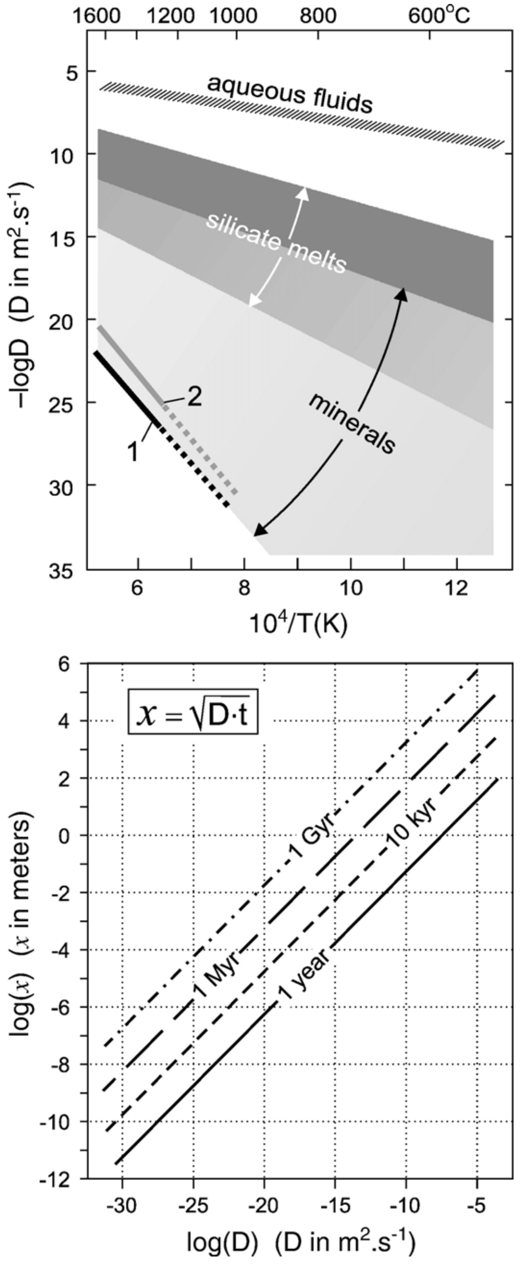


Fig. 4. *Top*: Arrhenius diagram showing generalized diffusion characteristics of geological materials. The lines labeled 1 and 2 represent the slowest-diffusing species known to the authors: self-diffusion of carbon in graphite [15] and diffusion of tetravalent ions in zircon [16], respectively. *Bottom*: Characteristic diffusive length scales for 4 different durations (1, 10^4, 10^6 and 10^9 yr) and the range of diffusivities shown in the top diagram. See text for discussion.

Despite the importance of pressure as a geologic variable, there exists comparatively little information on the effect of pressure (relative to temperature) on diffusion (see recent review by Béjina et al. [25]). Based on the available evidence, it seems safe to generalize that pressure has a minor influence over the P range relevant to the Earth's crust, where variations in D attributable to ΔP would rarely be as high as a factor of

3. In the mantle, however, the pressure effect may rise to prominence, as suggested by recent studies (e.g., [26–28]). Because we see pressure effects as a frontier in diffusion research, this topic will be revisited later.

2.4.3. Diffusivities in Earth materials

A comprehensive summary of the vast literature reporting diffusion measurements on natural materials is precluded here (see Brady [29]; Béjina et al. [25]). A practical, broad-brush characterization is presented in Fig. 4, which illustrates the overall range of D values and their temperature dependence for both crystals and fluids. In order to convey the length scale over which diffusion could be effective in various geologic media, the figure shows characteristic diffusion distance, $x \approx \sqrt{Dt}$, as a function of D for time scales ranging from 1 to 10^9 yr.

3. Solid-Earth diffusion frontiers

3.1. Prologue

Several areas of diffusion research are particularly exciting in terms of both recent discoveries and foreseeable future developments. Due to space constraints, the following sections can convey only the flavor of current frontiers in diffusion rather than an exhaustive discussion. In some instances, we will focus upon specific findings; in other cases we will offer an integrative perspective that we hope will enable the reader to appreciate key phenomena, applications and challenges.

3.2. Diffusion in heterogeneous media

Diffusion in earth systems frequently occurs through complex, heterogeneous media, where more than one phase or pathway exists and each phase has its own distinct chemical and physical properties (Fig. 2; Text Box 4). Complexities could include multiple phases characterized by distinct diffusivities, differences in diffusive length scales (grain sizes), variations in interconnectivity of fast pathways (e.g., fluids), and differences in the concentration of the diffusant within each phase or pathway. Diffusive mass transfer within such poly-phase and/or heterogeneous systems is commonly referred to as *bulk diffusion* (Text Box 4). In its simplest conceptualization, the bulk diffusivity, D_{bulk}, is a continuum property of a heterogeneous material that captures its overall diffusion behavior, and at sufficiently large length scale – much larger than any individual heterogeneities – D_{bulk} can be invoked using the equations in Section 2. However, the concepts and formalisms of bulk diffusion can be applied at a number of scales (Fig. 2), including individual mineral grains (lattice + defects) as well as rocks (minerals + ITM).

A familiar example of bulk diffusion is diffusive mass transfer through a porous medium (e.g., fluid saturated soil, sediment or rock), such as mineral grains permeated by an intergranular fluid medium. Diffusion in the fluid is much faster than in the solid grains, so long-distance diffusive transport is mediated entirely by the fluid (this is analogous to *type c* grain boundary diffusion in the classification of Harrison [30]). Baxter and DePaolo [31] used the term *intergranular transporting medium* (ITM; conceptually similar to Brady's [32] IGR) in reference to this high-diffusivity medium. The properties of the ITM represent the bulk continuum properties of the intergranular region, which in actuality may comprise grain boundaries alone or a combination of one or more C–O–H fluids and/or melt in addition to partially wetted grain boundaries (see Fig. 2). If the solid phases are assumed to be free of (and inert to) the diffusant of interest (e.g., hydrocarbons diffusing through a pure quartz sandstone) then an "effective diffusivity" may be defined:

$$D_{\mathrm{eff}} = bD_{\mathrm{ITM}}\phi \tag{5}$$

where ϕ is the porosity (volume fraction of ITM) and b is the tortuosity of the interconnected fluid pathway.

In many earth systems, the solid grains themselves hold much of the diffusant and at high temperatures may influence the bulk diffusive behavior of the system (e.g., Sr diffusion through a partially molten rock). Here, the bulk diffusivity becomes a strong function of the *partitioning* of the diffusant between the ITM (where long-range transport occurs) and the solid (where some or most of the diffusant is stored). Assuming, for the moment, that the solid grains maintain local equilibrium with the ITM (with respect to the diffusant), then at any location in the system, the ratio between the diffusant concentration in the bulk solid and the ITM is, by definition, the solid/ITM partition coefficient, denoted here as $K_{\mathrm{ITM}}^{\mathrm{solid}} = C_{\mathrm{solid}}/C_{\mathrm{ITM}}$. The effective bulk diffusivity is obtained by modifying Eq. (5) to account for the fraction of the diffusant held in the solids:

$$D_{\mathrm{bulk}}^{*} = \frac{\rho_{\mathrm{ITM}} bD_{\mathrm{ITM}}\phi}{\rho_{\mathrm{solid}}(1-\phi)K_{\mathrm{ITM}}^{\mathrm{solid}}} = \frac{bD_{\mathrm{ITM}}}{MK_{\mathrm{ITM}}^{\mathrm{solid}}} \tag{6}$$

where ρ is the density and M is the mass ratio of solid to ITM in the system. We can express a characteristic bulk diffusive timescale, τ_{bulk}, by introducing a relevant length scale, L, for the system as follows:

$$\tau_{\mathrm{bulk}} = \frac{L^2}{D_{\mathrm{bulk}}^{*}} \tag{7}$$

This bulk diffusive timescale describes the ease with which a particular diffusant is transported in a given bulk system, including the contributions of all solid and ITM phases. This parameter may more generally be called a "transmissive timescale" [33] because other transport processes (e.g., advection) might exist. The importance of the porosity, ϕ, of the system has long been appreciated by researchers studying chemical transport in porous media. More recent study has focused on the equal importance of K in controlling bulk diffusion. Transport through the ITM, however rapid, is only *efficient* if a significant amount of the diffusant is in the ITM. This can be quantified using the mineral/ITM partition coefficient, K, but data are scarce; acquisition of mineral/ITM partitioning data is a research frontier in itself.

The bulk diffusivity, D^*_{bulk}, defined above is applicable whenever it can be assumed that the solid and ITM can maintain equilibrium with each other over the time and length scale of interest. When this assumption breaks down, bulk diffusion in heterogeneous media becomes more complicated, but is still amenable to modeling. This equilibrium assumption is evaluated by comparing the characteristic timescales for diffusive transport within the ITM (τ_{ITM}) and the "equilibration" timescale of the solids with the ITM (τ_e),

$$\text{De} = \frac{\tau_{\text{bulk}}}{\tau_e} \tag{8}$$

where De is a "diffusive-exchange parameter". Equilibration of the solid with the ITM may proceed by a net transfer process such as dissolution-precipitation [31,34,35], grain boundary migration [36,37] or by solid-state diffusion [38,39]. When equilibration is controlled by solid-state diffusion, such systems have been called "double-diffusive" and represent one important subset of "multi-diffusion" systems (Text Box 4). An example of a double diffusive system with application to excess Ar in thermochronology is provided in Section 3.3.5.

