



# Theoretical constraints on the isotope effect for diffusion in minerals

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## Abstract

Isotopes of the same element generally diffuse at slightly different rates within a mineral, due to the difference in their masses. The magnitude of the mass dependence of the diffusion coefficient depends on the product of the correlation coefficient  $f$  (representing the degree to which the diffusion process deviates from a random walk) and the coupling coefficient  $K$  (representing the degree to which the motion of an atom during a single jump is coupled to that of other nearby atoms). Whereas  $K$  has been found to vary over a relatively narrow range,  $f$  can vary over a wide range from  $\sim 0$  to 1.

Diffusive isotope effects are expected to be large for trace and minor cations that diffuse slowly relative to the major cations that occupy the same sites and diffuse by the same mechanism. Diffusive isotope effects are also expected to be large for elements that diffuse rapidly by a simple interstitial mechanism. In both of these cases, the correlation coefficient is similar to or equal to unity. Diffusive isotope effects are reduced when the diffusion process is correlated, as for (1) rapid diffusion of trace and minor cations by a vacancy mechanism, with a low migration barrier for the jump to a vacancy; (2) diffusion by an interstitialcy process, or a process involving interstitial–vacancy pairs; (3) diffusion in grain boundaries and dislocations, where both dimensional restrictions and non-uniformity of the structure enhance correlation. The correlation coefficient can be determined from independent experimental data on the jump frequencies involved in the diffusion process, and/or from theoretical calculations of the jump energies. Quantitative estimates of the isotope effect are made for several cations in periclase, olivine, magnetite and rutile.

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## 1. INTRODUCTION

The slightly more rapid diffusion of light isotopes relative to their heavier counterparts in minerals, grain boundaries and melts may lead to significant isotope fractionation in magmatic and metamorphic systems (e.g. [Richter et al., 2003](#); [Teng et al., 2006](#); [Watson and Müller, 2009](#); [Dauphas et al., 2010](#)). In contrast to the equilibrium fractionation of isotopes between phases, which is proportional

to  $\sim 1/T^2$  in the high-temperature regime, the mass dependence of isotope diffusivity does not vanish at high temperatures; in fact, as will be shown here, the mass dependence often increases with temperature. Hence, isotope fractionation by diffusion remains viable at temperatures where equilibrium fractionation is negligible, and is likely to become more prevalent as temperature increases.

Solid-state diffusive fractionation of isotopes has been the subject of an increasing number of geochemical studies, especially during the last decade. Diffusion within minerals and/or grain boundaries has been inferred to be responsible for substantial observed fractionation of Li isotopes in upper mantle, contact metamorphic, and magmatic systems

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(e.g. [Lundstrom et al., 2005](#); [Teng et al., 2006](#); [Parkinson et al., 2007](#); [Rudnick and Ionov, 2007](#)). Iron and nickel isotopic fractionation in taenite and kamacite from iron meteorites has been attributed to diffusive isotope separation associated with exsolution and Fe–Ni exchange during cooling ([Dauphas, 2007](#)). Negatively correlated iron and magnesium isotope compositions in olivine from the Alexo komatiite ([Dauphas et al., 2010](#)) and Kilauea Iki lava lake ([Teng et al., 2011](#)) have also been shown to be due to diffusive separation of Fe and Mg isotopes as Mg diffused out and Fe diffused into the olivine during magmatic differentiation.

Fractionation of isotopes by diffusion has significant potential to provide information on geochemical processes and timescales, and detailed observations of isotope fractionation could benefit greatly from more data on the diffusion rates of different isotopes in minerals and melts. To date, only a few experimental measurements of the mass dependence of isotope diffusion in minerals have been made, e.g. for C in iron ([Mueller et al., 2014](#)), He in olivine and pyroxene ([Trull and Kurz, 1993](#)) and Li in rutile ([Johnson and Krouse, 1966](#)) and pyroxenes ([Richter et al., 2014](#)).

In geochemistry, the ratio of the diffusion coefficients ( $D$ ) of two isotopes  $L$  (light) and  $H$  (heavy) of the same element is commonly expressed as a function of the ratio of their masses ( $m$ ) as (e.g. [Richter et al., 1999](#)):

$$\frac{D_L}{D_H} = \left(\frac{m_H}{m_L}\right)^\beta \quad (1)$$

where the exponent  $\beta$  is an empirical parameter which can take values between  $\sim 0$  and  $0.5$ , the upper limit being the theoretical value for an ideal monatomic gas. Eq. (1) has been applied mainly to diffusive isotope fractionation in silicate melts, in which it has been observed that the values of  $\beta$  can vary widely and are positively correlated with the diffusivity of the ion ([Watkins et al., 2011, 2014](#); [Goel et al., 2012](#)). Cations that diffuse rapidly through silicate melts relative to Si and other network formers have a large isotope effect (high  $\beta$ ), while those that diffuse slowly tend to have a smaller isotope effect (low  $\beta$ ).

As shown below, these findings for silicate melts do not provide reliable guidance on the isotope effect in minerals. In minerals, diffusion is due to a series of jumps of an atom among specific lattice sites. The isotope effect depends upon two factors: (1) the degree to which the jumps deviate from a random walk, and (2) the degree to which the motion of an atom during a jump is coupled to that of other nearby atoms. The first of these factors, represented by a correlation coefficient  $f$ , has to do with the *sequence* of jumps an atom takes as it diffuses through the crystal. Often the direction of successive jumps is not completely random, and this has the effect of reducing the isotopic mass dependence of the diffusivity. The second factor concerns a *single* jump of an atom to an adjacent lattice site, and has to do with the coupling of the motion of the atom during this jump to lattice vibrations.

The basic theoretical description of the isotope effect in crystals is well established, and can be used to predict the isotope effect in cases where sufficient information exists

on the relative frequencies of the atomic jumps that are involved in the diffusion process. The primary purpose of this paper is to show how one can predict, estimate, or better interpret the magnitude of the isotope effect for diffusion in minerals.

## 2. THEORY OF THE ISOTOPE EFFECT IN CRYSTALS

The classical theory of the isotopic mass dependence of diffusion rates in crystalline solids was developed in the late 1950s and early 1960s. [Schoen \(1958\)](#) and [Tharmalingam and Lidiard \(1959\)](#) showed that the isotope effect for diffusion in crystalline solids diminishes in proportion to the degree to which the diffusion process deviates from that of a purely random walk. The basic equation that relates the diffusivities of two isotopes to their masses can be written as ([LeClaire, 1966](#)):

$$\left(\frac{D_L}{D_H} - 1\right) = f \left(\frac{w_L}{w_H} - 1\right), \quad (2)$$

where  $w_L$  and  $w_H$  represent the frequency of a jump of the isotope to an adjacent lattice site (vacancy or interstitial) and  $f$  is the correlation coefficient. In the simplest case of a random walk, with no correlation between successive jumps,  $f = 1$ . However, as discussed further below, there is often correlation between jumps, and in this case  $f < 1$ .

Within the classical model of atomic jumps in a crystal presented by [Vineyard \(1957\)](#), the ratio of jump frequencies of the two isotopes has a simple relation to the isotope mass ratio when there is no coupling between the vibration of the jumping atom and the vibrations of the rest of the crystal:  $(w_L/w_H) = (m_H/m_L)^{1/2}$  ([LeClaire, 1966](#)). However, when the motion of the atom during a jump is not fully decoupled from the vibrations of the surrounding atoms, the mass dependence of the jump frequency may be reduced ([Vineyard, 1957](#)) and can be described by [Mullen \(1961\)](#):

$$\left(\frac{w_L}{w_H} - 1\right) = K \left[ \left(\frac{m_H}{m_L}\right)^{1/2} - 1 \right] \quad (3)$$

where  $K$  reflects the degree of coupling, taking a maximum value of  $K = 1$  in the case of no coupling, and smaller values when coupling is significant. For a rigorous description of the meaning of  $K$  in terms of lattice vibrations, see [LeClaire \(1966\)](#). Note that the coupling coefficient is often expressed as  $\Delta K$  in the literature but is expressed throughout this paper simply as  $K$ . Combining Eqs. (2) and (3) leads to an equation for the isotopic mass dependence of the diffusion coefficient,  $E$ :

$$E \equiv \left(\frac{D_L}{D_H} - 1\right) / \left[ \left(\frac{m_H}{m_L}\right)^{1/2} - 1 \right] = fK \quad (4)$$

which is the expression that has generally been used to evaluate the isotopic mass dependence of diffusion in crystalline solids (e.g. [Peterson, 1975](#), and references therein). When the isotopes are not very different in mass, Eqs. (4) and (1) are nearly equivalent expressions, with  $E = fK \cong 2\beta$ , because  $\ln x \cong x - 1$  when  $x$  is near unity.

The advantage of Eq. (4) over the purely empirical Eq. (1) is that it connects the isotope effect to the atomic jump process that is responsible for diffusion. In physics and materials science, the primary goal of experimental studies on the isotope effect has been to elucidate the diffusion mechanism and gain insight on the relative frequencies of the various atomic jumps involved (see Peterson, 1975; Allnatt and Lidiard, 1993; and references therein). Turning this around, it is possible to place constraints on the magnitude of the isotope effect based on independent knowledge of the diffusion mechanism and the jump frequencies associated with it.

### 2.1. Limits of application of Eq. (4)

A few comments must be made about limits to the application of Eq. (4). First, the correlation coefficient for the light and heavy isotopes can be slightly different, and strictly speaking  $f$  in Eq. (4) should be written  $f_L$ . The relation between  $f_L$  and  $f_H$  is (LeClaire, 1966):

$$f_L = f_H \left[ \frac{(w_H/w_L)}{(1 - f_H + f_H(w_H/w_L))} \right]. \quad (5)$$

In most cases the difference between the correlation coefficients for two isotopes of the same element is negligible, but the difference is potentially significant for hydrogen or helium, if the correlation coefficients are substantially less than unity. The difference could also be significant for molecular dynamics simulations of the isotope effect, in which isotopic mass differences are often made artificially large (e.g. Bourg et al., 2010; Goel et al., 2012).

Also, Eqs. (2) and (4) are not exact unless  $K = 1$  (LeClaire, 1966). An assumption made in deriving Eq. (2) is that the jump frequency is only affected by the mass of the solute atom. However,  $K < 1$  means that the surrounding atoms have an influence on the jump frequency of the solute, which also implies that the mass of the solute atom affects not only its own jump frequency but also has some influence on the jump frequencies of the neighboring atoms. LeClaire (1966) proposed a correction to Eq. (4) for diffusion by a vacancy mechanism in a face-centered cubic (fcc) metal, which takes into account the influence of solute isotopic mass on the jump frequency of the nearest-neighbor solvent atoms that are also involved in diffusion. In general, the value of  $E$  obtained using this equation is expected to differ from that obtained using Eq. (4) by less than the error in experimental measurement of the isotope effect (Peterson, 1975). In non-metallic minerals, the correction is expected to be even smaller than it is in metals because the nearest neighbors to the jumping atom reside on a different sublattice. For example, the mass of a cation diffusing in MgO may have some influence on the jump frequencies of neighboring oxygen atoms, but jumps of the oxygen atoms do not contribute to diffusion of the cation. The mass of a cation would be expected to have a very small influence on the jump frequencies of other nearby cations.

