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Oxygen diffusion in grossular and some geological implications

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ABSTRACT

Computer simulation techniques were used to investigate defect formation and the diffusion of O and OH groups in grossular garnet. Diffusion of both species along an octahedral edge was simulated, and activation energies for the jump were calculated. This jump represents the greatest distance along the shortest diffusion route through the grossular lattice, and hence the calculated activation energy is comparable to experimentally determined values. The activation energy for O diffusion in the extrinsic regime is predicted to be 106 kJ/mol, whereas for the high-temperature intrinsic regime, we calculate an activation energy of 383 kJ/mol. Extrinsic diffusion of the OH group along the same pathway also has an activation energy of 106 kJ/mol. However, when structurally bound H_2O in the form of hydrogarnet defects is introduced into the system, the OH diffusion activation energy is reduced to 67 kJ/mol. The high activation energy combined with experimentally available diffusion coefficients for O in garnet suggest that O mobility is very low at metamorphic temperatures.

INTRODUCTION

The transport properties of O in silicate minerals have attracted growing interest in recent years because of the importance of the rates of stable isotope exchange and the control that O diffusion exerts on several geological processes. Knowledge of O diffusion coefficients at a range of temperatures and the resulting activation energies is critical for an understanding of the kinetics of O isotope exchange between coexisting minerals.

Many widely applicable geothermometers based on O isotope exchange are available. However, they often record reset or highly discordant apparent temperatures in rocks that have been cooled slowly (e.g., Dienes, 1977; Valley, 1986; Eiler et al., 1993). The immediate inference is that the rate of O self-diffusion within and between coexisting rock-forming minerals is comparatively rapid at low temperatures. Initial attempts to quantify formally the effect of diffusional exchange on stable isotope distributions have employed the Dodson equation and the concept of closure temperatures (Dodson, 1973). This model identifies the temperature for each mineral in the rock at which the concentration of a specific element is effectively fixed during retrograde reequilibration and the mineral isolated from its surroundings. Such models have been employed to determine cooling rates of plutons (e.g., Giletti, 1986; Farver, 1989) and to calculate the diffusion of O in magnetite in a slowly cooled host rock (Sharp, 1991). More recently, Eiler et al. (1993) adopted an alternative strategy using the so-called Fast Grain Boundary (FGB) model to describe stable isotope fractionation and intracrystalline zonation that result from closed system interdiffusion. This model assumes that grain-boundary diffusion is much faster than volume diffusion and accounts for the exchange between all minerals in a rock. Detailed ion microprobe mapping studies of magnetite (Valley and Graham, 1991) and garnet (Chamberlain and Conrad, 1991; Kohn et al., 1993) have revealed variations in O isotope ratios within individual grains. Interpretation of the processes that cause such heterogeneities and the exchange of O between coexisting minerals depends critically on the availability and quality of relevant O diffusion data.

Experimental studies of O diffusion have been performed for a wide range of silicate minerals (see for example Freer, 1981; Giletti, 1986; Graham and Elphick, 1991; Brady, 1995). The accumulated body of data suggests that O diffusion in several framework silicates under dry conditions is associated with high activation energies (typically 200–300 kJ/mol) and slow diffusion rates, whereas diffusion under wet, hydrothermal conditions is associated with lower activation energies (~120 kJ/mol) and faster diffusion rates. Such differences are now well established for the feldspar minerals (Elphick et al., 1988; Farver and Yund, 1990), and the diffusion data for quartz (Elphick and Graham, 1988) show a similar trend.

Among the important rock-forming minerals, there are comparatively few O diffusion data for garnets. Such data are required, however, for the interpretation of O isotope heterogeneities (Jamtveit and Hervig, 1994; Valley et al.,

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1994) and models to calibrate geothermometers (e.g., Eiler et al., 1993). This paucity of garnet diffusion data in part reflects the difficulties associated with experiments. Preliminary data for O diffusivity in grossular at 850 and 1050 °C were reported by Freer and Dennis (1982). The results were ambiguous because of the marked dog-leg shape of the recast inverse error function profiles, possibly reflecting both volume and grain-boundary diffusion. Coghlan (1990) also presented limited data for O diffusion in spessartine-almandine under hydrothermal conditions.