3.3. The diffusive closure concept and thermochronology

3.3.1. The Dodson equation

Because so many interpretive geochemical applications (e.g. geo- and thermochronology, geothermobarometry) rely on the assumption or knowledge of equilibration between phases, it is fundamental to rigorously predict the last time and conditions after which diffusive re-equilibration between phases is no longer significant and geochemical/geochronological information is locked in. This non-instantaneous transition between open (equilibrating) and closed (locked in) behavior is called "closure". Jaeger [40] suggested long ago that different minerals close to diffusive loss of certain radiogenic daughter elements (such as Ar, Sr, Pb, He) at different temperatures (their "closure temperatures")–an observation soon understood in the context of the temperature-dependent character of diffusion (Eq. (3)). Dodson [41] formalized the concept of mineral closure and derived what is now known as the "Dodson Equation", which includes the important effects of Arrhenius diffusion parameters (the constants in Eq. (3)) for the element in the mineral of interest, the characteristic diffusion length scale and geometry, and the cooling rate (Dodson used monotonic cooling, $T \propto t^{-1}$, in his derivations). The Dodson equation has proven valuable in illuminating many of the key factors that determine a mineral's closure temperature, but several of the assumptions of the Dodson formulation must be carefully assessed in any given situation. Limitations of the Dodson Equation have been discussed at length elsewhere [42,43]; Cherniak and Watson [44] discuss diffusive closure in the context of thermal events other than monotonic cooling, showing (among other things) that simple heating of an initially cool mineral to its 'closure' temperature for a particular diffusant will result in 40% loss of that diffusant (this statement holds for any heating rate as long as it is equivalent to that used to calculate the closure temperature). Here we focus mainly on issues arising from the gradual nature of closure and the complexities of natural systems.

3.3.2. The partial retention zone

The assumption of monotonic cooling from an arbitrarily high temperature does not apply to every system. Many minerals dwell for extended periods in a "partial retention zone" between complete diffusive openness and complete diffusive closure. Ganguly and Tirone [45] have dealt with this problem for high temperature thermochronometers and thermometers, and much of modern low-temperature thermochronology involves quantification and modeling of these effects, for example in He-thermochronology [46]. While more cumbersome and sometimes non-unique, rigorous numerical approaches are easily applied to even the most complex thermal histories.

3.3.3. Characteristic length scale and diffusivity for mineral closure

Dodson assumed that the macroscopic mineral grain radius and the lattice diffusivity determine the characteristic timescale for diffusive loss. The sub-microscopic complexities of natural minerals (Fig. 2) raise doubt about the validity of these assumptions, especially for noble gases. It is now clear, for example, that the macroscopic grain size has virtually no bearing on the diffusive loss characteristics of Ar from K feldspar [47]. Rather, multiple intracrystalline domains of varying size control Ar diffusive loss. Individual domains conform to the Dodson formulation, and thus each domain carries with it information about a different temperature on a T–t path. While questions persist about the physical basis for the MDD concept, recent work [48] has begun to illuminate the intragrain properties that lead to MDD behavior in feldspars. Ongoing research suggests that multi-path diffusion may characterize other minerals such as titanite and quartz [49,50], fundamentally changing the way diffusive loss (or uptake) should be modeled.

3.3.4. Boundary conditions for mineral closure

Dodson's formulation carries an important yet too-often overlooked assumption—namely that the surroundings of the mineral of interest behave as an effectively infinite sink for the escaping diffusant. Common practice is thus to ignore the surroundings of the mineral of interest in applying the closure concept—indeed, there are no parameters describing the rest of the rock system within Dodson's equation. But as different minerals close at different times and temperatures and as the capacity for the ITM to accept and transport a diffusant varies, this assumption may break down. Stated differently, even if a mineral remains diffusively open (according to Dodson's equation), if it has nothing to exchange chemistry with, it will be effectively closed. Eiler et al. [51] and Jenkin et al. [52] have discussed this issue as it applies to oxygen isotope thermometry and Rb–Sr geochronology, respectively, by assuming rapid diffusion within the ITM and modeling the progressive closure of all local mineral phases. The situation for noble-gas based geochronometers is slightly different, as discussed below.

3.3.5. Case study: the importance of bulk diffusion in thermochronology

In the case of noble-gas based thermochronometers (K–Ar and U/Th–He), the infinite sink assumption of Dodson's equation implies that the concentration of the escaping noble gas at the mineral surface is always effectively zero. If true, this zero-concentration boundary condition prevents Ar (or He) accumulation in the mineral of interest before its closure interval, conveniently linking the closure temperature with the measured radiogenic age—the basis of thermochronology. While this assumption seems to be valid in many cases, and may almost always be true for helium [53], the ubiquitous occurrence of "excess Argon" shows that it does not always hold [54,55]. Baxter [33] showed that the zero-concentration boundary condition can be met in one of two ways: 1) if the Ar (or He) released into the surroundings can be transported away from the system significantly faster than it is produced, and/or 2) if the partitioning of Ar (or He) between the mineral of interest and its surroundings strongly favors the surroundings. Here, the importance of partitioning between minerals, fluids and melts [55], and dry grain boundaries [56] is illuminated. These effects are encapsulated in a single equation showing how excess Ar (expressed as an age-equivalent) builds up in a mineral *prior* to its closure. Two factors are important: 1) the "transmissive timescale", τ_T, for transport of Ar out of the system to an effective sink a distance L away, and 2) the "total local sink capacity" (TLSC) of the surroundings relative to the mineral of interest

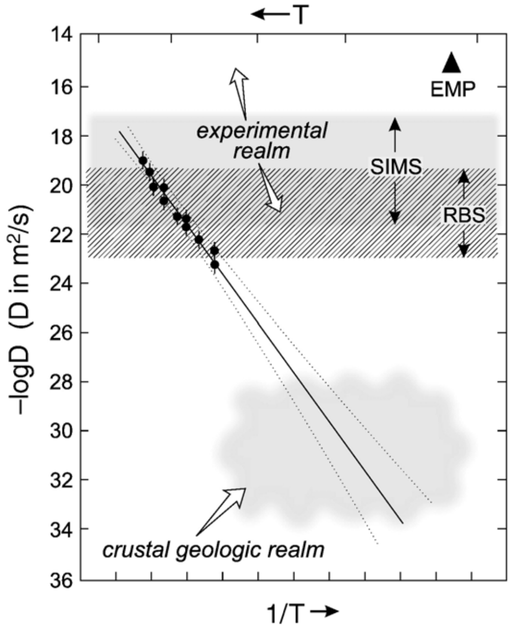


Fig. 5. Arrhenius diagram illustrating the nature of the extrapolation often required to apply laboratory diffusion data to crustal geologic systems. The temperature scale is arbitrary because no particular diffusion law is assumed, but the diffusivity scale has meaning in terms of what can be measured in the laboratory. The minimum measurable value is determined by the available time (realistically, a few months) and the spatial resolution of the analytical technique. Rutherford backscattering spectroscopy (RBS) and secondary-ion mass spectrometry (SIMS) have the best resolution available in depth-profiling mode. The minimum diffusivity measurable using RBS (depth resolution ~10 nm) is ~10^{-23} m^2/s. This value is high enough to result in appreciable diffusion over the vast time scales of some natural diffusion phenomena (10 s of microns in 1 Myr; ~1 cm in 1 Gyr).

including equilibrium partitioning and modal abundance effects:

$$^{40}Ar_{age-equivalent}(L,t) \cong \frac{\tau_T^{Ar}}{2}\left(1-\exp\left(-5/2\cdot\frac{t}{\tau_T^{Ar}(1+TLSC^{Ar})}\right)\right) \tag{9}$$

(note the minus sign preceding the 5/2 constant is a correction from Baxter [33]). Here, τ_T is defined as the bulk diffusive timescale for Ar (or He) as in Eq. (7). This equation is valid for Ar bulk diffusion through the ITM with the required assumption that all minerals in the system (Ar sources and sinks) are open and able to maintain equilibrium with each other and with the ITM. In practice, noble gas thermochronology is most rigorously modeled as a double-diffusive system (cf. Text Box 4) including the diffusion of Ar within the mineral of interest and the surrounding sink minerals, as well as bulk diffusion of Ar out of the system through the ITM. When any minerals in the system begin to pass through their respective closure intervals, the above equation breaks down because the system must be treated as double-diffusive, and further calculations must be performed numerically. This is an example of the applicability and importance of bulk and double-diffusive regimes in geochronology.

3.4. ‘Natural’ vs. ‘laboratory’ diffusion

There is a marked contrast between the time scales available in the laboratory to study diffusion and the time scales relevant to natural transport processes. This unavoidable fact necessitates care and wisdom in the comparison (and reconciliation) of observations from the two realms (e.g., [43]). Experimentalists who characterize diffusion in the laboratory cling to the theoretical principle that lattice diffusivities are true constants that apply for all time under appropriate and comparable conditions. Although generally defensible, this viewpoint does not circumvent the unavoidable reality that laboratory determinations of D are commonly made at temperatures significantly higher (and timescales much shorter) than those of interest in nature, particularly when the experiments target a crustal phenomenon. Down-temperature extrapolation of measured diffusivities to geologically realistic temperatures is often necessary (see Fig. 5). The principal risk in this approach is that low-temperature diffusion behavior may be dominated by a different pathway, in which case the high-temperature data paint an inaccurate picture. Wartho et al. [57] showed, for example, an apparent change in Arrhenius laws for Ar diffusion in K feldspar below about 725 °C. The prevalence of such behavior is unknown, but frequent agreement between high-temperature data and natural constraints on diffusion (see below) suggests that the problem is not pervasive. Lattice diffusivities measured in the laboratory should not be assumed, indiscriminately, to apply to all natural cases, but this does not lessen the value of the measurements: at some length (and time) scale, it is lattice diffusion specifically that governs diffusive