The isotope effect for diffusion in crystalline solids can be predicted using Eq. (4) given independent constraints on the correlation coefficient ( $f$ ) and coupling coefficient

( $K$ ). The primary focus of this paper is on  $f$ , for two reasons. First, while it is possible to calculate  $K$  based on the vibrational modes that contribute to the jump of an atom to a nearby lattice site (LeClaire, 1966) this has seldom been attempted, and to our knowledge no theoretical constraints on  $K$  exist for minerals. The value of  $K$  has instead usually been determined empirically, from measurements of the isotope effect where  $f$  is known independently from theoretical arguments. Such empirical determinations of  $K$  are available almost exclusively for self-diffusion by a vacancy mechanism in pure crystals (i.e.  $f = 0.7815$ ) and for simple interstitial diffusion where  $f = 1$  (e.g. Peterson, 1975). It is often assumed that the value of  $K$  for diffusion of a solute impurity in a crystal is similar to that for self-diffusion in the pure crystal, and the available experimental data appear to be consistent with this assumption (e.g. Chen and Peterson, 1972).

Secondly, values of  $K$  vary over a much smaller range than do values of  $f$ . The values of  $K$  determined from isotope effect measurements for self-diffusion in a wide range of crystals vary only over a factor of  $\sim 2$ , falling between  $\sim 0.5$  and 1 (see Allnatt and Lidiard, 1993, Table 10.2, and references therein). For nearly close-packed lattices, the range of  $K$  values is narrower,  $\sim 0.7$ –1, averaging 0.87. In contrast, the value of  $f$ , especially for dilute “impurity” atoms, can take a much wider range of values, between  $\sim 0$  and 1, even for impurities diffusing in the same mineral by the same mechanism. Thus, to obtain a first-order constraint on the magnitude of the isotope effect for diffusion, it is critical to know the correlation coefficient,  $f$ .

It is, of course, also important to know the coupling coefficient,  $K$ . We anticipate that theoretical constraints on  $K$  for minerals will become available in the future. It is also possible to determine  $K$  experimentally, by combining measurements of the isotopic mass dependence of the diffusion coefficient with calculations of the correlation coefficient, based on independent measurements of the relevant atomic jump frequencies.

### 3. CALCULATING THE CORRELATION COEFFICIENT

The correlation coefficient  $f$  can be calculated given sufficient information on the jump frequencies involved in the diffusion process. In general, correlation arises from the tendency of an atom to move back in the direction it came from with a greater than random probability. This happens, for example, during self-diffusion in a pure crystal by a vacancy mechanism. An atom that has just exchanged sites with a vacancy is more likely to reverse the jump immediately than it is to execute a jump to any other adjacent site, which is very likely to be occupied and hence unavailable for an immediate site exchange. Correlation may be even more prominent for a trace impurity in a crystal, when the impurity exchanges more readily with vacancies than do the adjacent solvent atoms. In this case, the impurity is likely to make many back-and-forth site exchanges with the vacancy before the vacancy exchanges sites with a solvent atom. The jump sequence in this case is highly correlated.

This section reviews theoretical approaches to the calculation of the correlation coefficient. Dilute systems, which involve a relatively small number of jump types, are considered first in Section 3.1. Concentrated systems, which involve many more jump types and are hence much more complicated, are considered in 3.2, and diffusion in grain boundaries is addressed in 3.3.

### 3.1. Dilute systems

Much of the theoretical work on the correlation coefficient has focused on systems in which an impurity is present at dilute concentrations within an essentially pure crystal. The discussion here focuses first on diffusion by a vacancy mechanism, where both impurities and vacancies are present at low concentrations. Correlation effects are also significant for some interstitial mechanisms, and are considered afterward.

#### 3.1.1. Vacancy mechanism

Diffusion of an impurity by a vacancy mechanism involves atomic jumps of several different types, in addition to jumps of the impurity atom into an adjacent vacancy. If only impurity-vacancy exchanges were possible, no net diffusion would take place; an impurity atom and vacancy on adjacent sites would simply exchange sites back and forth, the correlation coefficient would be zero (indicating perfectly correlated jumps), and the diffusion coefficient would also be zero (because there would be no net motion of the impurity). Atoms other than the impurity must exchange sites with the vacancy in order to allow the impurity atom to diffuse through the lattice.

In general, the correlation coefficient for diffusion of a dilute substituent by a vacancy mechanism can be expressed in the form (LeClaire, 1970):

$$f = \frac{u}{u + w_2}, \quad (6)$$

where  $w_2$  is the frequency of impurity-vacancy exchange, and  $u$  is a function that contains the vacancy exchange frequencies for other atoms that are involved in diffusion of the impurity. The function  $u$  has been evaluated analytically for diffusion on some simple lattices, where a limited number of jump types are involved, but becomes cumbersome for the more complex lattices that are relevant to most minerals. However, even in cases where no explicit expression for  $u$  has been derived Eq. (6) nevertheless illustrates the essential features of the correlation coefficient.

Consider the case in which the impurity-vacancy exchange frequency is small compared to the other atom-vacancy exchanges involved in diffusion ( $w_2 \ll u$ ), so that the impurity diffuses slowly relative to major elements that diffuse using the same vacancies. In this case, the correlation coefficient  $f \rightarrow 1$ : the vacancy is able to hop around and away from the impurity, randomizing its position between infrequent impurity-vacancy exchanges, and hence there is little correlation in the direction of successive jumps of the solute. In this situation the overall diffusion of the solute is controlled by the jump frequency of the solute,

and thus will depend strongly on the solute's mass. In general, then, we would anticipate that slowly diffusing impurities have a large isotope effect, close to a square root of mass dependence (i.e.,  $E \cong 1$ ,  $\beta \cong 1/2$ ).

On the other hand, if the impurity-vacancy exchange frequency is large relative to the other atom-vacancy exchange frequencies ( $w_2 \gg u$ ), the correlation coefficient will be small ( $f \rightarrow 0$ ). Hence, impurities that exchange readily with vacancies, and diffuse rapidly compared to the major elements that use the same population of vacancies for diffusion, will have a small isotope effect. In this case, the diffusivity of the solute is controlled by *other* atoms exchanging sites with vacancies, and the mass of the impurity atom is not a significant factor in determining its diffusion coefficient.

Analytical expressions for the function  $u$  in the expression for the correlation coefficient (Eq. (6)) have been derived for diffusion of dilute impurities in some simple lattices, and can be found in LeClaire (1970) and Ghate (1964). Here we focus on the example of the face-centered cubic (fcc) lattice, which is directly relevant to diffusion in taenite, periclase and halite (in the rock-salt structure that periclase and halite share, both the cation and the anion sublattices are fcc). Lidiard (1955) developed a five-frequency model (illustrated in Fig. 1) to describe diffusion on the fcc lattice, for which  $u = w_1 + 3.5Fw_3$ , and the impurity correlation coefficient is given by:

$$f = \frac{2w_1 + 7Fw_3}{2w_2 + 2w_1 + 7Fw_3}. \quad (7)$$

In this equation,  $w_2$  is the frequency of exchange between the substitutional impurity atom and an adjacent vacancy;  $w_1$  is the exchange frequency between a solvent atom that is a nearest neighbor to the impurity atom and the vacancy (with the vacancy remaining a nearest-neighbor of the impurity after exchange);  $w_3$  is the frequency of a dissociating jump of the vacancy away from the impurity atom (moving the vacancy out of the nearest-neighbor position); and  $F$  is the escape probability of the vacancy, given by (Allnatt and Lidiard, 1993; their Eq. (11).2.8):

$$F = 1 - \frac{10(w_4/w_0)^4 + B_1(w_4/w_0)^3 + B_2(w_4/w_0)^2 + B_3(w_4/w_0)}{72(w_4/w_0)^4 + B_4(w_4/w_0)^3 + B_5(w_4/w_0)^2 + B_6(w_4/w_0) + B_7}, \quad (8)$$

where  $w_4$  is the frequency of the associating jump of a vacancy into a nearest-neighbor position of the impurity atom (opposite of the  $w_3$  jump), and  $w_0$  is the exchange frequency between a vacancy and solvent atom that resides far from the substitutional cation, which is equivalent to the frequency of solvent-vacancy exchange in the pure crystal. It is often the case that  $w_1 \cong w_0$  (e.g. Barr and Lidiard, 1970), such that only four independent frequencies must be known to calculate the correlation coefficient using Eq. (7). The coefficients  $B_i$  in Eq. (8) were determined by Koiwa and Ishioka (1983) and are also given in Allnatt and Lidiard (1993, their Table 11.2).

The five jump frequencies are all functions of temperature:

$$w_i = v_i \exp\left(\frac{S_i}{R}\right) \exp\left(\frac{-H_i}{RT}\right), \quad i = 0 \text{ to } 4 \quad (9)$$



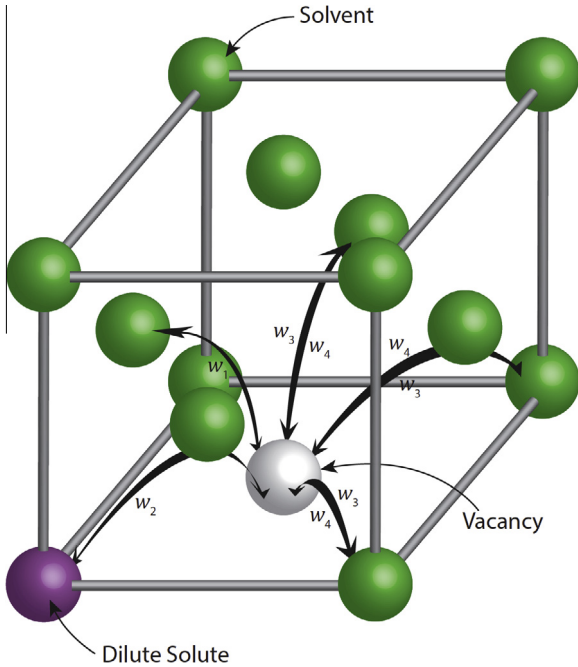


Fig. 1. One unit cell of an fcc lattice in the vicinity of dilute solute (purple) adjacent to a lattice vacancy (white). Arrows indicate the different types of jumps considered in the five-frequency model. The vacancy can exchange sites with a solvent atom (green) that is also a nearest neighbor to the impurity (with frequency  $w_1$ ); with a solvent atom that is not a nearest neighbor to the impurity, dissociating the impurity-vacancy pair (with frequency  $w_3$ ); or with the impurity (with frequency  $w_2$ ). A vacancy on a site that is a 2nd or 3rd nearest-neighbor to the impurity can also make an associating jump (the reverse of the  $w_3$ -type jump) to form an impurity-vacancy pair, with frequency  $w_4$ . Not shown is  $w_0$ , which refers to the frequency of solvent atom–vacancy jumps in the absence of an impurity. In general,  $w_1$  is found to be nearly identical to  $w_0$  for ionic crystals Barr and Lidiard (1970). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

where  $v_i$  is the jump attempt frequency,  $S_i$  the entropy and  $H_i$  the enthalpy of the jump of atom  $i$  to an adjacent vacancy. Note that, in the classical theory, the migration enthalpy and entropy are independent of isotopic mass; the mass of the isotope affects only the jump attempt frequency. Therefore, the ratio of jump frequencies for two isotopes of the same element is independent of temperature. However, the different types of jump involved in diffusion do in general have different activation enthalpies. This means that the correlation coefficient, and hence the isotope effect, generally does depend on temperature. At high temperatures, the different jump frequencies become more similar to each other, and as temperature increases the correlation coefficient for a solute generally becomes closer to the value for self-diffusion in the pure crystal (where  $w_1 = w_2 = w_3 = w_4 = w_0$ ).

