Jibamitra Ganguly · Weiji Cheng · Sumit Chakraborty

Cation diffusion in aluminosilicate garnets: experimental determination in pyrope-almandine diffusion couples

Abstract Diffusion couples made from homogeneous gem quality natural pyrope and almandine garnets were annealed within graphite capsules under anhydrous conditions at 22–40 kbar, 1057–1400 °C in a piston-cylinder apparatus. The concentration profiles that developed in each couple were modeled to retrieve the self diffusion coefficients [D(I)] of the divalent cations Fe, Mg, Mn and Ca. Because of their usually low concentrations and lack of sufficient compositional change across the interface of the diffusion couples, only a few reliable data can be obtained for D(Ca) and D(Mn) from these experiments. However, nine sets of D(Fe) and D(Mg) data were retrieved in the above *P-T* range, and cast in the form of Arrhenian relation, $D = D_0 \exp\{-[Q(1\ \text{bar}) + P\Delta V^+]/RT\}$. The values of the activation energy (Q) and activation volume (ΔV^+) depend on whether f_{O_2} is constrained by graphite in the system C-O or held constant. For the first case, we have for Fe: $Q(1\ \text{bar}) = 65{,}532 \pm 10{,}111\ \text{cal/mol}$, $D_0 = 3.50 (\pm 2.30) \times 10^{-5}\ \text{cm}^2/\text{s}$, $\Delta V^+ = 5.6(\pm 2.9)\ \text{cm}^3/\text{mol}$, and for Mg: $Q(1\ \text{bar}) = 60{,}760 \pm 8{,}257\ \text{cal/mol}$, $D_0 = 4.66 (\pm 2.48) \times 10^{-5}\ \text{cm}^2/\text{s}$, $\Delta V^+ = 5.3(\pm 3.0)\ \text{cm}^3/\text{mol}$. Here the ΔV^+ values have been taken from Chakraborty and Ganguly (1992). For the condition of constant f_{O_2}, the Q values are ~9 kcal lower and ΔV^+ values are ~4.9 cm³/mol larger than the above values. Lower temperature extrapolation of the Arrhenian relation for D(Mg) is in good agreement with the Mg tracer diffusion data (D^*_{Mg}) of Chakraborty and Rubie (1996) and Cygan and Lasaga (1985) at 1 bar, 750–900 °C, when all data are normalized to the same pressure and to f_{O_2} defined by graphite in the system C-O. The D^*_{Mg} data of Sch-

wandt et al. (1995), on the other hand, are lower by more than an order of magnitude than the low temperature extrapolation of the present data, when all data are normalized to the same pressure and to f_{O_2} defined by the graphite buffer. Comparison of the D(Fe), D(Mg) and D(Mn) data in the pyrope-almandine diffusion couple with those in the spessartine-almandine diffusion couple of Chakraborty and Ganguly (1992) shows that the self diffusion of Fe and Mn are significantly enhanced with the increase in Mn/Mg ratio; the enhancement effect on D(Mg) is, however, relatively small. Proper application of the self diffusion data to calculate interdiffusion coefficient or **D** matrix elements for the purpose of modeling of diffusion processes in natural garnets must take into account these compositional effects on D(I) along with the effects of thermodynamic nonideality, f_{O_2}, and pressure.

Introduction

Garnets in natural rocks show a variety of compositional zoning of both divalent and trivalent cations, which have been reviewed extensively by Chakraborty and Ganguly (1991). These zonings preserve memory of the thermal and growth histories of the minerals which could be retrieved if the appropriate cation diffusion data were available (e.g. Smith and Barron 1991; Lindstrom et al. 1991; Florence and Spear 1991; Chakraborty and Ganguly 1991, 1992: Spear and Parrish 1996; Ganguly et al. 1995, 1996; Lasaga and Jianxin 1995; Okudaira 1996). Because of the large range of composition encompassed by common natural garnets, experimental measurement of cation diffusion needs to be carried out in several major compositional groups. Of these, the most important are: (1) the relatively Mn-rich metapelitic garnets which show growth zoning of the divalent cations in low grade and diffusion-relaxation of the zoning at higher grade; (2) Mn-poor ferromagnesian garnets which are often found to develop diffusion

J. Ganguly (✉) · W. Cheng
Department of Geosciences, University of Arizona,
Tucson, AZ 85721, USA

S. Chakraborty
Mineralogisch-Petrographisches Institut, Zulpicherstrasse 49b,
D-50674 Köln, Germany

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zoning during cooling after they have been homogenized at granulite facies conditions, or during uplift from the Earth's mantle.

Chakraborty and Ganguly (1992) presented the self diffusion coefficients[1] [D(I)] of Fe^{2+}, Mg and Mn, which are suitable for modeling the relaxation of growth zoning of relatively Mn-rich garnets. The diffusion data were obtained by numerical simulation of experimentally induced multicomponent diffusion profiles at 14–43 kbar, 1100–1480 °C in diffusion couples made of natural *spessartine* and *almandine* crystals. These results also incorporated the data from Loomis et al. (1985), who used similar diffusion couples and the same experimental and modeling procedures. Cygan and Lasaga (1985), Chakraborty and Rubie (1996) and Schwandt et al. (1995) determined the tracer diffusion coefficient of Mg (D^*_{Mg}) in ferromagnesian garnets using tracer isotopes of ^{25}Mg or ^{26}Mg in chemically homogeneous ferromagnesian garnets. Although there is a formal distinction between self and tracer diffusion coefficients (e.g., Hermeling and Schmalzreid 1984), the ratio of D(I) to D^*_I does not usually depart very significantly from unity, so that we are unlikely to introduce any significant error in our analysis by equating these two diffusion coefficients.