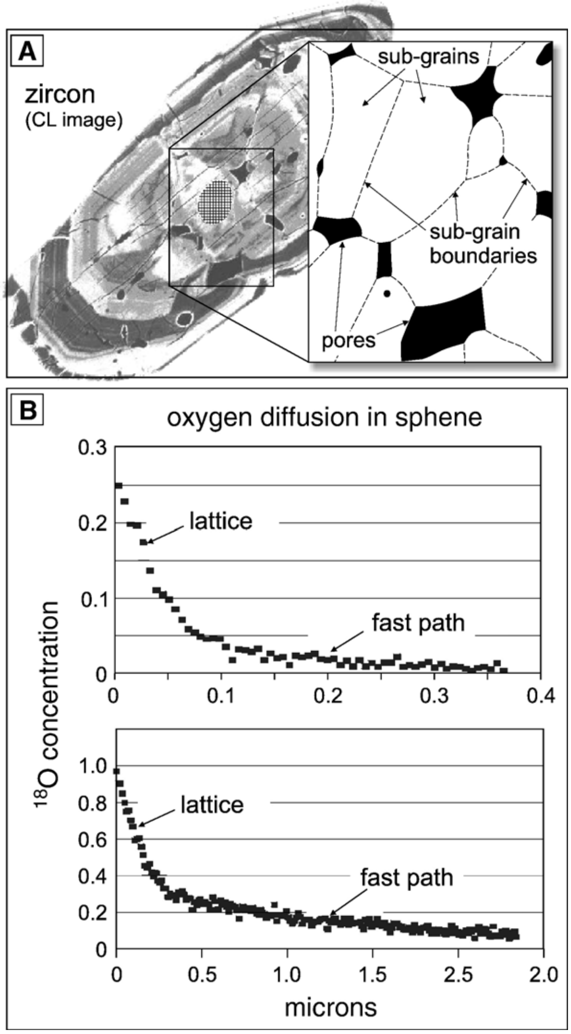


Fig. 6. Evidence of diffusion ‘fast paths’ in what appear to be single crystals. A: Cathodoluminescence (CL) image of a zircon containing melt inclusions (black) with distinct ‘cusps’ indicating the presence of sub-grain boundaries (inclusions within a true single crystal would be nearly spherical). The sub-grain boundaries appear as dashed curves in the enlarged sketch. Note that the CL banding is generally concentric with the outer rim of the zircon, suggesting that it grew as a single crystal. Image courtesy of E. Belousova and S. O’Reilly. B: Experimentally produced ^{18}O diffusive uptake profiles in natural sphene showing ‘tails’ caused by fast path diffusion [49].

exchange between a mineral and its surroundings. Because of the high temperatures prevailing in the mantle relative to the crust, experiments can often be conducted at the temperatures of direct interest, so down-temperature extrapolations are not always necessary.

The diffusivities governing *in situ* diffusion in natural systems can sometimes be estimated directly from measurements on rocks and minerals. Diffusion behavior can be deduced from isotopic closure systematics and from observed chemical gradients coupled with independent constraints on thermal history. Additional insights into diffusion in natural samples can be gained from the diffusive loss characteristics of Ar and He in the extraction line of a mass spectrometer. 'Real-world' characterizations of diffusion are often in good agreement with laboratory measurements; examples include: Pb diffusion in zircon (e.g., [58,59]), monazite (e.g., [60–62]), titanite [63,64] and apatite [65,66]. Carlson [67] noted generally good agreement between laboratory and natural constraints on divalent cation diffusion in garnet.

The most common cause of discrepancies between lab and nature may be 'imperfect' growth conditions of natural crystals or a history of deformation and recrystallization, either of which could result in fast paths [68,69]. Fig. 6 depicts two forms of direct evidence that fast-path contributions will complicate the diffusion behavior of what are apparently single crystals. The abundant evidence for multi-path diffusion of noble gases also underscores this point, although it is not yet known whether other diffusants are subject to similar effects. Other factors besides the mere existence of high diffusivity pathways are important in this context, most notably the partitioning of the diffusant between the fast path and the lattice (see 3.2).

In summary, the advantage of laboratory-determined diffusivities is that we can usually be fairly certain what has been characterized; the disadvantage is that downward extrapolations in temperature are often required to apply the data to natural systems, and if natural samples are dominated by fast-paths not present in the lab sample, the laboratory value represents only part of the information needed. The strength of diffusion information obtained from natural rocks is that it can be applied with confidence to the specific material that was characterized; the drawback is the uncertainty about the transport path and the soundness of generalizing to other samples and conditions. Continued effort to 'reconcile' laboratory with nature are an important frontier in diffusion studies; for the most part, this means discovering the full range of factors that contribute to multi-path diffusion and the circumstances under which these come into play.

3.5. *Effect of H_2O and H species on diffusion*

Dissolved H_2O in magmas has a pronounced enhancing effect on diffusion of most constituents [70], which is reasonable given the de-polymerization of the melt that accompanies H_2O dissolution (e.g., [71]). The effect of H species on diffusion in crystals is less well understood, but it stands to reason that intracrystalline diffusion can be affected only if H species enter the lattice. It has been recognized for some time that the presence of H_2O in the system of interest can dramatically affect lattice diffusion of oxygen in the crystalline phases present, including quartz [72–75], calcite [76,77], alkali feldspar [75,78]; clinopyroxene [79], zircon [80], monazite [81], rutile [82], olivine [83,84] and sphene [49]. The effect is almost always an enhancement of oxygen diffusion by the presence of H_2O, but in rutile the relationship is more complex [82]. In some cases, $D_{\text{oxygen}}^{\text{lattice}}$ shows a systematic increase with increasing P_{H_2O} [74,79], but in other instances the relationship between $D_{\text{oxygen}}^{\text{lattice}}$ and H_2O appears to be 'binary': i.e., fast diffusion is 'turned on' at some low threshold value of P_{H_2O} but changes relatively little over large subsequent increases in P_{H_2O}. [80]. The generally accepted explanation for H_2O-enhanced oxygen diffusion is that neutral water molecules are somewhat soluble and highly mobile in the crystal lattice [85,86]. These mobile H_2O molecules serve as 'long-distance carriers' of oxygen, and exchange oxygen with the lattice locally.

Given the probable mechanism of oxygen diffusion enhancement by H_2O, it is perhaps not surprising that lattice diffusion of *cations* appears generally insensitive to changes in P_{H_2O}, with certain important exceptions. Existing experimental studies suggest a limited role for H in lattice diffusion of cations at crustal P–T conditions. Kronenberg et al. [87], for example, concluded that the presence of H_2O does not affect C diffusion in calcite. Cherniak and Watson [58] showed that D_{Pb} in zircon in the presence of hydroxyapatite (but no fluid phase) is indistinguishable from D_{Pb} in zircon under H-absent conditions. Perhaps more convincing is the fact that independent characterizations of Sr diffusion under dry and H_2O-present conditions for both feldspar and apatite are in substantial agreement [88–90,65], and there are numerous examples of agreement between inferred isotopic closure behavior in natural systems (reasonably inferred to contain some H species) with laboratory characterizations of diffusion under dry conditions (see Section 3.4). Watson and Cherniak [91] examined Ar diffusion in quartz under nominally dry and H_2O-present conditions and did not find a significant difference. Cherniak and Watson [44] showed that Ti diffusion in zircon is unaffected by a change from dry conditions at atmospheric pressure to $P_{H_2O}=0.6$ GPa.

The effect of H_2O on lattice diffusion of cations in deep-seated mantle phases is a quite different story, perhaps because the available lattice solution mechanisms for H-bearing species are different. Recent studies have revealed significant enhancement by H_2O of Si self-diffusion [84] and Fe–Mg interdiffusion in olivine [92,93]. These effects are probably responsible for enhancement of kinetic properties such as viscosity, grain-growth rate and phase transformation kinetics [94–98]. In the Fe–Mg case, diffusion enhancement has been traced to the entry of H^+ into the lattice and consequent changes in point-defect concentrations (cation vacancies). The enhancement of $\tilde{D}_{Fe-Mg}$ is roughly proportional to the increase in water fugacity, leading to a ~50-fold increase in 'wet' Fe–Mg interdiffusion over the dry case at 5 GPa and 1100 °C. A similar but smaller effect has been observed for Fe–Mg interdiffusion in ferro-periclase [99].

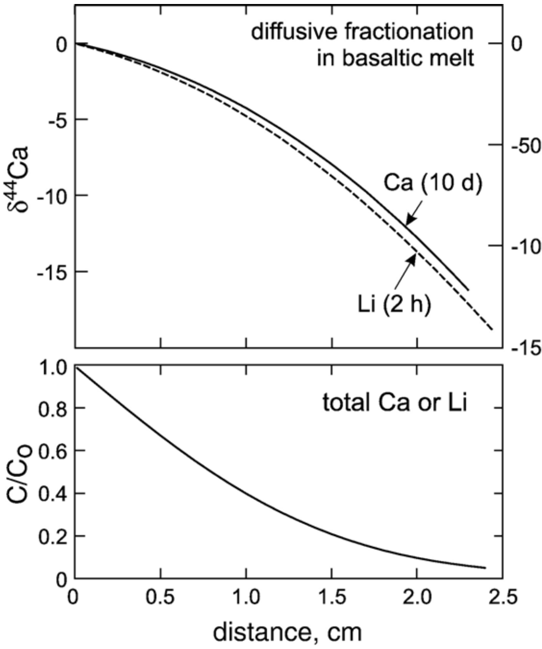


Fig. 7. Diffusive fractionation in silicate melt illustrated with isotopes of Ca (masses 40 and 44) and Li (masses 6 and 7) using the β values determined by Richter et al. [101]; see text. The hypothetical scenario involves diffusion into a melt reservoir initially free of both Ca and Li from a surface source held at constant concentration (at 0 cm). Top panel shows δ values as a function of distance for diffusion times of 10 days for Ca and 2 h for Li. The δ values are conventional $^{44}Ca/^{40}Ca$ and $^7Li/^6Li$, referenced to source ratios equivalent to the natural isotopic abundances: $^{44}Ca/^{40}Ca=0.0212$; $^7Li/^6Li=12.333$). This scenario–i.e., diffusion into a reservoir initially lacking the element of interest–maximizes the effects of subtle differences in isotope diffusivities. See Richter et al. [106] for a general discussion.