The diffusion coefficient of the impurity is related to the correlation coefficient, and is given by:

$$D_{solute} = \frac{r^2}{2} w_2 x_v f \left( \frac{w_4}{w_3} \right) \quad (10)$$

where  $r$  is the distance between nearest-neighbor sites on the fcc lattice, and  $x_v$  is the atomic fraction of vacancies. Note that there is a trade-off between  $w_2$  and  $f$ : a solute with large  $w_2$  will also have a small correlation coefficient (Eq. (7)). Solutes with small migration enthalpy (large  $w_2$ ) have larger diffusion coefficients than those with larger migration barriers, but the difference is less than it would be in the absence of correlation effects.

To maintain equilibrium concentrations of impurity-vacancy pairs requires that:

$$w_4/w_3 = \exp(-G_b/RT) \quad (11)$$

where  $G_b$  is the Gibbs free energy of association between solute and vacancy, which is often referred to as the binding energy (and is negative when solute and vacancy are attracted). A negative binding energy enhances the diffusivity of the solute, because it increases the probability that a vacancy will be adjacent to the solute; a positive binding energy (repulsion between solute and vacancy) inhibits diffusion because the solute has less access to vacancies. When the binding energy is zero, there is no driving force to pair vacancies with impurities, or to repel them, and  $w_4 = w_3 \cong w_1$ .

The diffusion coefficient for the solvent in the pure crystal is:

$$D_{solvent} = \frac{r^2}{2} w_0 x_v f_0 \quad (12)$$

where the correlation coefficient  $f_0 = 0.7815$  for the fcc lattice. Combining Eqs. (10)–(12) gives an expression for the ratio of a solute’s diffusion coefficient to that of the solvent in the infinitely dilute limit:

$$\frac{D_{solute}}{D_{solvent}} = \frac{w_2}{w_0} \frac{f}{f_0} \frac{w_4}{w_3} = \frac{w_2}{w_0} \frac{f}{f_0} \exp\left(\frac{-G_b}{RT}\right) \quad (13)$$

The solute correlation coefficient is shown in Fig. 2, as a function of the diffusivity ratio, for three different values

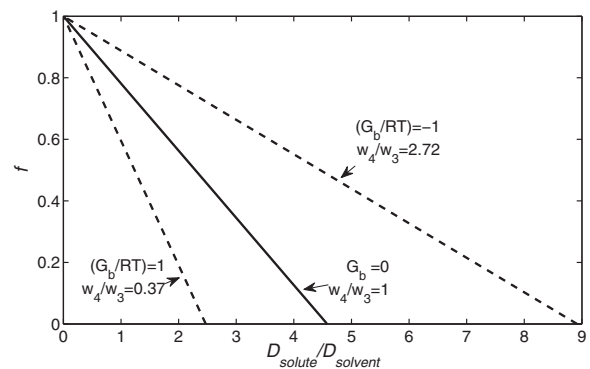


Fig. 2. Variation of the correlation coefficient with the ratio of dilute solute diffusivity to solvent self-diffusivity in the pure crystal, for diffusion on an fcc lattice by a vacancy mechanism where  $w_1 = w_0$ . The solid line represents the case of no binding between solute and vacancy, and the two dashed lines to the left and right represent modest repulsion and attraction, respectively. The curves are independent of temperature. The two dashed lines represent, for example, binding energies of +10 and –10 kJ/mol at a temperature of 930 °C.

of  $w_4/w_3$ . Each of these curves is independent of temperature. As noted above, solutes that diffuse rapidly by a vacancy mechanism generally have highly correlated motion (small correlation coefficient), while those that diffuse slowly move through the lattice with little correlation in the direction of atomic jumps ( $f \sim 1$ ). Note that the lines in Fig. 2 approach but do not extend to  $f = 0$ , which can be obtained only if  $w_2$  is infinite or if both  $w_1$  and  $w_3$  are equal to zero. Neither of these possibilities is physically realistic, but it is possible for  $f$  to approach zero closely if the solute jump energy is very small compared to the energies of the solvent jumps.

The correlation coefficient for a particular solute–solvent system can be calculated if the jump frequencies are known, or can be estimated. For several fcc metal alloys, the jump frequencies have been determined using a combination of data on the solute and solvent self-diffusion coefficients, measurements of the solvent atom diffusivity as a function of solute concentration, measurements of the electromigration drift velocity as a function of solute concentration (Doan and Bocquet (1975), and measurements of the shift in position of inert markers in binary interdiffusion experiments (Kirkendall effect) (Bocquet et al., 1983; Allnatt and Lidiard, 1993). Currently we are aware of six cases where sufficient data exist to both calculate  $f$  using Eqs. (7) and (8), and to independently estimate  $f$  based on measurements of the isotope effect, under the assumption that  $K_{\text{solute}} = K_{\text{solvent}}$ . In these six cases, the values of  $f$  obtained by these independent methods are in good agreement (Table 1; Fig. 3). This lends credence to the idea that  $f$ , and therefore the isotope effect  $E$ , can be predicted with fair accuracy in cases where independent information on the jump frequencies exists.

Another case in which measurements of the diffusive isotope effect can be compared with predictions based on independent experimental diffusion data is for the diffusion of cobalt in NiO. From measurements of the self-diffusion coefficients of Co and Ni in both nominally pure NiO and in samples containing up to 1.5 at.% Co, Chen and Peterson (1972) deduced that the Co–vacancy binding energy is negligible, such that  $w_3 \cong w_4 \cong w_1 \cong w_0$ . Hence, the situation is equivalent to the zero binding energy case depicted in Fig. 2, and the correlation coefficient can be

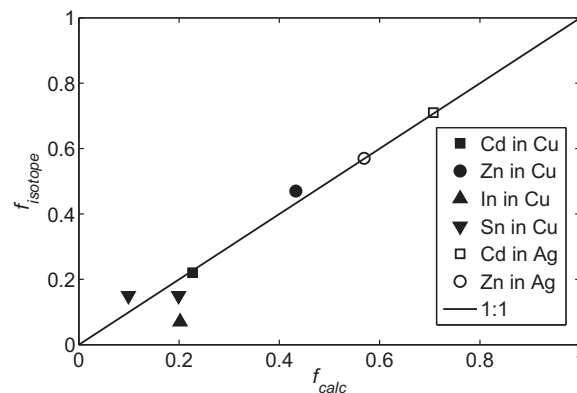


Fig. 3. Correlation coefficients for diffusion of several dilute impurities in the fcc metals Cu and Ag, calculated using Eq. (7) with atomic jump frequencies inferred from various experimental measurements ( $f_{\text{calc}}$ ), and from independent measurements of the isotope effect for diffusion ( $f_{\text{isotope}}$ ). Data are from Bocquet et al. (1983), and references therein.

determined from the ratio of self-diffusion coefficients,  $D_{\text{Co}}/D_{\text{Ni}}$ . Because Co and Ni have slightly different activation energies for self-diffusion, the correlation coefficient is a function of temperature. The isotope effect  $E$  can be calculated from the correlation coefficient, assuming that  $K$  for Co is the same as for Ni in NiO ( $K = 0.784$ ; Volpe et al., 1971). The calculated isotope effect is in reasonable agreement with direct measurements (Fig. 4), in absolute value and temperature dependence. The calculated values are systematically low, but could be brought into agreement with the measurements by increasing the assumed value of  $K$  for Co by  $\sim 15\%$ , or by assuming a small attractive (negative) binding energy between Co and vacancies, on the order of  $-5$  kJ/mol.

### 3.1.2. Interstitial mechanism

Diffusion of a trace element by a simple interstitial mechanism is uncorrelated ( $f = 1$ ): the direction of successive jumps is random, because all adjacent interstitial sites of the same type are equivalent. Because  $K$  also tends to be close to unity for interstitial diffusants (LeClaire, 1966), the isotope effect for diffusion by a purely interstitial

Table 1

Comparison of correlation coefficient determined from experimental data on the jump frequency ratios ( $f_{\text{calc}}$ ) with that determined from measurements of the isotope effect ( $f_{\text{isotope}}$ ), for dilute solute diffusion in face-centered cubic (fcc) metals.

Solvent	Solute	$T$ (K)	$w_2/w_1$	$w_3/w_1$	$w_4/w_0$	$F$	$f_{\text{calc}}$	$f_{\text{isotope}}$
Cu	Cd	1076	10	1	3	0.552	0.23	0.22
Cu	Zn	1168	3	0.5	1	0.736	0.43	0.47
Cu	In	1089	11	1	4	0.508	0.20	0.07
Cu	Sn	1014	13	0.2	2	0.619	0.10	0.15
		1089	7	0.33	3	0.552	0.19	0.15
Ag	Cd	1153	0.5	0.07	0.46	0.846	0.71	
		1133						0.71
Ag	Zn	1153	1.25	0.26	1.12	0.717	0.57	0.57

All data for  $w_2/w_1$ ,  $w_3/w_1$ ,  $w_4/w_0$  and  $f_{\text{isotope}}$  were obtained from Bocquet et al. (1983) and references therein. The values for  $F$  and  $f_{\text{calc}}$  were calculated based on the jump frequency data using Eqs. (7) and (8). A typographical error was found in the value for  $w_2/w_1$  reported for Cd in Cu by Bocquet et al. (1983), and was corrected here by consulting the original reference.