To complement the experimental studies, we used atomistic computer simulation techniques based on the Born model of solids to investigate defects and O diffusion in grossular garnet. In addition, we investigated the probability of enhanced diffusion in garnet under hydrothermal conditions by simulating OH diffusion in the lattice. Over the past two decades, studies using atomistic methods have demonstrated that reliable values can be calculated for defect formation and migration energies (Catlow, 1994), and indeed these methods are now routinely predictive in this respect.

METHODOLOGY

Computer simulation techniques have been widely and successfully used to study both the perfect and defective lattice properties of a range of geologically important materials (Catlow and Price, 1990), such as feldspars (Purton and Catlow, 1990; Patel et al., 1991), perovskite (Wright and Price, 1993), the Mg_2SiO_4 polymorphs (Price et al., 1987), magnetite (Lewis et al., 1985), and quartz (Leslie, 1989). These methods employ an atomistic approach, by which an interatomic potential function is defined to describe the total energy of the system in terms of atomic positions. The lattice energy includes contributions from ionic, covalent, and van der Waals type bonding. For ionic or semi-ionic solids, the dominant component of the cohesive energy, U_T, is the electrostatic or Coulombic term, U_C. However, because ions are not simple point charges, it is necessary to take into account the short-range repulsive interactions, U_{ij}, produced by the overlap of nearest-neighbor electron clouds. This short-range component is well modeled by the Buckingham potential:

$$U_{ij} = \sum_{ij} A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - C_{ij} r_{ij}^{-6} \qquad (1)$$

where A, ρ, and C are parameters obtained by fitting either to theoretical energy surfaces or empirically to crystalline properties. The O-O short-range parameters used in this study were derived theoretically using Hartree-Fock methods (Catlow, 1977), whereas those for Ca-O, Al-O (Lewis and Catlow, 1985), and Si-O (Sanders et al., 1984) were fitted to experimental data. When modeling defects, it is essential to describe the local polarization effects of the defect, and so in our models O polarizibility is described by means of a simple harmonic shell model. The potential parameters used in this study are listed in Table 1. For the O-H interaction, we used a Morse potential, which is especially suited to more molecular species; the overall charge of the OH is set to −1. The interactions between cations and hydroxyl O were modeled by a modified Buckingham potential, calculated using the methodology of Schröder et al. (1992). All the above parameters were successfully used in a previous study of defects in grossular (Wright et al., 1994), which found that the calculated bulk properties and the structure of the hydrogarnet defect agree well with experimental data.

TABLE 1. Potential parameters used for grossular and hydrogrossular

Interaction	Buckingham Potential A (eV)	 ρ (Å)	 C (eV·Å^6)
Si^{4+}-O^{2-}	1283.907	0.32052	10.66158
Al^{3+}-O^{2-}	1460.3	0.29912	
Ca^{2+}-O^{2-}	1090.40	0.34370	
O^{2-}-O^{2-}	22764.0	0.149	27.88
Si^{4+}-$O^{1.4-}$	983.556	0.32052	10.66158
Al^{3+}-$O^{1.4-}$	1142.6775	0.29912	
Ca^{2+}-$O^{1.4-}$	777.27	0.34370	
O^{2-}-$O^{1.4-}$	22764.0	0.149	27.88
$H^{0.4+}$-$O^{1.4-}$	311.97	0.25	
$H^{0.4+}$-O^{2-}	311.97	0.25	
$O^{1.4-}$-$O^{1.4-}$	22764.0	0.149	27.88

Interaction	Morse potential D_e (eV)	 a (Å^{-1})	 r_0 (Å)
$H^{0.4+}$-$O^{1.4-}$	7.0525	2.1986	0.9485

Note: all parameters involving $O^{1.4-}$ refer to hydroxyl O. Harmonic force constant for O^{2-} core shell is 74.92 eV/Å^2. Three-body force constant for O-Si-O is 2.097 eV/rad.