The presence of free H_2O in the ITM of a given rock system significantly enhances the rates of ITM-mediated bulk diffusion. Aqueous fluid in the ITM can play a first-order role in determining, for example: 1) the rates at which local chemical reactions can proceed [100,38]; 2) the rheology of rocks, particularly within the diffusion creep regime (e.g., [76,101]); and 3) the bulk diffusive transport of elements or isotopes of geochemical significance. The possible role of H species in grain boundaries of fluid-absent rocks is unknown.

3.6. Diffusive fractionation of isotopes

The phenomenon of (isotopic) mass-dependent diffusion in gases has been recognized for decades, and formed the basis of early efforts to separate isotopes. Until recently, the effect has been considered only sporadically for geologically relevant diffusants and condensed phases. In olivine and clinopyroxene, Trull and Kurz [102] observed a significant difference in the diffusivities of ^{3}He and ^{4}He (for which the mass effect might be relatively large), and Tsuchiyama et al. [103] made theoretical predictions about isotopic effects on diffusion of heavier elements in molten MgO. Trull and Kurz [104] later noted differences in He isotope diffusivities of several percent in basaltic glass. Also in 1999, Richter et al. [105] demonstrated experimentally for the first time that isotopes of a relatively heavy element (^{40}Ca and ^{44}Ca) have slightly different diffusivities in $CaO–Al_2O_3–SiO_2$ melts. This mass effect on diffusion was later extended by Richter et al. [106] to melts of basaltic and rhyolitic composition. It was also confirmed for Li isotopes (^{6}Li and ^{7}Li), where a substantially larger effect was observed. Richter et al. [105] adopted the mathematical form of the mass dependence expected from the kinetic theory of gases

$$(D_1/D_2) = (M_2/M_1)^{\beta} \tag{10}$$

where the D ratio is the diffusivity of isotope 1 over that of isotope 2, and M refers to isotope mass. For gases, the exponent β is 0.5, but the results for Li and Ca isotopes in silicate melts reveal smaller β values of 0.215 and 0.075, respectively. These β values lead to small absolute differences in D for two isotopes (the difference appears in the second or third decimal place), but these differences can produce rather large isotope fractionations under the "right" circumstances. As discussed by Richter et al. [106], the potential for diffusive fractionation is maximized when two interdiffusing reservoirs have markedly different concentrations of the element whose isotopes are under consideration. The most extreme case is when one of the reservoirs is essentially devoid of the element of interest, as illustrated in Fig. 7. These dramatic diffusive fractionations require special circumstances in order to develop in natural systems, but plausible scenarios do exist. Fractionation effects due to diffusion in melts might be expected in the margins of mafic magma bodies emplaced in the continental crust, in vapor bubbles exsolving from a magma, and in magmatic double-diffusive situations.

Richter et al. [107] extended their studies of diffusive isotopic fractionation to aqueous solutions at near-ambient conditions, where substantial smaller effects are observed (β in Eq. (10) is $\sim 0.01-0.03$). The documentation of mass-dependent diffusivities in silicate melts at high temperatures and in aqueous solutions at low temperatures raises the likelihood that geologic media 'intermediate' between these two – e.g., supercritical fluids laden with silicate solute – might exhibit the same effect. This has not yet been demonstrated experimentally, but the recent study by Teng et al. [108] of amphibolite country rock against an alkalic pegmatite strongly suggests fractionation of Li isotopes by diffusion in either a fluid phase or in the grain boundaries of the amphibolite (^{7}Li/^{6}Li fractionation >20‰ was observed). Whichever diffusion medium is responsible, similar effects might be envisioned for the interaction between down-going slab and overlying mantle wedge in subduction zones.

The documentation of mass-dependent diffusion in a variety of geologic media (gases, aqueous solutions, and molten silicates) begs the question as to whether it also occurs in minerals for elements other than light noble gases. Studies of metals (e.g., [109]) suggest that the answer is yes, but direct measurements on minerals will be difficult because diffusion distances achievable in the lab are generally small and depth-profiling analytical techniques may therefore be required. The mass effect appears largest in gases at low pressures, markedly smaller in dense (silicate) liquids, and still smaller in aqueous solutions. On the basis of observed behavior in gases and silicate melts, we speculate that the mass effect will be quite small in dense crystalline oxides, where the kinetic energy of the atoms is almost entirely vibrational (see Section 2.2).

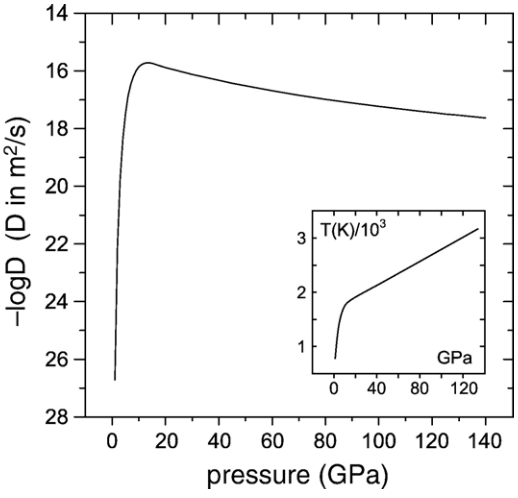


Fig. 8. Diffusivity along the mantle geotherm in a hypothetical phase that is stable over the entire pressure range. Typical diffusion parameters were assumed as follows (see Eqs. (3) and (4)): $D_o = 1\text{E}^{-6}$ m^2 s^{-1}; $E_a = 300$ kJ·mol^{-1}; $V_a = 3$ cm^3·mol^{-1}. The geotherm (inset) is an average based mainly on the information in Duffy and Hemley [165], and is given for $P = 1–15$ GPa by $T(K) = 1900–1420\cdot(0.8^P)$ and for $P = 16–140$ GPa by $T(K) = 1680 + 11.1\cdot P$.

In closing this section, we note that, unlike equilibrium fractionation, diffusive fractionation does not go away at high temperature — it can occur at all temperatures where diffusion is effective [106]. This does not mean that we should expect ubiquitous occurrences, however, because diffusive fractionation will be apparent only in a system that fails to reach equilibrium: it is a consequence of an interrupted process. Lastly, the magnitude of an observed mass effect on diffusion of a particular element will depend strongly upon the identity of the diffusing species. Aqueous solute ions, for example, carry large spheres of hydration, and it is the mass (and size) of the entire complex that will determine the value of D. Differences arising from the identity of the solute isotope of interest will be minimized in this case [107]. The same effect could operate in magmas, where elements of potential interest dissolve (and may diffuse) as molecules or complex anions (e.g., CO_3^{2-} or CO_2 in the case of carbon [110]).

3.7. Diffusion in the deep Earth

Studies of diffusion have been conducted on Earth materials for several decades, but it is only recently that the experimental technologies (and computational approaches (e.g. [111])) have been available to explore diffusion in the deep Earth — i.e., at $P > 3$ or 4 GPa (see [25] and references therein). Given the form of Eqs. (3) and (4) and knowledge of the deep geothermal gradient, the key question is how the enhancing effect of increased T on diffusion plays off against the suppressing effect of increased pressure. In this regard, it is important to bear in mind (given the form of Eq. (3)) that a temperature increment of, say, 100° has a progressively smaller effect as temperature rises along the geothermal gradient. The interplay of the effects of temperature and pressure along the geotherm is illustrated in Fig. 8 for a hypothetical phase that is stable over the entire range of $P–T$ conditions in the mantle. No such phase exists, but the plot is nevertheless useful in revealing the dominance of the temperature effect at shallow depth and the counteracting effect of pressure deep in the Earth. The diffusivity along the entire lower-mantle geotherm changes by only about 2 orders of magnitude despite a temperature difference of ~1400°. Real-world phase transitions would obviously affect this oversimplified picture [26,112].

Revisiting the approach of Hofmann and Hart [113], Holzapfel et al. [28] applied their new data for Fe–Mg interdiffusion in the perovskite lattice to evaluate diffusive equilibration time scales in the lower mantle, concluding that the length scale of diffusion over the entire age of the Earth is only about 1 m. This result contrasts with that of Van Orman et al. [114] for cation and oxygen diffusion in MgO at pressures up to 25 GPa. Lattice diffusion in this phase is fast enough to lead to diffusive length scales of 1–10 km over the age of the Earth (100 km if grain boundary transport controls the diffusive flux). Given a perovskite-dominated lower mantle, the question of whether subordinate magnesiowüstite grains are interconnected becomes of paramount importance (isolated grains of a high-diffusivity phase would have little effect on bulk transport).

One of the key questions concerning deep-Earth diffusion is to what extent the metallic core communicates with the silicate mantle, and what elements are involved. This topic was addressed in early studies by Knittle and Jeanloz [115] and Goarant et al. [116] focusing specifically upon the rate of reaction between metal and oxides. A broader attack on this general problem will undoubtedly occur over the coming decade, given the ongoing debate about possible core–mantle 'communication' with respect to certain siderophile elements [117–121]. Some siderophile elements have been shown to be extremely mobile in MgO grain boundaries at modest pressures [122,123].