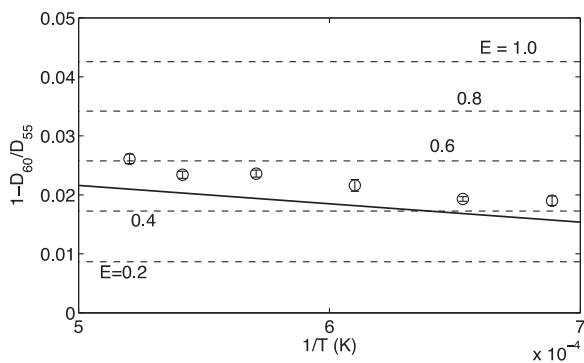


Fig. 4. Comparison of calculated (solid line) and measured (circles with  $2\sigma$  error bars) ratios of  $^{60}\text{Co}$  and  $^{55}\text{Co}$  diffusion coefficients in NiO [Chen and Peterson \(1972\)](#), as a function of temperature. The calculations are based on Eq. (4), where  $f$  is obtained from independent measurements of the ratio of Co and Ni tracer diffusion coefficients in NiO, as described in the text, and the value of  $K$  for Co diffusion is assumed to be the same as that measured for Ni self-diffusion in NiO [Volpe et al. \(1971\)](#), i.e.  $K = 0.784$ . The dashed horizontal lines correspond to different values of  $E$  ( $=fK$ ).

mechanism is generally expected to be large, close to a square root of mass dependence. (However, see [Mueller et al. \(2014\)](#), who found a smaller than expected isotope effect for interstitial diffusion of carbon in fcc-iron).

Correlation effects do come into play in interstitial diffusion if the interstitial atom also makes jumps to regular lattice sites (as in an interstitialcy mechanism), and/or if the interstitial atom preferentially occupies positions adjacent to lattice vacancies to form bound interstitial–vacancy pairs. In such cases many distinct types of jump must be considered, and no global analytical model like the five-frequency model considered above exists to evaluate the correlation coefficient. However, some simple limiting cases have been evaluated.

[Miller \(1969\)](#) developed a model for diffusion of interstitial atoms on an fcc lattice by bound interstitial–vacancy pairs, motivated by the finding that rapid diffusion of Cd in Pb is not consistent with a vacancy mechanism – hence suggesting an interstitial mechanism – but is also highly correlated, with a very small isotope effect. If the interstitial and vacancy are strongly bound, so that jumps of the interstitial and vacancy that keep the two on adjacent sites are much more frequent than jumps that break up the pair, and if the interstitial always remains as an interstitial, never jumping into the vacant lattice site, then the correlation coefficient for the interstitial impurity can be expressed as:

$$f \cong \left( \frac{u_2}{k_2 + u_2} \right), \quad (14)$$

where  $k_2$  is the jump frequency of the interstitial to another interstitial site that is adjacent to the vacancy, and  $u_2$  is the exchange frequency of the vacancy with a solvent atom that is also adjacent to the impurity. If the interstitial is much more mobile than the vacancy ( $k_2 \gg u_2$ ), then the interstitial atom will orbit about the vacancy with no net diffusion until the vacancy exchanges places with a solvent atom. In this case diffusion is controlled by the solvent–vacancy

exchanges rather than the interstitial jumps, diffusion of the interstitial is highly correlated, and the isotope effect is small (as with Cd diffusion in Pb).

This model may be applicable to interstitial carbon diffusion in fcc-Fe (taenite) under certain circumstances. It has been inferred that C interstitials in fcc-Fe are quite strongly attracted to vacancies, with a binding energy of  $-30$  to  $-40$  kJ/mol ([Slane et al., 2004](#); [Hepburn et al., 2013](#)). This may result in significant correlation for C diffusion, and a reduced isotope effect, if the interstitial jumps are rapid enough compared to the vacancy jumps, and a substantial fraction of the carbon is bound as pairs. It is unlikely, however, that such C–vacancy binding could explain the smaller than expected isotope effect for C diffusion determined by [Mueller et al. \(2014\)](#), because the carbon concentrations in their experiments ( $\sim 0.1$ – $5$  at.%) are much higher than the vacancy concentrations (expected to be on the order of 1 ppm, for a vacancy formation energy of 164 kJ/mol ([Kim and Buyers, 1978](#))). In this case there will be very few carbon–vacancy pairs, compared to the concentration of carbon interstitials, and carbon would be expected to diffuse predominantly by a purely interstitial mechanism with little correlation. Although vacancy concentrations are likely to be enhanced by the presence of carbon ([Mead and Birchenall, 1956](#)), it seems unlikely that C–vacancy pairing would lead to significant correlation effects in carbon diffusion unless the carbon concentration is less than  $\sim 100$  ppm.

### 3.1.3. Interstitialcy mechanism

Correlation effects also come into play for diffusion by an interstitialcy mechanism, wherein an interstitial atom hops to an occupied lattice site, displacing the lattice occupant to another adjacent interstitial site. In magnetite, for example, cation self-diffusion at low  $f_{\text{O}_2}$  has been clearly linked to an interstitialcy mechanism, based on measurements of the isotope effect for Fe ([Peterson et al., 1980](#)), direct inferences of the correlation coefficient from point defect relaxation measurements ([Dieckmann and Schmalzried, 1986](#)) and analysis of Mössbauer spectra ([Becker et al., 1993](#)). An interstitialcy mechanism has also been inferred for the self-diffusion of Ti in rutile ([Hoshino et al., 1985](#)). The involvement of more than one atom in the interstitialcy jump process leads not only to correlation effects but also to a violation of some of the assumptions made in deriving Eq. (4) for the isotope effect. In general, Eq. (4) has to be replaced by a more general expression:

$$\left( \frac{D_L}{D_H} - 1 \right) / \left( \left[ \frac{m + m_H}{m + m_L} \right]^{1/2} - 1 \right) = F(f)K \quad (15)$$

in which (1) the correlation coefficient  $f$  is replaced by a function of the correlation coefficient,  $F(f)$ , and (2) the mass term is modified to include the average mass  $m$  of the non-tracer atoms that also move during the interstitialcy jumps. The function  $F(f)$  often differs from  $f$  by only a few percent ([Peterson et al., 1980](#)), and hence may be closely approximated by  $f$  in many cases. The additional mass of the non-tracer atom participating in the jump, on the other hand, typically leads to  $E$  only about half as large

as would be predicted by Eq. (4) for the same correlation and coupling coefficients.

LeClaire (1970) presented equations for the correlation coefficient of an impurity atom diffusing by an interstitialcy mechanism, in terms of the relevant jump frequencies, in two simple lattices. However, to our knowledge there is not yet enough information on the jump frequencies to apply these equations to calculate the correlation coefficient for any impurity diffusing by an interstitialcy process.

### 3.2. Concentrated systems

The general problem of calculating correlation effects in concentrated mineral solid solutions is much more complicated than for the dilute systems considered above, where a trace element diffuses within an essentially pure crystal. Even in a simple binary solid solution, where diffusion occurs by a vacancy mechanism, the local environment of an atom–vacancy pair varies throughout the crystal, and there are many different types of jump to consider, each of which may have a different frequency depending on the configuration of the two types of atoms around the atom–vacancy pair. Similarly, there are many different types of jump to consider for a dilute impurity diffusing in a binary solid diffusion (e.g. a trace element diffusing in (Mg,Fe)O or (Mg,Fe)<sub>2</sub>SiO<sub>4</sub>). Correlation effects are more difficult to address rigorously in these cases, and in general the problem must be solved numerically, for example by using kinetic Monte Carlo calculations (e.g. Van der Ven and Ceder, 2005; Ammann et al., 2011).

However, correlation effects have been analyzed in terms of a simple model of a random solid solution (Manning, 1971), which is useful for analyzing the correlation coefficient for diffusion in mineral solid solutions with ideal, or nearly ideal, mixing. In this model, the atoms on the sublattice of interest, as well as the vacancies, are assumed to have a random distribution (i.e. there is no local ordering, including no binding between atoms of any type and vacancies). Furthermore, the rate of exchange between an atom of type *i* and an adjacent vacancy is assumed to be independent of the detailed arrangement of atoms around the vacancy – i.e., for each type of atom there is a single characteristic vacancy exchange frequency, *w<sub>i</sub>*, that does not depend on the local configuration of atoms.

On the basis of this simplified model for a disordered solid solution, Manning (1971) derived a simple expression for the correlation coefficient in terms of the self-diffusion coefficients, which can be written for a particular chemical species *a* as:

$$f_a = 1 - \frac{D_a(1 - f_0)}{\sum_i x_i D_i}, \quad (16)$$

where *f<sub>0</sub>* is the correlation coefficient for self-diffusion in a pure crystal (*f<sub>0</sub>* = 0.7815 for an fcc lattice), and *x<sub>i</sub>* is the atom fraction of chemical species *i* on the sublattice of interest. The denominator of Eq. (16) is the weighted mean of diffusion coefficients of all species on the sublattice, where the weights are the atomic concentrations.

In the limit of a nearly pure crystal, where *b* is the solvent and *a* is a trace element, Eq. (16) reduces to:

$$f_a = 1 - \frac{D_a}{D_b}(1 - f_0). \quad (17)$$

This equation reproduces the zero binding energy curve shown in Fig. 2, which is based on the five-frequency model for diffusion of a dilute impurity on an fcc lattice. As *f<sub>a</sub>* → 1, *D<sub>a</sub>/D<sub>b</sub>* → 0, and as *f<sub>a</sub>* → 0, *D<sub>a</sub>/D<sub>b</sub>* → 1/(1-*f<sub>0</sub>*). Note that because the correlation coefficient cannot be negative, there is an upper limit on the diffusion coefficient of the trace element; for the fcc lattice, it cannot be greater than 4.58*D<sub>b</sub>*, in the nearly pure crystal, and more generally cannot exceed 1/(1-*f<sub>0</sub>*)∑*x<sub>i</sub>**D<sub>i</sub>*. Diffusion coefficients that exceed this limit are an indication that one or more of the assumptions underlying the Manning (1971) model have been violated. A larger than expected cation diffusion coefficient could be explained, for example, by a negative (attractive) binding energy between the cation and a vacancy (e.g., Fig. 2).

Recall from above that in a pure crystal, dilute solutes that diffuse rapidly generally have highly correlated jump sequences, with small values of *f*. For major elements in mineral solid solutions, atomic jumps are also more highly correlated (the correlation coefficient is smaller) when the jump frequency, and therefore the diffusivity, of the atom is relatively high. However, correlation effects are less extreme than in the dilute case, because the frequency of a particular jump is not as different from the *average* frequency as it is in the case of a dilute impurity.