We used the computer code CASCADE (Leslie, 1981), supported by the British Science and Engineering Research Council, to evaluate the energy of the defect configurations of interest. In ionic materials, defects are charged species that cause long-range disruption in the lattice. These long-range perturbations are effectively modeled by the Mott-Littleton approach (Mott and Littleton, 1938), by which the crystal is divided into two concentric spherical regions. In region 1, which contains the defect at its center, an explicit atomistic simulation is performed to adjust the coordinates of all ions within the region until they are at positions where no net forces act on them, i.e., they are relaxed around the defect. In region 2, the effects of the defect are relatively weak, and the relaxation is calculated essentially as the polarization response to the effective charge of the defect. In practice an interface region between regions 1 and 2, referred to as 2A, is normally used. The resulting defect energy is a measure of the perturbation by the defect of the static lattice energy of the crystal. In this approach, no account is taken of zero-point energy or, more important, entropic effects. For further details on this method see Catlow (1986). In the present study, we used a maximum region 1 size of 8.5 Å, containing around 240 ions, to evaluate the defect configurations of interest.

TABLE 2. Defect formation energies (eV) in grossular

	ΔE	ΔE/defect
Unbound pseudo-Schottky		
CaO	7.96	3.98
Al_2O_3	24.52	4.90
SiO_2	19.52	6.51
$Ca_3Al_2Si_3O_{12}$	99.66	4.98
Unbound Frenkel defects		
O	9.64	4.82
Ca	11.60	5.80
Al	13.95	11.60
Si	21.80	10.90
Bound defects		
CaO pseudo-Schottky	5.75	2.87
O Frenkel	7.86	3.93

RESULTS

Defects in grossular

Above 0 K, all solids contain an equilibrium number of point defects (vacancies and interstitials) in the lattice. Such defects may be formed intrinsically or extrinsically. In the intrinsic case, vacancies are charge balanced by the formation of equally charged interstitials or by equal and oppositely charged vacancies. This first case is termed Frenkel disorder, and the formation energy of Frenkel defects is simply the sum of the individual vacancy and interstitial energies:

$$E_{Fr} = V_n + n_i \tag{2}$$

where V denotes a vacancy of species n, and the subscript i indicates an interstitial of species n. The generation of charge-balanced vacancy defects in stoichiometric proportions is known as Schottky disorder. However, in complex materials such as garnet we may define nonstoichiometric vacancy defects. For example, a stoichiometric defect in grossular would consist of three Ca vacancies, two Al vacancies, three Si vacancies, and 12 O vacancies (one formula unit of grossular). Forming one Ca vacancy and one O vacancy maintains charge neutrality but results in a local change in composition. The ions removed are assumed to form another phase on the surface, thus maintaining bulk stoichiometry of the system. The formation energy of these pseudo-Schottky defects (E_{pS}) is defined as the energy of the composite vacancies plus the lattice energy (U) of the phase removed to the crystal surface:

$$E_{pS} = \sum_{j=1}^{N} V_j + U. \tag{3}$$

Extrinsic defects are commonly formed at low temperatures in response to some charge imbalance introduced by substitution reactions. For example, substitution of two Fe^{2+} ions for two Al^{3+} ions in grossular leads to an excess charge of 2−, which may be balanced by the formation of an O vacancy.

The intrinsic pseudo-Schottky and Frenkel defect formation energies are given in Table 2 and were calculated by assuming that individual vacancies and interstitials are isolated and noninteracting. When comparing defect formation energies, it is more useful to consider the energy per point defect rather than the total balanced formation energy. Table 2 shows that the most favorable defect, with the lowest energy per point defect (3.98 eV), is predicted to be the CaO vacancy pair, where the formation of a Ca vacancy is charge balanced by an accompanying O vacancy, and a unit of CaO is formed at the surface. The lowest energy interstitial defect is the O Frenkel (4.82 eV/defect). We also calculated the binding energy (ΔE_B) associated with these two defects. For the pseudo-Schottky, V_{CaO}, $\Delta E_B = -2.21$ eV, and for the Frenkel, $\Delta E_B = -1.78$ eV. Thus, the energy for both defects is less when they are bound. The most favorable defect then is the bound CaO, with a formation energy of 2.87 eV (277 kJ/mol).