3.8. Bulk diffusion of molecular H_2O

Water, and its transport within the Earth, is central to many important geochemical questions which go far beyond the scope of this paper. Consider, for example, the global water cycle represented by the hydration of the oceanic lithosphere, the subduction and de-watering of the slab, the release of H_2O into the fore-arc and mantle wedge, and the fluxing of arc magmatism. The processes within this cycle are topics of concentrated research in the geoscience community, and yet the mechanisms and rates by which H_2O is transported and exchanged within these systems are not well constrained. Certainly, advection of aqueous fluids (or supercritical fluids) operates in many systems [124–126], but if that flow is channelized, then at some local length scale, diffusive transport of water to and from such channels (e.g.,[127,128]) is rate limiting in the net hydration or dehydration of a rock system.

On the input side of the subduction zone, Ranero et al. [129] suggest that hydration of the oceanic crust and mantle is promoted by channelized flow down flexure cracks. However, the overall effectiveness of hydration depends upon the extent of H_2O migration from the cracks into the adjacent rock. This would occur via either grain-boundary diffusion of H_2O molecules or penetration of fluid along grain edges by dissolution/precipitation processes [130], or both. The latter process is controlled by solute diffusion through interconnected fluid, but can occur only if grain-edge wetting is energetically favorable [130]. In either case, the bulk diffusive length scale, L, would be represented by the half width between flexure cracks. Experimental constraints and modeling of the bulk diffusion of H_2O coupled with hydration and dehydration reaction kinetics within subduction zones is another important frontier.

3.9. Geospeedometry: constraining the durations of geologic processes

Geospeedometry [131] refers to the use of diffusion profiles within minerals to extract information about the timescale of a particular geologic process. Whereas geochronology is generally geared toward the specific age of an event, geospeedometry is theoretically capable of providing unique information about the duration or episodicity of that event. Further interpretations may in some cases permit evaluation of the rate of a particular process — i.e., the 'speed' in geospeedometry. Conceptually, if the Arrhenius law of a particular species in a mineral is well known, and if an 'unfinished' diffusion profile is captured in a mineral, then the duration over which diffusion occurred can be determined. Geospeedometry is thus capable of elucidating very short-lived events that traditional geochronology cannot resolve. Recent years have seen a resurgence of this methodology, in particular as chemical diffusion data have continued to improve. Examples include the use of chemical profiles in igneous phenocrysts to constrain eruptive timescales and cooling rates (e.g. [132–135]) and chemical profiles in metamorphic minerals to constrain the duration of metamorphism and related processes (e.g., [136–138]). Watson and Harrison [139] described a method to extract *T–t* information from stranded profiles of two diffusants governed by independent Arrhenius laws. As additional high-quality experimental data on diffusion become available, this and other approaches in geospeedometry may reach their full potential.

3.10. Computational sources of data

This discussion would not be complete without brief mention of theoretical means to obtain diffusion 'data' for use in modeling geochemical systems, as this is an important frontier in itself. Oelkers and Helgeson [140] were early contributors in this area who constrained diffusion of a variety of ions in supercritical aqueous fluids using available electrical conductance measurements and the Nernst–Einstein equation. Recently, theorists have turned to computational approaches to generate diffusion 'data' for both solids and liquids. Molecular dynamics simulations–which explore large assemblages of atoms using interatomic potentials to calculate equilibrium and transport properties–are particularly promising (e.g., [103,141–154]). These approaches have not yet eliminated the need for constraints from the experimental lab and natural systems, but we can expect computational modeling and direct measurements to go increasingly hand in hand in future studies.

Acknowledgements

Some of the research described in this paper was supported by the National Science Foundation, through grant nos. EAR 0440228 and EAR 0337481 to EBW and EAR-0337527 to EFB. During the course of the writing, discussions with D.J. Cherniak, D.A. Wark, J.B. Thomas, and Dustin Trail were invaluable, as was their input on the manuscript itself. Official reviews by Jim Van Orman and an anonymous reviewer are greatly appreciated. We probably would not have finished the manuscript without Alex Halliday's encouragement.

References

[1] P.G. Shewmon, Diffusion in Solids, McGraw-Hill, New York, 1963.

[2] J.R. Manning, Diffusion Kinetics for Atoms in Crystals, Wiley, New York, 1968.

[3] E.L. Cussler, Diffusion: Mass Transfer in Fluid Systems, 2nd ed., Cambridge Univ. Press, Cambridge, U.K., 1997.

[4] M.E. Glicksman, Diffusion in Solids: Field Theory, Solid-State Principles, and Applications, John Wiley, Hoboken, N.J., U.S.A., 2000.

[5] J. Crank, The Mathematics of Diffusion, 2nd ed.Clarendon Press, Oxford, 1975.

[6] V.C. Kress, M.S. Ghiorso, Multicomponent diffusion in MgO–Al_2O_3–SiO_2 and CaO–MgO–Al_2O_3–SiO_2 melts, Geochim. Cosmochim. Acta 57 (1993) 4453–4466.

[7] S. Chakraborty, D.B. Dingwell, D.C. Rubie, Multicomponent diffusion in ternary silicate melts in the system K_2O–Al_2O_3–SiO_2. 1. Experimental measurements, Geochim. Cosmochim. Acta 59 (1995) 255–264.

[8] Y. Liang, F. Richter, E.B. Watson, Diffusion in silicate melts: II. Multicomponent diffusion in CaO–Al_2O_3–SiO_2 at 1500 °C and 1 GPa, Geochim. Cosmochim. Acta 60 (1996) 5021–5035.

[9] E.B. Watson, A conceptual model for near-surface kinetic controls on the trace-element and stable-isotope composition of abiogenic calcite, Geochim. Cosmochim. Acta 68 (2004) 1473–1488.

[10] G.W. Fisher, Nonequilibrium thermodynamics as a model for diffusion controlled metamorphic processes, Am. J. Sci. 273 (1973) 897–924.

[11] A.C. Lasaga, Kinetic Theory in the Earth Sciences, Princeton University Press, Princeton, N.J., 1998.

[12] E.B. Watson, J.M. Brenan, Fluids in the lithosphere. 1. Experimentally-determined wetting characteristics of CO_2–H_2O fluids and their implications for fluid transport, host-rock physical properties, and fluid inclusion formation, Earth Planet. Sci. Lett. 85 (1987) 497–515.

[13] B.K. Holtzman, N.J. Groebner, M.E. Zimmerman, S.B. Ginsberg, D.L. Kohlstedt, Stress-driven melt segregation in partially molten rocks, Geochem. Geophys. Geosyst. 4 (2003) 8607–8633.

[14] D.A. Wark, E.B. Watson, Interdiffusion of H_2O and CO_2 in metamorphic fluids at 490–690 °C and 1 GPa, Geochim. Cosmochim. Acta 68 (2004) 2693–2698.

[15] K.T. Koga, M.J. Walter, E. Nakamura, K. Kobayashi, Carbon self-diffusion in natural diamond, Phys. Rev., B 72 (2005) (art. no. 024108).

[16] D.J. Cherniak, J.M. Hanchar, E.B. Watson, Diffusion of tetravalent cations in zircon, Contrib. Mineral. Petrol. 127 (1997) 383–390.

[17] S.M. Fortier, B.J. Giletti, An empirical model for predicting diffusion coefficients in silicate minerals, Science 245 (1989) 1481–1484.

[18] J.A. Van Orman, T.L. Grove, N. Shimizu, Rare earth element diffusion in diopside: influence of temperature, pressure, and ionic radius, and an elastic model for diffusion in silicates, Contrib. Mineral. Petrol. 141 (2001) 687–703.

[19] D.J. Cherniak, REE diffusion in feldspar, Chem. Geol. 193 (2003) 25–41.

[20] J. Naghizadeh, S.A. Rice, Kinetic theory of dense fluids, X. Measurement and interpretation of self-diffusion in liquid Ar, Kr, Xe, and CH4, J. Chem. Phys. 36 (1962) 2710–2720.

[21] E.B. Watson, M. Sneeringer, A. Ross, Diffusion of dissolved carbonate in magmas: Experimental results and applications, Earth Planet. Sci. Lett. 61 (1982) 346–358.

[22] S.D. Hamann, The influence of pressure on electrolytic conduction in alkali silicate glasses, Aust. J. Chem. 18 (1965) 2–8.

[23] D.J. Misener, Cation diffusion in olivine, in: A.W. Hofmann, B.J. Giletti, H.S. Yoder, R.A. Yund (Eds.), Geochemical Transport and Kinetics, vol. 634, Carnegie Inst. Wash. Publ., 1974, pp. 117–129.

[24] I. Kushiro, Effect of pressure on the diffusivity of network-forming cations in melts of jadeitic composition, Geochim. Cosmochim. Acta 47 (1983) 1415–1422.

[25] F. Béjina, O. Jaoul, R.C. Liebermann, Diffusion in minerals at high pressure: a review, Phys. Earth Planet. Int. 139 (2003) 3–20.

[26] D.L. Farber, Q. Williams, F.J. Ryerson, Divalent cation diffusion in Mg_2SiO_4 spinel (ringwoodite), beta phase

(wadsleyite), and olivine: implications for the electrical conductivity of the mantle, J. Geophys. Res. 105 (B1) (2000) 513–529.

[27] C. Holzapfel, D.C. Rubie, S. Mackwell, D.J. Frost, The effect of pressure on Fe–Mg interdiffusion in $(Fe_XMg_{1-X})O$ ferropericlase, Phys. Earth Planet. Int. 139 (2003) 21–34.

[28] C. Holzapfel, D.C. Rubie, D.J. Frost, F. Langenhorst, Fe–Mg interdiffusion in $(Mg,Fe)SiO_3$ perovskite and lower mantle reequilibration, Science 309 (2005) 1707–1710.