The Manning (1971) model has been found to be consistent with experimental data in a number of relevant cases. Measurements of the isotope effect for diffusion of both atomic species in α-CuZn and equiatomic FeCo confirm that the Manning model is applicable to these disordered metallic alloys (Bakker, 1984, and references therein). The Manning (1971) model was also found to be consistent with tracer diffusion data in (Co,Mg)O (Schnehaage et al., 1982) and (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> olivine (Hermeling and Schmalzried, 1984). In each of these solid solutions there is a strong variation in the diffusivities with composition, but – consistent with the Manning (1971) model – the jump frequency ratio of the two cations is essentially independent of composition. The Manning (1971) model therefore appears to be useful for evaluating the correlation coefficient in nearly ideal solid solutions, for cations that do not bind significantly to vacancies.

### 3.3. Grain boundaries

Only some general comments can be made regarding correlation and the isotope effect for diffusion along grain boundaries, because very few experimental measurements are available and the theoretical picture is inherently more complicated and less well described than for diffusion in crystals. Robinson and Peterson (1972) examined the isotope effect for silver diffusion within grain boundaries, using (1) silver polycrystals, (2) silver bicrystals, and (3) copper polycrystals. To our knowledge, these remain the only experimental measurements of the isotope effect in grain boundaries. For Ag self-diffusion in silver, it was found that the isotope effect for diffusion along grain boundaries, both in the bicrystals and polycrystals, was significantly less than



that for diffusion (by a vacancy mechanism) within the crystal, with  $E = 0.46$  for grain boundaries and  $E = 0.705$  for single crystals. Although the smaller value for grain boundaries may be attributed in part to a smaller coupling coefficient  $K$  within the less close-packed grain boundary, this seems unlikely to fully explain the difference, and hence it seems likely that Ag jumps within grain boundaries are also more correlated than they are in the crystal. Silver diffusion along grain boundaries in polycrystalline copper has an even smaller isotope effect ( $E = 0.18$ ) and hence appears to be even more highly correlated. Although the grain boundary diffusion mechanism cannot be uniquely identified based on the [Robinson and Peterson \(1972\)](#) isotope effect results, it is clear that diffusion in grain boundaries involves atomic jumps that can be significantly correlated, leading to a reduced isotope effect.

[Ma and Balluffi \(1994\)](#) examined correlation effects for self-diffusion by vacancy, interstitialcy and interstitial mechanisms in idealized grain boundaries. They identify two sources of correlation in grain boundaries. For vacancy and interstitialcy mechanisms, there are correlation effects that arise from the non-random position of the defect after making an exchange with the tracer atom. These effects are of the same character as those discussed above for diffusion in crystals, but are enhanced when diffusion is confined to one or two dimensions in the grain boundary. The other source of correlation arises from the non-uniform grain boundary structure, which leads to a number of jump types of varying difficulty that must be executed to enable long-range diffusion. The easiest jumps in the sequence are the ones most likely to be immediately reversed, leading to correlation. This source of correlation applies to interstitial as well as interstitialcy and vacancy diffusion mechanisms in grain boundaries, and becomes more prominent as the difference in activation energy among the jumps in the sequence becomes larger ([Ma and Balluffi, 1994](#)).

In simple oxides, there is evidence from the  $f_{O_2}$  dependence and from theoretical calculations on volume and grain boundary diffusion that the diffusion mechanism in grain boundaries is often the same as the diffusion mechanism in the crystal ([Sutton and Balluffi, 1995](#), p. 506–508, and references therein). Because correlation effects are enhanced in grain boundaries, it may therefore be anticipated that the isotopic mass dependence for diffusion in grain boundaries is generally less than for volume diffusion.

[Qin and Murch \(1993\)](#) presented an approximate expression for the correlation coefficient of a dilute impurity diffusing by a vacancy mechanism in an idealized dislocation core within a simple cubic crystal. Because grain boundaries can be modeled as arrays of dislocations, these equations may be useful for evaluating the isotope effect for impurities in grain boundaries. The [Qin and Murch \(1993\)](#) expression for the impurity correlation coefficient in the dislocation core,  $f'$ , can be written as:

$$f' = \frac{(2 - Y_0)w'_0 + 2.905w_0}{2Y_0w'_2 + (2 - Y_0)w'_0 + 2.905w_0} \quad (18)$$

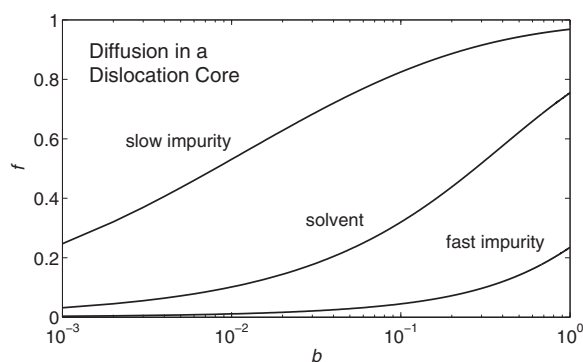
where  $w_0$  is the jump frequency of the solvent in the crystal lattice,  $w'_0$  is the solvent jump frequency in the dislocation,  $w'_2$  is the impurity jump frequency in the dislocation, and

$$Y_0 = 2(1 + b) \left\{ 1 + 2b - 2[b(b + 1)]^{1/2} \right\}, \quad (19)$$

where  $b = w_0/w'_0$ .

[Fig. 5](#) shows how the correlation coefficient  $f'$  for diffusion in the dislocation varies with  $b$ , for solvent self-diffusion and for “slow” and “fast” impurity diffusion (with the impurity-vacancy exchange frequency being 10 times slower or faster than the solvent-vacancy exchange frequency within the dislocation). For  $b = 1$ , there is no enhancement of diffusivity within the dislocation, and hence the correlation coefficient is equivalent to that in the 3D lattice. As  $b$  decreases, the diffusivity in the dislocation core becomes more rapid relative to that in the lattice, diffusion is increasingly confined to the dislocation core, and the jumps become more correlated. Although the value of  $b$  is not well constrained for any real case, it is likely to be fairly small given that diffusion in grain boundaries is typically enhanced by a large factor ( $\sim 10^4$  or more) relative to volume diffusion. Some of this enhancement may be due to higher vacancy concentrations within the dislocation cores, but it is likely that the vacancies are also significantly more mobile in the dislocation cores, and hence that  $b$  is relatively small.

For highly charged impurities that tend to bind to vacancies, the jumps are expected to be even more highly correlated. Impurity-vacancy binding is not considered in the [Qin and Murch \(1993\)](#) model but should have a greater influence on the correlation coefficient in dislocations and grain boundaries than it does for volume diffusion. In volume diffusion, a vacancy can randomize its position relative to the impurity even if it is strongly bound, because it is free to hop around the impurity in three dimensions. Along a dislocation core, it is much more difficult for a bound vacancy to randomize its position because jumps of the vacancy outside the core are much less frequent than jumps within the core. Hence, it may be expected that there are many back-and-forth exchanges between the bound vacancy and impurity before the pair is reoriented by a jump of the vacancy outside the dislocation core, with a



[Fig. 5](#). Correlation coefficient for diffusion in a dislocation by a vacancy mechanism, according to the model of [Qin and Murch \(1993\)](#). As  $b$  (the ratio of solvent-vacancy exchange frequency in the lattice to the solvent-vacancy exchange frequency in the dislocation) decreases, vacancies are increasingly confined to the dislocation and atomic jumps become more correlated. Slow impurity:  $w'_2/w'_0 = 0.1$ ; solvent:  $w'_2/w'_0 = 1$ ; fast impurity:  $w'_2/w'_0 = 10$ .

correspondingly small correlation coefficient, and isotope effect, for the impurity.

#### 4. APPLICATIONS

In some minerals, enough data are available on the diffusion mechanism and jump frequencies to make quantitative estimates of the correlation coefficient, and predictions of the isotope effect. Results are presented below for cation diffusion in periclase, olivine, magnetite and rutile.

##### 4.1. Periclase (MgO)

Periclase is an important constituent of Earth's lower mantle, and has the simple rocksalt structure, which consists of interpenetrating fcc cation and anion sublattices. Although the isotopic mass dependence for diffusion in periclase does not appear to have been studied, enough is known about its diffusion properties – from both experimental data and first-principles calculations – to make testable predictions of the isotope effect for diffusion of several cations.

It is possible to make some simplifying approximations to the five-frequency model discussed in (3.1.1) in the case of cation diffusion in MgO by a vacancy mechanism. First, in simple ionic crystals it is typically found that  $w_1 \cong w_0$ . For example, in various alkali halide crystals a large database exists on the reorientation frequency of solute–vacancy pairs (controlled by  $w_1$ ) and on the migration of the vacancy in pure crystals (controlled by  $w_0$ ), which in almost every case are found to be nearly identical (Barr and Lidiard, 1970). Secondly, it is assumed that the entropy for  $w_0$ ,  $w_1$  and  $w_2$  type jumps is correlated with the enthalpy (Zener, 1952). For cation diffusion in MgO, the relationship between the migration entropy and migration enthalpy is  $S_m^i = (1.42 \times 10^{-4} K^{-1}) H_m^i$  (Crispin et al., 2012). Third, it is assumed that the binding energy affects the associating and dissociating jumps symmetrically, and that the binding entropy is negligible, as it appears to be for trivalent cations in periclase (Van Orman et al., 2009; Crispin and Van Orman, 2010), such that  $w_3^i = w_0 \exp(H_b^i/2RT)$  and  $w_4^i = w_0 \exp(-H_b^i/2RT)$ , where  $H_b$  is the binding enthalpy. Finally, the jump attempt frequency ( $\nu$  in Eq. (9)) is assumed to be the same for all jump types.