O diffusion in grossular

Garnet minerals are densely packed; this and the calculated defect formation energies (Table 2) suggest that O diffusion is predominately governed by a vacancy mechanism by which ions migrate by moving to successive vacant sites. To simulate O diffusion in grossular by means of this mechanism, two adjacent O vacancies were created in the lattice to represent the initial and final sites of the migrating ion; an O ion was then placed at fixed points between the two sites. At each point the defect energy was calculated, and in this way it was possible to build a potential energy surface, enabling the saddle point for the jump to be calculated.

The garnet structure consists of a network of interconnected octahedra and tetrahedra, and thus several different O jumps are possible, each having a different activation energy. For O to migrate through the lattice, jumps along both tetrahedral and octahedral edges are required, with the overall activation energy for atomic migration determined by the higher energy jump. The octahedral jump represents the longest jump on the shortest migration route through the grossular lattice and therefore can be compared with experimental values of activation energy. The O migration pathway along an octahedral edge is shown in Figure 1, with the saddle point located approximately halfway between the two O sites. The value of the migration energy (ΔE_M) is found by subtracting the energy of the initial state (i.e., with one O vacancy present) from that of the activated state where the migrating ion is at the saddle point. The value of ΔE_M was then found to be 1.1 eV or 106 kJ/mol. This calculated value should correspond to the extrinsic diffusion Arrhenius energy, where all vacant sites are formed by extrinsic processes. At high temperatures, the majority of defects may be formed thermally rather than in response to impurities, provided the formation energies are sufficiently low. In this case, to determine the intrinsic diffusion Arrhenius energy, it is necessary to add a fraction of the defect formation energy to the migration energy (Lasaga, 1981). If we assume that the O vacancy is part of a bound CaO defect (Table 2), then the intrinsic diffusion activation energy (ΔE_D) is given by

$$\Delta E_D + \Delta E_M + \left(\frac{E_{def}}{2}\right) \qquad (4)$$

where E_{def} is the defect formation energy. Using the CaO value in Table 2 (2.87 eV) and the value of ΔE_M (1.1 eV) yields a value of 3.97 eV (383 kJ/mol) for ΔE_D. The predicted activation energies for O diffusion in grossular are then 106 and 383 kJ/mol for extrinsic and intrinsic diffusion, respectively.

OH diffusion in grossular

In view of the geological importance of O diffusion under hydrothermal conditions, we studied the effect of H_2O on O diffusion in grossular. H_2O is certainly present in natural grossular in the form of the hydrogarnet defect configuration, which was successfully modeled in an earlier study of defects in grossular by Wright et al. (1994). In the present work, the diffusion activation energy for OH was determined by moving the OH unit along the same path as that taken by the O. The O in the OH was fixed at a series of points along the octahedral edge as before, whereas the H was allowed to find its own minimum energy position. The route taken by the OH was very similar to that taken by O alone and had the same migration activation energy of 1.1 eV (106 kJ/mol). However, when the OH pair was migrating from a hydrogarnet defect to an adjacent SiO_4 tetrahedron along an octahedral edge, the activation energy was found to decrease to 0.7 eV (67.5 kJ/mol). This reduction is probably due to a local distortion of the lattice, caused by the presence of the hydrogarnet defect, providing an easier migration route.