[29] J.B. Brady, Diffusion data for silicate minerals, glasses, and liquids, in: T.J. Ahrens (Ed.), Mineral Physics and Crystallography, a Handbook of Physical Constants, Am. Geophys. Union, Washington, D.C., 1995.

[30] L.G. Harrison, Influence of dislocations on diffusion kinetics in solids with particular reference to alkali halides, Trans. Faraday Soc. 57 (1961) 1191–1199.

[31] E.F. Baxter, D.J. DePaolo, Field measurement of slow metamorphic reaction rates at temperatures of 500–600 °C, Science 288 (2000) 1411–1414.

[32] J.B. Brady, Intergranular diffusion in metamorphic rocks, Am. J. Sci. 283-A (1983) 181–200.

[33] E.F. Baxter, Quantification of the factors controlling the presence of excess ^{40}Ar or ^{4}He, Earth Planet. Sci. Lett. 216 (2003) 619–634.

[34] C.I. Steefel, D.J. DePaolo, P.C. Lichtner, Reactive transport modeling: an essential tool and new research approach for the Earth Sciences, Earth. Planet. Sci. Lett. 240 (2005) 539–558.

[35] D.J. DePaolo, S.R. Getty, Models of isotopic exchange in fluid-rock systems: Implications for geochronology in metamorphic rocks, Geochim. Cosmochim. Acta 60 (1996) 3933–3947.

[36] E.F. Baxter, D.J. DePaolo, Field Measurement of High Temperature Bulk Reaction Rates II: interpretation of results from a field site near Simplon Pass, Switzerland, Am. J. Sci. 302 (2002) 465–516.

[37] M. Nakamura, H. Yurimoto, E.B. Watson, Grain growth control of isotope exchange between rocks and fluids, Geology 33 (2005) 829–832.

[38] E.F. Baxter, Natural Constraints on Metamorphic Reaction Rates, in: Vance Muller, Villa (Eds.), Geochronology-linking the isotopic record with petrology and textures, vol. 220, Geol. Soc. London, Spec. Publ., 2003, pp. 183–202.

[39] J.A. Van Orman, T.L. Grove, N. Shimizu, Diffusive fractionation of elements during production and transport of melt in Earth's upper mantle, Earth Planet. Sci. Lett. 198 (2002) 93–112.

[40] E. Jaeger, Rb–Sr age determination on minerals and rocks from the Alps, Sci. Terre 10 (1965) 395–406.

[41] M. Dodson, Closure temperature in cooling geochronological and petrological systems, Contrib. Mineral. Petrol. 40 (1973) 259–274.

[42] I. McDougall, T.M. Harrison, Geochronology and Thermochronology by the $^{40}Ar/^{39}Ar$ Method, Oxford University Press, New York, 1999.

[43] I.M. Villa, From nanometer to megameter: isotopes, atomic-scale processes, and continent-scale tectonic models, Lithos 87 (2006) 155–173.

[44] D.J. Cherniak, E.B. Watson, Ti diffusion in zircon, Chem. Geol. (submitted for publication).

[45] J. Ganguly, M. Tirone, Diffusion closure temperature and age of a mineral with arbitrary extent of diffusion: theoretical formulation and applications, Earth Planet. Sci. Lett. 170 (1999) 131–140.

[46] P.W. Reiners, T.A. Ehlers (Eds.), Low-temperature thermochronology, Reviews in Mineralogy and Geochemistry, vol. 58, Mineralogical Society of America, 2005.

[47] O.M. Lovera, F.M. Richter, T.M. Harrison, The $^{40}Ar/^{39}Ar$ geothermometry for slowly cooled samples having a distribution of diffusion domain sizes, J. Geophys. Res. 94 (1989) 17,917–17,935.

[48] J.D. Fitz Gerald, I. Parsons, N. Cayzer, Nanotunnels and pull-aparts: defects of exsolution lamellae in alkali feldspars, Am. Mineral. 91 (2006) 772–783.

[49] X.Y. Zhang, D.J. Cherniak, E.B. Watson, Oxygen diffusion in titanite: lattice diffusion and fast-path diffusion in single crystals, Chem. Geol. 235 (2006) 105–123.

[50] E.F. Baxter, P.L. Clay, S.P. Kelley, E.B. Watson, D.J. Cherniak, J.B. Thomas, Two diffusive pathways for Ar in quartz and feldspar, Goldschmidt Conference, Melbourne Australia, 2006.

[51] J.M. Eiler, J.W. Valley, L.P. Baumgartner, A new look at stable isotope thermometry, Geochim. Cosmochim. Acta 57 (1993) 2571–2583.

[52] G.R.T Jenkin, G. Rogers, A.E. Fallick, C.M. Farrow, Rb–Sr closure temperatures in bi-mineralic rocks: a mode effect and test for different diffusion models, Chem. Geol. 122 (1995) 227–240.

[53] K.A. Farley, (U–Th/He) Dating: techniques, calibrations, and applications, in: D. Porcelli, C.J. Ballentine, R. Weiler (Eds.), Rev. Min. Geochem., vol. 47, 2002, pp. 819–844.

[54] E.F. Baxter, D.J. DePaolo, P.R. Renne, Spatially Correlated Anomalous $^{40}Ar/^{39}Ar$ "Age" variations about a lithologic contact near Simplon Pass, Switzerland: a mechanistic explanation for excess Ar, Geochim. Cosmochim. Acta 66 (2002) 1067–1083.

[55] S.P. Kelley, Excess argon in K–Ar and Ar–Ar geochronology, Chem. Geol. 188 (2002) 1–22.

[56] E.F. Baxter, P.D. Asimow, K.A. Farley, Grain boundary partitioning of Ar and He, Geochim. Cosmochim. Acta. (in press).

[57] J.A. Wartho, S.P. Kelley, R.A. Brooker, M.R. Carroll, I.M. Villa, M.R. Lee, Direct measurement of Ar diffusion profiles in a gem-quality Madagascar feldspar using the ultra-violet laser ablation microprobe (UVLAMP), Earth Planet. Sci. Lett. 170 (1999) 141–153.

[58] D.J. Cherniak, E.B. Watson, Pb diffusion in zircon, Chem. Geol. 172 (2001) 5–24.

[59] K. Mezger, E.J. Krogstad, Interpretation of discordant U–Pb zircon ages; an evaluation, J. Metamorp. Geol. 15 (1997) 127–140.

[60] D.J. Cherniak, E.B. Watson, M. Grove, T.M. Harrison, Pb diffusion in monazite: a combined RBS/SIMS study, Geochim. Cosmochim. Acta 68 (2004) 829–840.

[61] A. Cocherie, E. Mezeme, O. Legendre, C.M. Fanning, M. Faure, P. Rossi, Electron-microprobe dating as a tool for determining the closure of Th–U–Pb systems in migmatitic monazite, Am. Mineral. 90 (2005) 607–618.

[62] D. Bosch, D. Hammor, O. Bruguier, R. Caby, J.-M. Luck, Monazite 'in situ' $^{207}Pb/^{206}Pb$ geochronology using a small geometry high-resolution ion probe; application to Archaean and Proterozoic rocks, Chem. Geol. 184 (2002) 151–165.

[63] D.J. Cherniak, Lead diffusion in titanite and preliminary results on the effects of radiation damage on Pb transport, Chem. geol. 110 (1993) 177–194.

[64] D.J. Scott, M.R. St-Onge, Constraints on Pb closure temperature in titanite based on rocks from the Ungava Orogen, Canada; implications for U–Pb geochronology and P–T–t path determinations, Geology 23 (1995) 1123–1126.

[65] D.J. Cherniak, F.J. Ryerson, a study of strontium diffusion in apatite using Rutherford backscattering spectroscopy and ion-implantation, Geochim. Cosmochim. Acta 57 (1993) 4653–4662.

[66] E.J. Krogstad, R.J. Walker, High closure temperatures of the U–Pb system in large apatites from the Tin Mountain Pegmatite, Black Hills, South Dakota, USA, Geochim. Cosmochim. Acta 58 (1994) 3845–3853.

[67] W.D. Carlson, Rates of Fe, Mg, Mn, and Ca diffusion in garnet, Am. Mineral. 91 (2006) 1–11.

[68] W.J. Dunlap, A.K. Kronenberg, Argon loss during deformation of micas: constraints from laboratory deformation experiments, Contrib. Mineral. Petrol. 141 (2001) 174–185.

[69] A. Mulch, M.A. Cosca, M.R. Handy, In-situ UV-laser Ar-40/Ar-39 geochronology of a micaceous mylonite: an example of defect-enhanced argon loss, Contrib. Mineral. Petrol. 142 (2002) 738–752.

[70] E.B. Watson, Diffusion in volatile-bearing magmas, in: M.R. Carroll, J.R. Holloway (Eds.), Volatiles in Magmas, Reviews in Mineralogy, vol. 30, Mineralogical Society of America, Washington D.C., 1994, pp. 371–411.

[71] H. Eckert, J.P. Yesinowski, L.A. Silver, E.M. Stolper, Water in silicate glasses — quantitation and structural studies by H-1 solid echo and MAS-NMR methods, J. Phys. Chem. (92) 2055–2064.

[72] B.J. Giletti, R.A. Yund, Oxygen diffusion in quartz, J. Geophys. Res. 89 (1984) 4039–4046.

[73] P.F. Dennis, Oxygen self-diffusion in quartz under hydrothermal conditions, J. Geophys. Res. 89 (1984) 4047–4057.

[74] J.R. Farver, R.A. Yund, Oxygen diffusion in quartz: dependence on temperature and water fugacity, Chem. Geol. 90 (1991) 55–70.

[75] S.C. Elphick, P.F. Dennis, C.M. Graham, An experimental study of the diffusion of oxygen in quartz and albite using an overgrowth technique, Contrib. Mineral. Petrol. 92 (1986) 322–330.