With these simplifying assumptions, only three parameters are required to calculate the correlation coefficient for a dilute solute cation diffusing by a vacancy mechanism in MgO: (1) the migration enthalpy of Mg, (2) the migration enthalpy of the solute, and (3) the binding energy between solute and vacancy. Information on these parameters can be obtained both from experimental measurements and theoretical calculations. Contour plots of the mass dependence of isotope diffusion ( $E$ ) for cations in MgO, as a function of solute migration enthalpy and solute–vacancy binding energy, are shown in Fig. 6, based on Eq. (4). No measurements of  $K$  exist for diffusion in MgO, but measurements of  $K$  for self-diffusion in NiO (Volpe et al., 1971) and CoO (Chen et al., 1969), which share the same rocksalt structure, are very similar to each other ( $K = 0.78$  for NiO;  $K = 0.75$

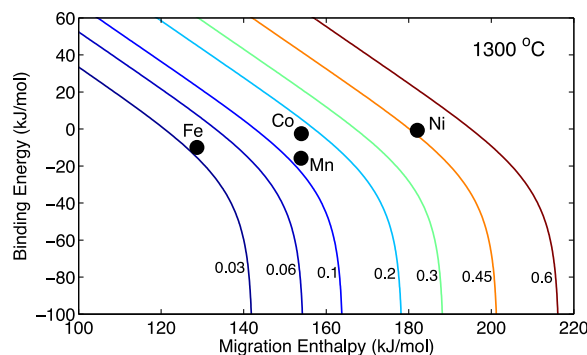


Fig. 6. Contour maps of the isotope effect for cation diffusion by a vacancy mechanism in MgO, as a function of the migration enthalpy and binding energy to vacancies. The migration enthalpy for Mg self-diffusion used in the calculations (196.6 kJ/mol) as well as the migration enthalpies and binding energies for Fe, Co, Mn and Ni, are from the DFT calculations reported in Crispin et al. (2012). The numbers on the curves are values of  $E$ . A constant value of  $K$  is assumed (0.78, the measured value for Ni self-diffusion in NiO).

for CoO). For the calculations presented here we adopt the value  $K = 0.78$  determined for Ni self-diffusion in NiO. The migration enthalpy for Mg diffusion is assumed to be 196.6 kJ/mol, the value obtained from calculations based on density functional theory (DFT) by Crispin et al. (2012).

Values of the migration energy and binding energy have also been calculated for the divalent transition metal cations Mn, Fe, Co and Ni in MgO (Table 2), using the same DFT techniques used to calculate the Mg migration energy (Crispin et al., 2012). The diffusion coefficients obtained from these calculations are in reasonable agreement with independent experimental data, for samples with controlled vacancy concentrations (Crispin et al., 2012). The DFT values for the migration and binding energy of these cations are also plotted on Fig. 6, and predict a significant dispersion in the mass dependence of isotope diffusion, with Fe having the smallest isotope effect and Ni the largest.

As discussed previously, the isotope effect for diffusion by a vacancy mechanism is expected to be temperature dependent due to differences in the activation energy for the various jumps involved. The predicted temperature dependence for transition metals in periclase is shown in Fig. 7, based on the parameters given in Table 2. With increasing temperature, solute jump frequencies ( $w_2$ ) become more similar to the Mg jump frequency ( $w_1$ ). Hence, in general the correlation coefficient converges toward the value for Mg self-diffusion ( $f = 0.7815$ ) at high temperatures. For Mn, Fe, Co and Ni, which exchange more readily with vacancies than does Mg, the isotope effect hence becomes stronger with increasing temperature. For cations that diffuse more slowly than Mg and have large correlation coefficients, the isotope effect would be expected to diminish with increasing temperature.

The correlation coefficient determined by Schnehage et al. (1982) for Co diffusion in MgO, based on measurements of Co and Mg tracer diffusivities in (Co,Mg)O at 1573 K, is in excellent agreement with the correlation

Table 2

Diffusion parameters for divalent transition metals and Mg in MgO, from density functional theory calculations Crispin et al. (2012).

	Migration enthalpy, $H_m$ (kJ/mol)	Binding enthalpy, $H_b$ (kJ/mol)
Mn <sup>2+</sup>	153.9	−15.8
Fe <sup>2+</sup>	128.7	−10.0
Co <sup>2+</sup>	154.0	−2.5
Ni <sup>2+</sup>	182.1	−0.7
Mg <sup>2+</sup>	196.6	

$$w_0 = w_1 = v \exp\left(0.0001424 \frac{H_m^{Mg}}{R}\right) \exp\left(\frac{-H_m^{Mg}}{RT}\right); \quad w_2 = v \exp\left(0.0001424 \frac{H_m^i}{R}\right) \exp\left(\frac{-H_m^i}{RT}\right); \quad w_3 = w_1 \exp\left(\frac{H_b^i}{2RT}\right); \quad w_4 = w_1 \exp\left(\frac{-H_b^i}{2RT}\right)$$

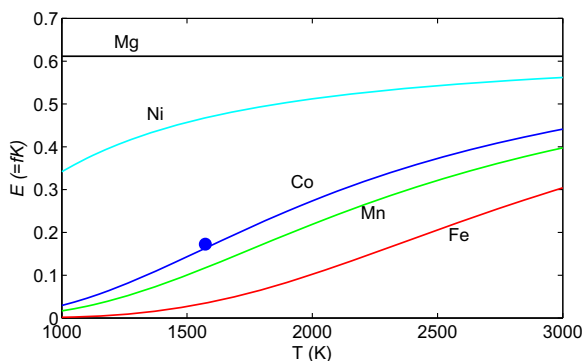


Fig. 7. Predicted isotope effect as a function of temperature for divalent transition metal cations in MgO, based on DFT calculations of migration and binding energies (Crispin et al., 2012) and assuming  $K = 0.78$ . Also shown (blue circle) is the predicted isotope effect for Co in MgO based on the correlation coefficient determined from experimental measurements of Co and Mg tracer diffusion coefficients in (Co, Mg) O Schnehage et al. (1982). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

coefficients predicted by the DFT calculations at the same temperature, using Eq. (4) (Fig. 7).

It is important to point out that while the DFT calculations correctly predict the relative order of experimentally determined diffusion coefficients among the divalent transition metals in MgO, as well as their absolute values within at worst a factor of  $\sim 3$ , the difference in diffusivity between the fastest (Fe) and slowest (Ni) cation is over-predicted by the DFT calculations (Crispin et al., 2012). Hence, the differences in correlation coefficients among these cations, and the consequent dispersion in the isotope effect, may not be as large as suggested by Figs. 6 and 7. Further experimental work is needed to test the DFT predictions.

The predicted large difference in correlation coefficients for Fe and Ni diffusion in periclase has important consequences for the fractionation of their isotopes by diffusion. Fig. 8 shows a simple example of diffusive fractionation of Fe and Ni isotopes, for diffusion in an effectively infinite medium at constant temperature (1500 K). Initially, the isotopic compositions for each element are homogeneous and there is a step function in the elemental concentrations, with elemental concentration  $C_0$  on the right side of the interface and zero on the left. The concentration of each isotopic species as a function of distance from the initial interface  $x$  and isothermal anneal time  $t$  is given by:

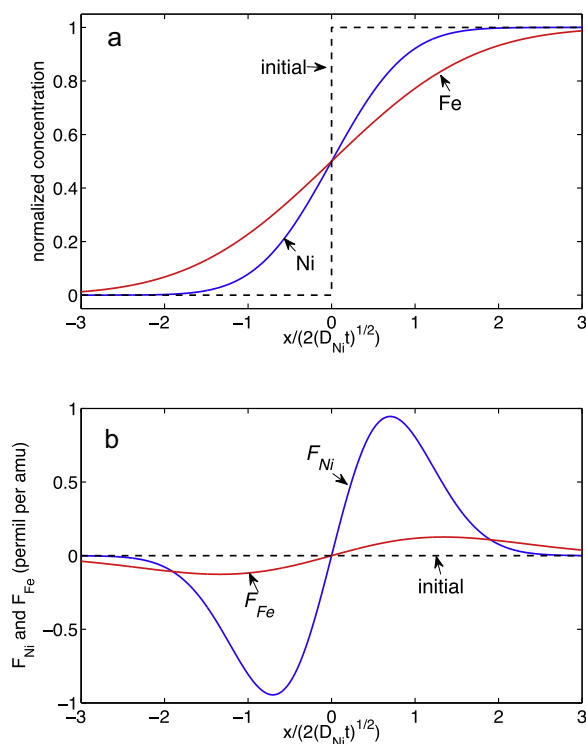


Fig. 8. Fractionation of Fe and Ni isotopes by diffusion in periclase at 1500 K. Iron and nickel are both present at dilute concentrations, with an initial step function in their elemental concentration profiles. The isotopic composition of each element is homogeneous initially, but becomes fractionated as light isotopes are concentrated at the leading edge of the diffusion profile, and depleted behind it. The length scale  $x$  is normalized by the Ni diffusion coefficient  $D_{Ni}$  and isothermal annealing time  $t$ , and is assumed to be sufficiently short that diffusion is occurring in an effectively infinite medium. (a) Elemental diffusion profiles for Fe (red) and Ni (blue). The diffusion coefficients are obtained from the DFT results presented in Crispin et al. (2012). (b) Isotopic fractionation of Fe and Ni isotopes along the diffusion profiles shown in (a). Isotopic fractionation of Ni and Fe isotopes are represented by  $F_{Ni}$  and  $F_{Fe}$ , the ‰ per amu difference from the initial (homogeneous) isotopic composition. For example,  $F_{Fe}$  can be calculated as  $\delta^{56/54}/(56-54)$ , or as  $\delta^{57/54}/(57-54)$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\frac{C - 0.5C_0}{0.5C_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right). \quad (20)$$

Differences in diffusivity for the isotopes of Fe and Ni are small enough that the relative concentration profiles of

the isotopes are indistinguishable in the plot of elemental concentrations (Fig. 8a). The fractionation of Ni isotopes is significantly greater than the fractionation of Fe isotopes (Fig. 8b), due to the greater mass dependence  $E$  for Ni diffusion. Nickel isotopic fractionation also peaks closer to the original interface than Fe isotopic fractionation, due to the faster diffusion of Fe relative to Ni. Again, it should be noted that this behavior is quite different from the observed behavior in silicate melts. In silicate melts, the mass dependence of isotope diffusion decreases as the diffusivity of the element decreases (Watkins et al., 2014). In minerals, the isotope effect is usually expected to increase as the diffusivity of the element decreases.

## 4.2. Olivine

The Manning (1971) model for diffusion in concentrated solid solutions has been found to provide a reasonable description of Fe and Mg diffusion rates in olivine (Hermeling and Schmalzried, 1984) and can be used to calculate correlation coefficients for these cations. The ratio of self-diffusion coefficients  $D_{\text{Fe}}/D_{\text{Mg}}$  across the forsterite-fayalite solid solution series at 1130 °C was found to have a nearly constant value of 3.6, and the value of  $f_0$  for cation self-diffusion in olivine (which is difficult to calculate rigorously, because of the large number of jump types involved) is estimated to be 0.745 (Hermeling and Schmalzried, 1984). Based on these values, the correlation coefficients for Fe and Mg, calculated using Eq. (16), are shown as a function of olivine composition in Fig. 9. These results predict that the isotope effect (1) depends significantly on olivine composition for both cations, especially Fe; and (2) is significantly smaller for Fe than for Mg.