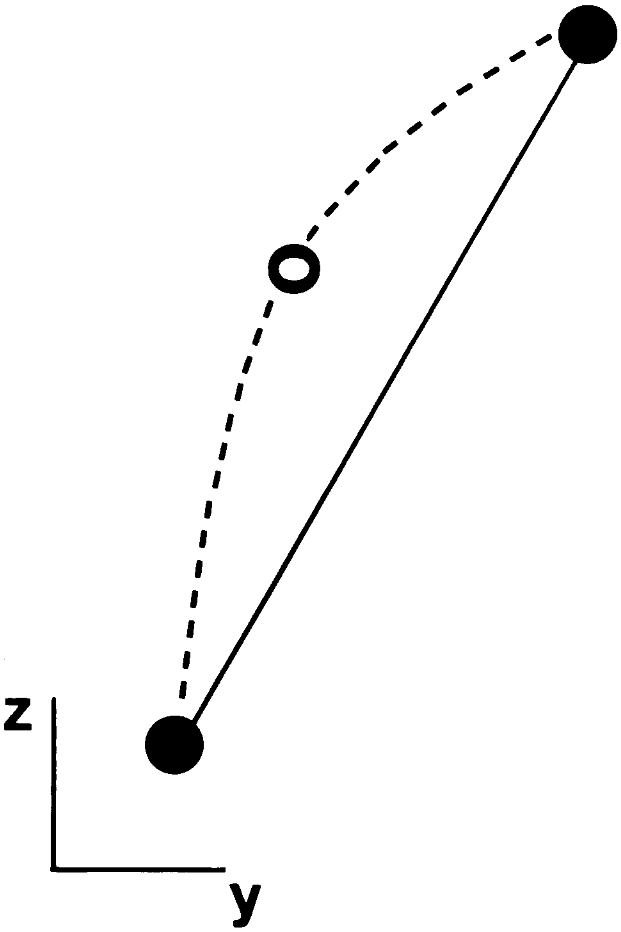

Fig. 1. The diffusion pathway for O along an octahedral edge. The O does not move in a straight line but is displaced by interactions with adjacent ions. The saddle point position is shown by the open circle.

DISCUSSION

The results of our simulations indicate that intrinsic defect formation energies (both Schottky and Frenkel) are high, and therefore the concentration of thermally generated defects is expected to be low. Thus, in the intrinsic regime O diffusion is likely to occur by a vacancy-controlled mechanism. Intrinsic diffusion of O is likely to be restricted to high temperatures but would be energetically more favorable than an interstitial mechanism.

Although the methodology used in this study does not allow the calculation of absolute diffusion rates, it can give quantitative information on defect formation and migration energies, which can be compared with measured values. Experimental data on O diffusion rates in any kind of garnet are limited. The study of Freer and Dennis (1982) was carried out under hydrous conditions on rather impure grossular ($Ca_{2.92}Fe_{0.10}Al_{1.96}Si_3O_{12}$) at temperatures of 850 and 1050 °C and pressures of 2 and 8 kbar, respectively. Ignoring the effects of differences in experimental conditions, this yields, to a first approximation, an activation energy of 102 kJ/mol. Since the samples used for experiments had a high degree of impurities, we may assume that the experiments were performed at conditions well within the extrinsic regime. The charge imbalance brought about by, say, substitution of Fe^{2+} for Al^{3+} or Fe^{3+} for Si^{4+} would lead to the generation of O vacancies. If this is the case, then our predicted activation energy of 106 kJ/mol is in excellent agreement with the experimentally obtained value of 102 kJ/mol.

Other experimental and theoretical studies have provided information about O transport in other garnet structure compounds. The activation energies from these investigations are summarized in Table 3. Paldino et al. (1964) performed bulk-exchange experiments with powdered yttrium iron garnet (YIG) under dry gas conditions and obtained an intrinsic activation energy of 273 (±25%) kJ/mol. More recently, Coghlan (1990) (data cited in Brady, 1995) examined O diffusion in single crystals of spessartine-almandine composition under hydrothermal conditions and found an activation energy of 301 kJ/mol. Schuh et al. (1991) simulated defects in yttrium alumi-

TABLE 3. Summary of O diffusion data in garnets

Garnet	*Q* (kJ/mol)	D_0 (m²/s)	Details	Reference
Grs	102	6.1×10^{-16}	Exp., S, wet, 850 °C, 2 kbar, 1050 °C, 8 kbar	Freer and Dennis (1982)
YIG	273	4.0×10^{-5}	Exp., S, P, dry, 1100–1473 °C	Paldino et al. (1964)
Sps-Alm	301	6.0×10^{-9}	Exp., S, wet, 800–1000 °C	Brady (1995)
YAG	145		Calc. extrinsic	Schuh et al. (1991)
Grs	287		Calc.	Fortier and Giletti (1989)
Grs	106		Calc. extrinsic	this study
Grs	383		Calc. intrinsic	this study

Note: S = single crystal, P = powder sample, Exp. = experimental, Calc. = calculated, wet = hydrous experiment, and dry = anhydrous experiment.

num garnet (YAG) using the same techniques as those employed in the present study and calculated an activation energy for O migration along an octahedral edge to be 146 kJ/mol. Finally, the empirical model of Fortier and Giletti (1989) yields an activation energy of 287 kJ/mol for O diffusion in grossular under hydrothermal conditions.