[76] A.K. Kronenberg, J. Tullis, Flow strengths of quartz aggregates — grain size and pressure effects due to hydrolytic weakening, J. Geophys. Res. 89 (1984) 4281–4297.

[77] J.R. Farver, Oxygen self-diffusion in calcite: dependence on temperature and water fugacity, Earth Planet. Sci. Lett. (1994) 575–587.

[78] J.R. Farver, R.A. Yund, The effect of hydrogen, oxygen and water fugacity on oxygen diffusion in alkali feldspar, Geochim. Cosmochim. Acta 54 (1990) 2953–2964.

[79] J.R. Farver, Oxygen self-diffusion in diopside with applications to cooling rate determinations, Earth Planet. Sci. Lett. 92 (1989) 386–396.

[80] E.B. Watson, D.J. Cherniak, Oxygen diffusion in zircon, Earth Planet. Sci. Lett. 148 (1997) 527–544.

[81] D.J. Cherniak, X.Y. Zhang, M. Nakamura, E.B. Watson, Oxygen diffusion in monazite, Earth Planet. Sci. Lett. 226 (2004) 161–174.

[82] D.K. Moore, D.J. Cherniak, E.B. Watson, Oxygen diffusion in rutile from 750 to 1000 °C and 0.1 to 1000 MPa, Am. Mineral. 83 (1998) 700–711.

[83] S. Chakraborty, F. Costa, Fast diffusion of Si and O in San Carlos olivine under hydrous conditions, Geochim. Cosmochim. Acta 68 (2004) A275 (Suppl.).

[84] S. Chakraborty, Diffusion studies in Earth and planetary sciences, Defect Diffus. Forums 237–240 (2004) 1081–1092.

[85] Y. Zhang, E.M. Stolper, G.J. Wasserburg, Diffusion of a multi-species component and its role in oxygen and water transport in silicates, Earth Planet. Sci. Lett. 103 (1991) 228–240.

[86] J.D.C. McConnell, The role of water in oxygen isotope exchange in quartz, Earth Planet. Sci. Lett. 136 (1995) 97–107.

[87] A.K. Kronenberg, R.A. Yund, B.J. Giletti, Carbon and oxygen diffusion in calcite: effects of Mn content and P_{H_2O}, Phys. Chem. Miner. 11 (1984) 101–112.

[88] B.J. Giletti, J.E.D. Casserly, Strontium diffusion kinetics in plagioclase feldspars, Geochim. Cosmochim. Acta 58 (1994) 3785–3793.

[89] D.J. Cherniak, E.B. Watson, A study of strontium diffusion in plagioclase using Rutherford backscattering spectroscopy, Geochim. Cosmochim. Acta 58 (1994) 5179–5190.

[90] J.R. Farver, B.J. Giletti, Oxygen and strontium diffusion kinetics in apatite and potential applications to thermal history determinations, Geochim. Cosmochim. Acta 53 (1989) 1621–1631.

[91] E.B. Watson, D.J. Cherniak, Lattice diffusion of Ar in quartz, with constraints on Ar solubility and evidence of nanopores, Geochim. Cosmochim. Acta 67 (2003) 2043–2062.

[92] Z. Wang, T. Hiraga, D.L. Kohlstedt, Effect of H^+ on Fe–Mg interdiffusion in olivine, $(Fe,Mg)_2SiO_4$, Appl. Phys. Lett. 85 (2004) 209–211.

[93] S. Hier-Majumder, I.M. Anderson, D.L. Kohlstedt, Influence of protons on Fe–Mg interdiffusion in olivine, J. Geophys. Res. 110 (2005) B02202.

[94] P.N. Chopra, M.S. Paterson, The role of water in the deformation of dunite, J. Geophys. Res. 89 (1984) 7861–7876.

[95] S. Mei, D.L. Kohlstedt, Influence of water on plastic deformation of olivine aggregates: 1. Diffusion creep regime, J. Geophys. Res. 105 (2000a) 21,457–21,469.

[96] S. Mei, D.L. Kohlstedt, Influence of water on plastic deformation of olivine aggregates: 2. Dislocation creep regime, J. Geophys. Res. 105 (2000b) 21,471–21,481.

[97] S. Karato, Grain growth kinetics in olivine aggregates, Tectonophysics 168 (1989) 255–273.

[98] T. Kubo, E. Ohtani, T. Kato, T. Shinmei, K. Fujino, Effects of water on the α–β transformation kinetics in San Carlos olivine, Science 281 (1998) 85–87.

[99] S. Demouchy, S. Mackwell, D.L. Kohlstedt, Effect of hydrogen on Mg–Fe interdiffusion in ferro-periclase, Eos Trans. AGU 86 (2005) (Fall Meet. Suppl., Abstract MR41A-0902).

[100] W.D. Carlson, Scales of disequilibrium and rates of equilibration during metamorphism, Am. Mineral. 87 (2002) 185–204.

[101] G. Hirth, D.L. Kohlstedt, Rheology of the upper mantle and the mantle wedge: a view from the experimentalists, in: J. Eiler (Ed.), Inside the Subduction Factory, AGU Geophysical Monograph, vol. 138, 2003, pp. 83–105.

[102] T.W. Trull, M.D. Kurz, Experimental measurements of ^{3}He and ^{4}He mobility in olivine and clinopyroxene at magmatic temperatures, Geochim. Cosmochim. Acta 47 (1993) 1313–1324.

[103] A. Tsuchiyama, K. Kawamura, T. Nakao, C. Uyeda, Isotope effects on diffusion in MgO melt simulated by molecular dynamics (MD) method and implications for isotopic mass fractionation in magmatic systems, Geochim. Cosmochim. Acta 58 (1994) 3013–3021.

[104] T.W. Trull, M.D. Kurz, Isotope fractionation accompanying helium diffusion in basaltic glass, J. Mol. Struct. 485–486 (1999) 555–567.

[105] F.M. Richter, Y. Liang, A.M. Davis, Isotope fractionation by diffusion in molten oxides, Geochim. Cosmochim. Acta 63 (1999) 2853–2861.

[106] F.M. Richter, A.M. Davis, D.J. DePaolo, E.B. Watson, Isotope fractionation by chemical diffusion between molten basalt and rhyolite, Geochim. Cosmochim. Acta 67 (2003) 3905–3923.

[107] F.M. Richter, R.A. Mendybaev, J.N. Christensen, I.D. Hutcheon, R.W. Williams, N.C. Sturchio, A.D. Beloso, Kinetic isotope effect during diffusion of ionic species in water, Geochim. Cosmochim. Acta 70 (2006) 277–289.

[108] F.-Z. Teng, W.D. McDonough, R.L. Rudnick, R.J. Walker, Diffusion-driven extreme isotopic fractionation in country rocks of the Tin Mountain pegmatite, Earth Planet. Sci. Lett. 243 (2006) 701–710.

[109] N.L. Peterson, S.J. Rothman, Isotope effect in self-diffusion in zinc, Phys. Rev. 163, 645–649.

[110] G. Fine, E.M. Stolper, The speciation of carbon-dioxide in sodium aluminosilicate glasses, Contrib. Mineral. Petrol. 91 (1985) 105–121.

[111] J. Ita, R.E. Cohen, Effects of pressure on diffusion and vacancy formation in MgO from non-empirical free-energy integrations, Phys. Rev. Lett. 79 (1997) 3198–3201.

[112] S. Chakraborty, R. Knoche, H. Schulze, D.C. Rubie, D. Dobson, N.L. Ross, Enhancement of cation diffusion rates across the 410-kilometer discontinuity in Earth's mantle, Science 248 (1999) 362–365.

[113] A.W. Hofmann, S.R. Hart, An assessment of local and regional isotopic equilibrium in the mantle, Earth Planet. Sci. Lett. 38 (1978) 44–62.

[114] J.A. Van Orman, Y. Fei, E.H. Hauri, J. Wang, Diffusion in MgO at high pressures: constraints on deformation mechanisms and chemical transport at the core-manlte boundary, Geophys. Res. Lett. 30 (2003) 1056.

[115] E. Knittle, R. Jeanloz, Earth's core-mantle boundary: results of experiments at high pressures and temperatures, Science 251 (1991) 1438–1443.

[116] F. Goarant, F. Guyot, J. Peyronneau, J.P. Poirier, High-pressure and high-temperature reactions between silicates and iron alloys in the diamond-anvil cell, studied by analytical electron microscopy, J. Geophys. Res. 97 (1992) 4477–4487.

[117] R.J. Walker, J.W. Morgan, M.F. Horan, ^{187}Os enrichment in some mantle plume sources: evidence for core-mantle interaction? Science 269 (1995) 819–822.

[118] A.D. Brandon, R.J. Walker, J.W. Morgan, M.D. Norman, H.M. Prichard, Coupled ^{186}Os and ^{187}Os evidence for core-mantle interaction, Science 280 (1998) 1570–1573.

[119] A. Schersten, T. Elliott, C. Hawkesworth, M. Norman, Tungsten isotope evidence that mantle plumes contain no contribution from the Earth's core, Nature 427 (2004) 234–237.

[120] J.A. Baker, KK. Jensen, ^{186}Os–^{187}Os enrichments in the Earth's mantle–core–mantle interaction or recycling of ferromanganese crusts and nodules? Earth Planet. Sci. Lett. 220 (2004) 277–286.

[121] A.D. Brandon, R.J. Walker, The debate over core–mantle interaction, Earth Planet. Sci. Lett. 232 (2005) 211–225.

[122] E.B. Watson, Mobility of siderophile elements in grain boundaries of periclase and periclase/olivine aggregates, Eos Trans. AGU, 2002.