The isotopic mass dependence of diffusion for Fe and Mg has also been inferred from detailed observations of isotope fractionation along Fe–Mg interdiffusion profiles in natural olivine (Sio et al., 2013; Oeser et al., 2015). The inferred values of  $E$  (or  $\beta$ ) depend on the surface boundary condition assumed in modeling the profiles, but the ratio  $E_{\text{Fe}}/E_{\text{Mg}}$  is not sensitive to model parameters (Sio et al.,

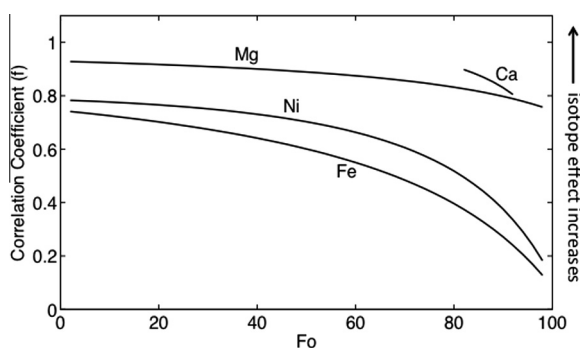


Fig. 9. Correlation coefficients for Mg, Ni, Fe and Ca diffusion parallel to [001] in olivine as a function of forsterite content at 1130 °C, using Eq. (16) Manning (1971) and assuming Ni and Ca are present as trace elements. The diffusion coefficients used in the calculations were obtained using the expressions recommended by Chakraborty (2010) (see text for details).

2013). Sio et al. (2013) found, for an olivine phenocryst from Kilauea Iki lava lake,  $E_{\text{Fe}}/E_{\text{Mg}} = 1.8 \pm 0.3$ . Oeser et al. (2015) similarly found  $E_{\text{Fe}}/E_{\text{Mg}} = 2.05 \pm 0.45$  for olivine phenocrysts and xenocrysts from several different intraplate volcanic regions. In contrast, if  $K$  is similar for Fe and Mg in olivine, the Manning (1971) model, combined with the Hermeling and Schmalzried (1984) tracer diffusion data, predict that  $E_{\text{Fe}}/E_{\text{Mg}} < 1$ , with  $E_{\text{Fe}}/E_{\text{Mg}} \sim 0.4$ – $0.5$  for Fo75–Fo85 olivine.

A possible explanation for this discrepancy is that there is significant local ordering in olivine, which is not accounted for in the Manning (1971) model. The isotope fractionation data from natural crystals (Sio et al., 2013; Oeser et al., 2015) suggest that the frequency of Mg hops to neighboring vacancies is greater than that for Fe, making Mg hops more correlated (with smaller  $f$ ). But the experimental data (Hermeling and Schmalzried, 1984) show that Fe diffuses more rapidly than Mg. This could potentially be explained if there is a substantial attraction (negative binding energy) between Fe and vacancies, which would enhance the diffusivity of Fe by increasing the probability that a vacancy occupies an adjacent site. If the binding is strong enough, Fe could diffuse more rapidly than Mg even if it hops to an adjacent vacancy at a lower frequency. For example,  $\text{Al}^{3+}$  diffuses much more rapidly than  $\text{Mg}^{2+}$  in MgO, despite apparently having a somewhat smaller jump frequency to vacancies, because Coulombic forces bind it strongly to vacancies (Van Orman et al., 2009).

It seems plausible that there is attractive binding between Fe and vacancies in olivine. A small fraction of the Fe is present as  $\text{Fe}^{3+}$ , which may be expected to bind strongly to negatively charged vacancies, and  $\text{Fe}^{2+}$  might also attract vacancies, as it does in MgO where the binding energy has been calculated from first-principles to be  $-10$  kJ/mol (Crispin et al., 2012). Although calculating the correlation coefficients in concentrated solid solutions that are ordered due to atom–vacancy interactions is a difficult problem, it has been done in fcc alloys, using first-principles calculations to determine the energies of many different atomic configurations as well as the jump energies, and kinetic Monte Carlo simulations to determine the correlation coefficients (Van der Ven and Ceder, 2005). Similar theoretical calculations for olivine would be very useful, as would experimental work on the isotopic mass dependence in olivine.

Although natural observations of Fe and Mg isotopic fractionation in olivine cast doubt on the applicability of the Manning (1971) model to olivine solid solutions, it is nevertheless useful as a point of reference to examine the predictions of this simple end-member model for other cations in olivine. We focus here on divalent cations, for which ordering effects are likely to be less significant than for trivalent (or monovalent) cations. Because the correlation coefficient within the Manning (1971) model depends on the diffusivity of the impurity relative to the diffusivities of the major cations Fe and Mg, it is critical to use self-consistent diffusion data sets to evaluate them, and to compare all diffusion coefficients at the same crystallographic orientation, and under the same conditions of temperature,  $f_{\text{O}_2}$  and olivine composition. Sufficient data exist



for Fe–Mg interdiffusion, Ni diffusion and Ca diffusion to develop robust expressions for the diffusion coefficients in the *c* direction as a function of temperature,  $f_{O_2}$ , and forsterite content (Chakraborty, 2010, and references therein), and use these to calculate the correlation coefficients according to the Manning (1971) model.

Because the forsterite-fayalite solid solution is nearly ideal, the Fe–Mg interdiffusion coefficient can be expressed as:

$$\tilde{D}_{Fe-Mg} = \frac{D_{Fe}D_{Mg}}{x_{Fa}D_{Fe} + (1 - x_{Fa})D_{Mg}}. \quad (21)$$

The self-diffusion coefficients for Fe and Mg at 1130 °C, as a function of olivine composition, are obtained from this expression using the interdiffusion coefficient from the expression recommended by Chakraborty (2010), originally presented by Dohmen and Chakraborty (2007), and  $D_{Fe}/D_{Mg} = 3.6$  (Hermeling and Schmalzried, 1984). The correlation coefficients for Ni and Ca are then obtained using Eq. (16), and are also shown in Fig. 9. It was assumed that Ni and Ca are present at dilute concentrations, so that only Fe and Mg contribute to the denominator in Eq. (16).

Spandler and O'Neill (2010) also reported an internally consistent set of diffusion coefficients that are suitable for determining correlation coefficients for divalent cations in olivine. The Spandler and O'Neill (2010) experiment involved element exchange between a natural olivine (Fo91) single crystal and a synthetic basaltic liquid at 1300 °C, and produced data on the diffusion coefficients for Fe–Mg as well as a large number of minor and trace elements, all under identical conditions. The Fe and Mg self-diffusion coefficients are inferred from the Fe–Mg interdiffusion coefficient measured in the Spandler and O'Neill experiment as above, using Eq. (21). The ratio  $D_{Fe}/D_{Mg}$  is temperature-dependent, due to a difference in the activation energies for Fe and Mg self-diffusion. Hence, the ratio determined by Hermeling and Schmalzried (1984) at 1130 °C must be corrected to 1300 °C. No information is available on the activation energy difference. Here it is assumed that the difference in diffusivity between Fe and Mg in olivine is a function only of the difference in their activation energy (i.e. the pre-exponential factors for Fe and Mg are the same), which implies that the activation energy difference is 15 kJ/mol. Under this assumption,  $D_{Fe}/D_{Mg} = 3.1$  at 1300 °C, and this ratio is assumed here to be independent of crystallographic orientation. The correlation factors for divalent cations are calculated from the Manning (1971) model using Eq. (16), assuming that the diffusion coefficients measured by Spandler and O'Neill at low concentrations are equivalent to tracer diffusion coefficients, and are shown in Fig. 10.

The diffusion coefficients for Be determined by Spandler and O'Neill are too large to be explained within the framework of the Manning (1971) model. The high mobility of Be is likely due to its diffusion by an interstitial mechanism, but could also be consistent with a vacancy mechanism if there is substantial attraction (negative binding energy) between Be and vacancies.

The correlation coefficients obtained from the Spandler and O'Neill (2010) data for Ni and Ca in the [001]

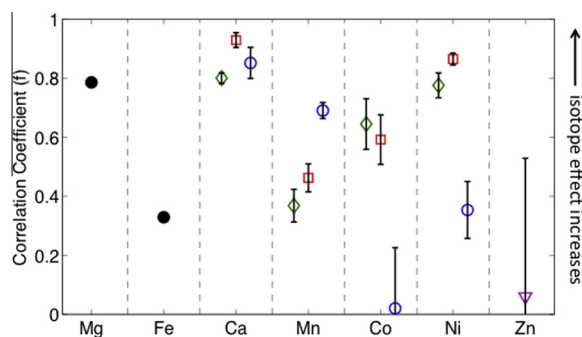


Fig. 10. Correlation coefficients for cations in Fo<sub>91</sub> olivine at 1300 °C, based on the experimental diffusion data of Spandler and O'Neill (2010) and the Manning (1971) model (Eq. (16)). A constant  $D_{Fe}/D_{Mg}$  ratio of 3.1 was assumed, independent of crystallographic orientation; hence, the correlation coefficients for Mg and Fe are independent of diffusion direction. Green diamonds represent diffusion in the [100] direction; red squares, diffusion in the [010] direction; blue circles, diffusion in the [001] direction; purple triangle (Zn) represents an average of diffusion in the [010] and [001] directions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

direction, shown in Fig. 10, are in good agreement with the values shown in Fig. 9, obtained using the expressions recommended by Chakraborty (2010). The Spandler and O'Neill (2010) data suggest that some cations may have significant anisotropy in the isotope effect, smaller in the fast [001] direction than in the [100] or [010] directions for Co and Ni, and larger in the [001] direction for Mn.

### 4.3. Magnetite

Diffusion in magnetite has been the subject of a number of careful studies. Dieckmann and Schmalzried (1977) showed, based on experimental measurements of Fe self-diffusion as a function of  $f_{O_2}$ , that the diffusion mechanism changes from one involving interstitials at low  $f_{O_2}$  to a vacancy mechanism at higher  $f_{O_2}$ . Later experiments on the isotope effect (Peterson et al., 1980), point defect relaxation (Dieckmann and Schmalzried, 1986) and Mössbauer spectroscopy (Becker et al., 1993) confirmed that the low- $f_{O_2}$  mechanism is an interstitialcy process. The isotope effect is smaller in the low- $f_{O_2}$  interstitialcy regime than in the high- $f_{O_2}$  vacancy regime, due both to a smaller correlation coefficient and to the involvement of a non-tracer atom in the jump.