The data for O diffusion in garnet structure compounds appear to divide into two main groups: (1) the experimental data of Freer and Dennis (1982), the modeling studies of Schuh et al. (1991), and the extrinsic results of this study; (2) the experimental data of Paldino et al. (1964) and Coghlan (1990), the results of the empirical study of Fortier and Giletti (1989), and the intrinsic values obtained in this work. Selected data are shown together on an Arrhenius plot in Figure 2. Clearly, it is tempting to associate the activation energies in (1) with the extrinsic transport of O in the garnet structure and those in (2) with genuine intrinsic diffusion. If we focus on the latter group of data (Fig. 2) we see large differences in the trends shown. Although there is good agreement between the results of Coghlan (1990) and the predictions of Fortier and Giletti (1989), the experimental data of Paldino et al. (1964) are typically five orders of magnitude faster. Caution must be exercised when comparing these data because the latter were obtained from bulk-exchange experiments with powders under dry conditions and the former from hydrothermal exchange experiments with single crystals. These differences in diffusion rate and activation energy are more likely the result of enhanced diffusion along grain boundaries in the powdered YIG samples than the presence of H_2O in the spessartine-almandine experiments.

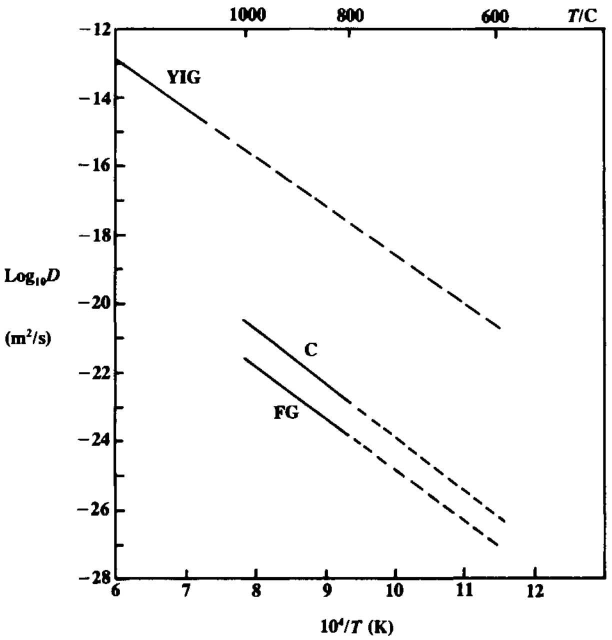

Fig. 2. Arrhenius plot of diffusion data. Data from Paldino et al., 1964 (YIG); Coghlan, 1990 (C); and Fortier and Giletti, 1989 (FG).

In the case of quartz and feldspars, O diffusion is enhanced when H_2O is present, possibly because of the presence of protons that somehow mediate in the jump process to lower the activation barrier (Graham and Elphick, 1991). However, in the case of grossular we find no evidence for this. The results of the calculations indicate that the activation energy is the same for both OH and O diffusion. The lower activation energy found for OH diffusion in the presence of a hydrogarnet defect is probably due to local distortion of the lattice and charge distribution around the defect complex. This would suggest that when grossular has a composition close to the hydrogrossular end-member, the activation energy is lower. To clarify this, a series of experiments on garnet along the grossular-hydrogrossular series is needed.

There is now a growing body of data obtained from both ion microprobe and laser probe analyses of natural garnet (e.g., Chamberlain and Conrad, 1991; Kohn et al., 1993; Jamtveit and Hervig, 1994; Valley et al., 1994) to show the persistence of O isotope profiles through geological time. Chamberlain and Conrad (1991) note that a characteristic length scale for O diffusion in garnet for 400 m.y. at 500 °C (with a diffusivity of 2.63×10^{-29} m²/s taken from the data of Coghlan) would be 0.6 μm. Such scalar diffusion rates coupled with activation energies $\geq$300 kJ/mol would preclude any significant modification of isotope ratios and profiles at metamorphic temperatures. Indeed geothermometers based on the fractionation of ^{18}O between garnet and quartz or feldspar have been used for some time (e.g., Dienes, 1977) and frequently yield temperatures in excess of 700 °C, which is consistent with the metamorphic conditions expected for the rocks concerned.

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