[123] L.A. Hayden, E.B. Watson, Grain boundary mobility of siderophile elements in MgO, Goldschmidt Conference Abstracts, 2006.

[124] J.J. Ague, Partial eclogitisation of gabbroic rocks in a late Precambrian subduction zone (Zambia): prograde metamorphism triggered by fluid infiltration, Contrib. Mineral. Petrol. 143 (2003) 38–55.

[125] C.M. Breeding, J.J. Ague, M. Brocker, E.W. Bolton, Blueschist preservation in a retrograded, high-pressure, low-temperature metamorphic terrane, Tinos, Greece: implications for fluid flow paths in subduction zones, Geochem. Geophys. Geosyst. 4 (2003) (art #9002).

[126] T. John, V. Schenk, Partial eclogitisation of gabbroic rocks in a late Precambrian subduction zone (Zambia): prograde metamorphism triggered by fluid infiltration, Contrib. Mineral. Petrol. 146 (2003) 174–191.

[127] D.J. DePaolo, Isotopic effects in fracture-dominated reactive fluid-rock systems, Geochim. Cosmochim. Acta 70 (2006) 1077–1096.

[128] M.J. Bickle, Transport mechanisms by fluid-flow in metamorphic rocks: oxygen and strontium decoupling in the Trois Seigneurs Massif—a consequence of kinetic dispersion? Am. J. Sci. 292 (1992) 289–316.

[129] C.R. Ranero, J. Phipps Morga, K.D. McKintosh, C. Reichert, Bending-related faulting and mantle serpentinization at the Middle America trench, Nature 425 (2003) 367–373.

[130] M. Nakamura, E.B. Watson, Experimental study of aqueous fluid infiltration into quartzite: implications for the kinetics of fluid re-distribution and grain growth driven by interfacial energy reduction, Geofluids 1 (2001) 73–89.

[131] A.C. Lasaga, Geospeedometry: an extension of geothermometry, in: S.K. Saxena (Ed.), Kinetics and Equilibrium Reactions, Advances in Physical Geochemistry, vol. 3, 1983, pp. 81–114.

[132] F.J. Tepley, J.P. Davidson, Mineral-scale Sr-isotope constraints on magma evolution and chamber dynamics in the Rum layered intrusion, Scotland, Contrib. Mineral. Petrol. 145 (2003) 628–641.

[133] L.A. Coogan, S.A. Kaseman, S. Chakraborty, Rates of hydrothermal cooling of new oceanic upper crust derived from lithium-geospeedometry, Earth Planet. Sci. Lett. 240 (2005) 415–424.

[134] A.H. Peslier, J.F. Luhr, Hydrogen loss from olivines in mantle xenoliths from Simcoe (USA) and Mexico: mafic alkalic magma ascent rates and water budget of the sub-continental lithosphere, Earth Planet. Sci. Lett. 242 (2006) 302–319.

[135] S. Demouchy, S.D. Jacobsen, F. Gaillard, C.R. Stern, Rapid magma ascent recording by water diffusion profiles in mantle olivine, Geology 34 (2006) 429–432.

[136] J.J. Ague, E.F. Baxter, Extremely short-duration peak metamorphism in the Barrovian zones, Scotland, AGU Annual Fall Meeting, 2006.

[137] A. Camacho, J.K.W. Lee, B.J. Hensen, J. Braun, Short-lived orogenic cycles and the eclogitization of cold crust by spasmodic hot fluids, Nature 435 (2005) 1191–1196.

[138] S.W. Faryad, S. Chakraborty, Duration of Eo-Alpine metamorphic events obtained from multicomponent diffusion modeling of garnet: a case study from the Eastern Alps, Contrib. Mineral. Petrol. 250 (2005) 306–318.

[139] E.B. Watson, T.M. Harrison, Accessory minerals and the geochemical evolution of crustal magmatic systems: a summary and prospectus of experimental approaches, Phys. Earth Planet. Int. 35 (1984) 19–30.

[140] E.H. Oelkers, H.C. Helgeson, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: aqueous tracer diffusion coefficients of ions to 1000 °C and 5 kb, Geochim. Cosmochim. Acta 52 (1988) 63–85.

[141] J.D. Kubicki, A.C. Lasaga, Molecular dynamics simulations of SiO_2 melt and glass: ionic and covalent models, Am. Mineral. 73 (1988) 941–955.

[142] A. Tsuchiyama, K. Kawamura, Sites and behaviors of noble gas atoms in MgO crystal simulated by the molecular dynamics (MD) method, in: J. Matsuda (Ed.), Noble Gas Geochemistry and Cosmochemistry, Terra Scientific Publishing, Tokyo, 1994, pp. 315–323.

[143] K. Wright, G.D. Price, Computer simulation of defects and diffusion in perovskites, J. Geophys. Res. B 98 (1993) 22,245–22,253.

[144] K. Wright, R. Freer, C.R.A. Catlow, Oxygen diffusion in grossular and some geological implications, Am. Mineral. 80 (1995) 1020–1025.

[145] K. Wright, R. Freer, C.R.A. Catlow, Water-related defects and oxygen diffusion in albite; a computer simulation study, Contrib. Mineral. Petrol. 125 (1996) 161–166.

[146] J. Bryce, F.J. Spera, Dependence of self diffusivity on *P* and *T* in molten $NaAlSi_2O_6$: comparison of laboratory and molecular dynamics experiments, Geophys. Res. Lett. 24 (1997) 711–715.

[147] C. Meis, J.D. Gale, Computational study of tetravalent uranium and plutonium lattice diffusion in zircon, Mat. Sci. Eng. B57 (1998) 52–61.

[148] D. Nevins, F.J. Spera, Molecular dynamics simulations of molten $CaAl_2Si_2O_8$: dependence of structure and properties on pressure, Am. Mineral. 83 (1998) 1220–1230.

[149] D. Derdau, R. Freer, K. Wright, Oxygen diffusion in anhydrous sanidine feldspar, Contrib. Mineral. Petrol. 133 (1998) 199–204.

[150] F. Azough, R. Freer, K. Wright, R. Jackson, A computer simulation study of point defects in diopside and the self-diffusion of Mg and Ca by a vacancy mechanism, Min. Mag. 62 (1998) 599–606.

[151] A. Jones, D. Palmer, M.S. Islam, M. Mortimer, Ion migration in nepheline: a dielectric spectroscopy and computer modeling study, Phys. Chem. Miner. 28 (2001) 28–34.

[152] A. Jones, M.S. Islam, M. Mortimer, D. Palmer, Alkali ion migration in albite and K-feldspar, Phys. Chem. Miner. 31 (2004) 313–320.

[153] M.S. Islam, Computer modelling of defects and transport in perovskite oxides, Solid State Ionics 154–155 (2002) 75–85.

[154] A.M. Royal, K. Wright, B. Slater, A computational study of oxygen diffusion in olivine, Phys. Chem. Miner. 30 (2003) 536–545.

[155] S.H. Chen, H.T. Davis, D.F. Evans, Tracer diffusion in polyatomic liquids, 2. Jour, Chem. Phys. 75 (1981) 1422–1426.

[156] A.R. Cooper, The use and limitation of the concept of an effective binary diffusion coefficient for multi-component diffusion, in: J.B. Wachtman, A.D. Franklin (Eds.), Mass Transport in Oxides, Nat. Bur. Stand. Spec. Publ., vol. 296, 1968, pp. 79–84.

[157] Y. Zhang, A modified effective binary diffusion model, J. Geophys. Res. 98 (1993) 11901–11920;
F.M. Richter, A method for determining activity-composition relations using chemical diffusion in silicate melts, Geochim. Cosmochim. Acta 57 (1993) 2019–2032.

[158] L. Onsager, Theories and problems of liquid diffusion, N. Y. Acad. Sci. Annals 46 (1945) 241–265.

[159] F.M. Richter, A method for determining activity-composition relations using chemical diffusion in silicate melts, Geochim. Cosmochim. Acta 57 (1993) 2019–2032.

[160] C.E. Lesher, The kinetics of Sr and Nd exchange in silicate liquids — theory, experiments, and applications to uphill diffusion, isotopic equilibration, and irreversible mixing of magmas, J. Geophys. Res. 99 (B5) (1994) 9585–9604.

[161] A.F. Trial, F.J. Spera, Measuring the multicomponent diffusion matrix — experimental design and data analysis for silicate melts, Geochim. Cosmochim. Acta 58 (1994) 3769–3783.

[162] J.W. Lee, Multipath diffusion in geochronology, Contrib. Mineral. Petrol. 120 (1995) 60–82.

[163] J.S. Turner, Buoyancy Effects in Fluids, Cambridge University Press, Cambridge, 1973.

[164] E.B. Watson, Diffusion in fluid-bearing and slightly-melted rocks: experimental and numerical approaches illustrated by iron transport in dunite, Contrib. Mineral. Petrol. 107 (1991) 417–434.

[165] T.S. Duffy, R.J. Hemley, Temperature structure of the Earth, Rev. Geophys. (1995) 5–9 (U.S. Nat. Rep. to I.U.G.G.).

Bruce Watson is an experimental geochemist whose research includes studies of both equilibrium and transport phenomena in the solid Earth at a variety of scales. He uses experimental constraints and simple models to gain insight into the conditions and time scales of processes affecting the behavior of the chemical elements and their isotopes in the crust and mantle. He received a PhD in geochemistry from MIT in 1976 and joined the Rensselaer faculty in 1977.

Ethan Baxter is an isotope geochemist and petrologist whose field-based and experimental research focuses on the rates, mechanisms, and timescales of processes such as chemical reaction and material flux occurring within the dynamic surface, crust, and mantle of the Earth. He earned his PhD from the University of California at Berkeley in 2000, and joined the Boston University faculty in 2002.