Cations other than Fe exhibit similar changes in diffusivity with changing  $f_{O_2}$ , suggesting a similar change in mechanism (see review by Van Orman and Crispin, 2010). At present there is not enough information, either theoretical or experimental, to predict the correlation coefficients for diffusion of cation impurities in magnetite by an interstitialcy mechanism. A large number of interstitialcy jump types are possible, each with a different correlation coefficient (Peterson et al., 1980) and it is not clear which predominate even for self-diffusion of Fe (Peterson et al., 1980; Dieckmann and Schmalzried, 1986; Becker et al.,

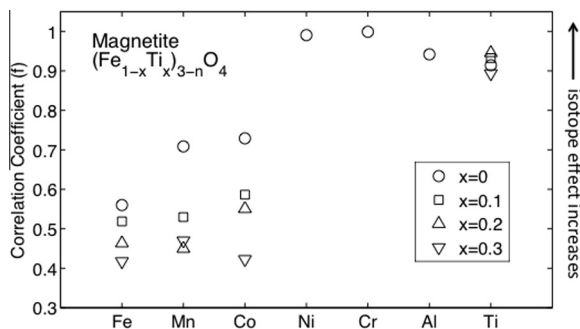


Fig. 11. Correlation coefficients for cation diffusion by a vacancy mechanism in pure magnetite and three different titanomagnetite compositions, calculated using the Manning (1971) model (Eq. (16)). The calculated values are based on diffusion data from Aggarwal and Dieckmann (2002) for Fe, Mn, Co and Ti, and from Dieckmann et al. (1987) for Ni, Cr and Al. (Note that these calculations apply only to diffusion in the high- $f_{O_2}$  vacancy regime.).

1993). For impurities, there are many different jump frequencies to consider for each type of interstitialcy jump, and virtually no constraints on their relative magnitudes from experimental studies. Valuable information could be obtained from DFT calculations of the jump energies, combined with kinetic Monte Carlo simulations, which would help identify the most favorable interstitialcy process for impurity atoms diffusing in magnetite at low  $f_{O_2}$ , and allow the correlation coefficient for this process to be calculated.

In the high- $f_{O_2}$  vacancy regime, the correlation coefficients for cation impurities can be estimated based on their diffusivities relative to Fe self-diffusion – neglecting any binding between cations and vacancies – using Eq. (16). Trivalent and tetravalent cations diffuse significantly more slowly than Fe in magnetite and are thus expected to have correlation coefficients near unity, even if they bind significantly to vacancies due to Coulombic attraction.

Iron self-diffusion by a vacancy mechanism has been determined to occur on the octahedral cation sublattice (Dieckmann and Schmalzried, 1986; Becker et al., 1993). For self-diffusion on this sublattice, the correlation coefficient  $f_0$  is 0.56 and the value of  $K$  determined from isotope effect measurements is 0.89 (Peterson et al., 1980).

Calculated correlation coefficients for several cations are shown in Fig. 11, for pure magnetite and three different titanomagnetite compositions. The correlation coefficients are shown at 1200 °C, a temperature at which experimental data exist for all cations. Except for Fe (in all cases) and Ti (in titanomagnetite), all cations are assumed to be present at low concentrations, such that the denominator in Eq. (16) depends only on Ti and/or Fe diffusion coefficients. The slowly-diffusing cations Ni, Cr, Al and Ti are calculated to have correlation coefficients close to unity in magnetite, and hence are predicted to have a large isotope effect, with  $E \sim 0.8$ –0.89 (assuming  $K = 0.89$ ). The correlation coefficient for Ti does not vary strongly with magnetite composition within the range studied experimentally, and correlation coefficients for Ni, Cr and Al are also expected

to be insensitive to the titanium content of the magnetite. The correlation coefficients for Fe, Co and Mn are similar to each other, and decrease with increasing titanium content of the magnetite.

It should be emphasized that the values shown in Fig. 11 apply only to the high- $f_{O_2}$  vacancy regime. In pure magnetite, the vacancy regime for most cations begins approximately one log unit above the Ni–NiO buffer. Addition of Ti expands the vacancy regime: for  $(Ti_{0.2}Fe_{0.8})_3O_4$  it begins about one log unit below the Ni–NiO buffer for most cations. At lower oxygen fugacities, cation diffusion in magnetite occurs by an interstitialcy mechanism. As discussed above, no information is available on the correlation coefficients for cations other than Fe in this regime. However, for Fe the isotope effect in the interstitialcy regime is less than half its value in the vacancy regime at 1200 °C (Peterson et al., 1980), and may become smaller still at temperatures below 1100 °C where a more highly correlated type of interstitialcy jump predominates (Dieckmann and Schmalzried, 1986). Thus, it might be anticipated that the isotope effect for other cations in magnetite also diminishes significantly in the low- $f_{O_2}$  interstitialcy regime.

#### 4.4. Rutile

In rutile, Ti self-diffusion has been inferred to occur by an interstitialcy mechanism, and the self-diffusion data combined with point defect relaxation, electrical conductivity and thermogravimetry measurements yields correlation coefficients in the range ~0.25–0.45 (Hoshino et al., 1985). Hence, the isotope effect for Ti diffusion in rutile is expected to be fairly small, with a maximum  $E \sim 0.12$ –0.23 assuming  $K \sim 1$ , and less if  $K < 1$  (for self-diffusion by an interstitialcy mechanism,  $E \cong 1/2fK$ ; see Eq. (15)).

Many divalent and monovalent cation impurities in rutile, such as Co, Mn, Fe, Ni (Sasaki et al., 1985), and Li (Johnson, 1964) diffuse rapidly in the  $c$  direction, with much slower diffusivities in the orthogonal direction. This has been attributed to interstitial diffusion within relatively open channels that parallel the  $c$  axis, and an interstitialcy mechanism along  $a$  where open channels do not exist (Sasaki et al., 1985). These cations are thought to predominantly occupy  $Ti^{4+}$  sites, but upon jumping to an interstitial site they are evidently able to make many jumps in the  $c$  direction before reoccupying a regular cation site. The anisotropy in diffusion mechanism for these cations is likely to give rise to significant anisotropy in the isotope effect as well. The jumps among interstitial sites along  $c$  are not likely to be correlated significantly, and hence the isotope effect is expected to be large in this direction. Consistent with this expectation, the isotope effect has been measured for diffusion in the  $c$  direction for Li and found to depend very nearly on the square root of mass (Johnson and Krouse, 1966). In the orthogonal direction, the isotope effect is likely to be much smaller, because both the tracer cation and Ti must move during an interstitialcy jump and because jumps of the tracer are likely to be significantly correlated, as they are for self-diffusion of Ti.

## 5. CONCLUSIONS

1. In minerals, the dependence of diffusion coefficients on isotopic mass (“isotope effect” for diffusion) is primarily a function of the degree of correlation (non-randomness) in the sequence of atomic jumps that leads to diffusion, which is expressed by the correlation coefficient  $f$ . The magnitude of the isotope effect can be predicted if the relative frequencies of the various jumps involved in the diffusion process are known.
2. For diffusion by a vacancy mechanism, trace or minor elements that have a large activation energy for the jump to an adjacent vacancy, and therefore diffuse slowly relative to major elements that occupy the same sublattice, have little correlation in their jumps ( $f \sim 1$ ) and therefore are expected to exhibit a large isotope effect ( $E$  close to 1;  $\beta$  close to 1/2). Rapidly diffusing elements with small activation barriers have highly correlated jumps, with smaller values of  $f$  and  $E$ . This behavior is quite different from that in silicate melts, where the isotope effect has been found to be small for slowly diffusing cations, and large for rapidly diffusing cations (Goel et al., 2012; Watkins et al., 2014).
3. The correlation coefficient, and therefore the isotope effect, for diffusion by a vacancy mechanism is temperature-dependent. With increasing temperature, the frequencies of the various jumps involved in diffusion generally become more similar to each other, and the correlation coefficient tends to converge toward the value for self-diffusion in the pure crystal. The isotope effect is expected to become stronger with increasing temperature for elements with small correlation coefficients (which tend to have small migration barriers and diffuse rapidly) and to become somewhat weaker with increasing temperature for elements with large correlation coefficients (which tend to have large migration barriers and diffuse slowly).
4. For solid solutions, the isotope effect for all cations diffusing on the same sublattice is, in general, a function of the major element composition of the mineral. This dependence on composition will be greatest when the major cations have significantly different jump frequencies, and when the jump frequency of the cation of interest is not much lower or higher than those of the major cations.
5. Diffusion of trace or minor elements by a simple interstitial mechanism is uncorrelated ( $f = 1$ ), and the isotope effect is therefore expected to be large. Correlation is significant, however, for diffusion by an interstitialcy mechanism (involving the coupled jump of an interstitial atom to an occupied lattice site, displacing the lattice atom to another interstitial site), or for diffusion by means of interstitial–vacancy pairs.
6. The isotope effect in non-cubic minerals may be anisotropic, either due to a change in mechanism with orientation (e.g., for small, low-charge cations that diffuse interstitially along  $c$  in rutile) or due to changes in the relative jump frequencies as a function of orientation (e.g., for cations in olivine).

7. In grain boundaries and dislocations, atomic jumps are generally more correlated than they are within the mineral. Hence, the isotope effect is expected to be smaller for “fast path” diffusion along grain boundaries and dislocations than for volume diffusion.

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## APPENDIX A. QUANTUM EFFECTS

The theory of the isotope effect discussed in this paper is a result of classical physics and does not take into account quantum effects, which may be significant for light atoms at low temperatures. In most cases, diffusion of atoms that substitute on regular lattice sites in minerals is significant only well above the Debye temperature. At these temperatures, quantum isotope effects are expected to be small, with corrections to Eq. (4) amounting to less than a few percent (e.g. LeClaire, 1966). However, quantum effects may be important for diffusion of light atoms by an interstitial mechanism, below the Debye temperature.

Quantum effects have been found to be particularly important for hydrogen diffusion in metals at low temperatures, with distinctly different effects in body-centered cubic (bcc) and face-centered cubic (fcc) metals (Völkl and Alefeld, 1975). In bcc metals, the activation energy is lower for hydrogen than deuterium in the low-temperature regime, so that  $D_H/D_D$  is strongly temperature dependent (with  $D_H/D_D \sim 20$  at  $-125$  °C). In fcc metals, the activation energy for hydrogen diffusion is larger than for deuterium, and deuterium diffuses *faster* than hydrogen at low temperatures (below  $\sim 500$  °C, in Pd; Völkl and Alefeld, 1975). Several distinct quantum effects may be important in the diffusivity of hydrogen isotopes: quantum statistics (Bose–Einstein phonon distributions), quantum tunneling, and zero-point energy effects (Franklin, 1975). An analysis of these effects is beyond the scope of this paper, which is focused on diffusion in minerals at high temperatures.

It is possible that quantum effects may be significant for light elements such as H, He and possibly Li in silicate minerals and glasses at low temperatures. However, the isotope effect for interstitial diffusion of H (Johnson et al., 1975) and Li (Johnson and Krouse, 1966) in rutile has been found to be consistent with classical theory at temperatures as low as 300 °C and 450 °C, respectively. Thus, it seems reasonable to assume that the classical theory presented here adequately describes the isotope effect in nearly all cases, at metamorphic and igneous temperatures.

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