Loomis et al. (1985) reported the result of a diffusion couple experiment with natural crystals of *pyrope* and *almandine*, enclosed in a graphite capsule, at 40 kbar, 1440 °C. They found that D(Mg) retrieved from the multicomponent diffusion profiles is similar to that retrieved from spessartine-almandine diffusion couples. However, D(Fe) in the pyrope-almandine diffusion couple was around an order of magnitude slower than that in a spessartine-almandine diffusion couple. This result suggests that the D(Fe) values derived from experiments with spessartine-almandine diffusion couples may not be quite appropriate for the modeling of diffusion zoning in Mn-poor ferromagnesian garnets.

The primary objective of this work has been to determine the self diffusion coefficients of Fe and Mg in Mn-poor ferromagnesian garnets using diffusion couples made from natural pyrope and almandine garnet crystals. The results would provide the much needed data required to model diffusion zoning in primarily ferromagnesian garnets, such as those found in granulite facies rocks and in the mantle samples, and also help evaluate compositional dependence of D(Fe) and D(Mg).

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[1] In our earlier works (Loomis et al. 1985; Chakraborty and Ganguly 1991, 1992), we referred to diffusion coefficients retrieved from modeling multicomponent diffusion profiles as tracer diffusion coefficients, but it is more appropriate to refer to them as self diffusion coefficients, as done in this paper. The self [D(I)] and tracer (D^*_I) diffusion coefficients are the diffusion coefficients of an element and of an isotope of the element, respectively, in response to their own concentration gradients. The multicomponent diffusion theory used in our earlier works permits retrieval of the self diffusion coefficients

Diffusion couple experiments

All experiments were carried out in a piston-cylinder apparatus using "talc-glass" pressure cells with anhydrous parts within a graphite internal resistance furnace. The diffusion couples were made from natural crystals of pyrope and almandine and were encased within tightly fitting graphite capsules. Special care was taken to dry the parts of the pressure cell inside the graphite furnace so that the f_{O_2} was defined very closely by graphite-O_2 equilibrium. The temperature was measured by W-W3Re/W-W25Re thermocouples. The experiments were run for as long as possible in order to induce sufficiently long profiles, but without unduly increasing the chance of failures (e.g., cracking of the carbide cores and pistons) at the chosen P-T conditions requiring expensive replacements, so that the convolution effects in the measurement of the diffusion profiles by microprobe spot analysis (Ganguly et al. 1988) were minimal. To decide experimental conditions, a set of synthetic profiles were produced as function of P, T and t using the full multicomponent simulation procedure and guessed values of D^*_i, based on our previous works (Loomis et al. 1985; Chakraborty and Ganguly 1992). The P, T, t conditions of the experiments were decided on the basis of the expected profile lengths and these estimates were continually updated with the acquisition of diffusion data as the work progressed.

The interested reader is referred to Chakraborty and Ganguly (1992) for the details of sample preparation, design of pressure cell, experimental procedure, method of recovery of samples, and friction calibration of the talc-glass pressure cell. The method of polishing the mating faces of the garnet-garnet couples has evolved during the course of our experimental investigation. It was found that a "mirror quality" finish can be obtained on the mating faces by first mechanically polishing them down to a 0.125 micron grit size of diamond, followed by around two minutes of chemical-mechanical polishing (at 300–350 rpm) using silica suspension on OP-chem cloth from Struers. As discussed in Chakraborty and Rubie (1996), this procedure greatly reduces the surface damage that develops during mechanical polishing.

We were unable to find large enough supply of gem quality crystals suitable for diffusion studies from a single source of either almandine or pyrope so that the compositional make-up of the diffusion couples was variable. The compositions of the garnet crystals used in the diffusion couple experiments are summarized in the table. These analyses are representative, but individual crystals in a given stock differed somewhat in composition. Each crystal was analyzed separately, and found to be essentially homogeneous, as determined by a large number of spot analyses in the microprobe. The total iron was treated as Fe^{2+}.

Measurement and modeling of diffusion profiles

A diffusion couple recovered from a high P-T experiment was sectioned after it was impregnated with low viscosity epoxy, polished, and the diffusion profiles of all divalent cations present in the natural garnet samples were measured by step scanning in an electron microprobe (Cameca SX-50) along a line normal to the interface. Each section was carefully oriented so that the surface exposed to electron microprobe analyses was normal to the interface. Several sets of diffusion profiles (typically 8–10 sets) in several different sections of each diffusion couple were measured in order to find the best set of profiles that should be modeled to retrieve the diffusion coefficients.

Each diffusion-couple was examined in high resolution (20 μm to ∼4 cm) in backscattered imaging in order to find suitable unfractured sections for the measure-

173

Table 1. Summary of annealing conditions and self diffusion data of divalent cations in pyrope-almandine diffusion couples. The diffusion coefficients are corrected for the convolution effect of the microprobe beam. (*Alm(1)* $Alm_{69}Pyr_{28}Gr_2Spess_1$, *Alm(2)* $Alm_{80-}Pyr_{19}Gr_1$, *Alm(3)* $Alm_{73}Pyr_5Gr_1Spess_{21}$, *Alm(4)* Alm_{70-} $Pyr_{21}Gr_{4.5}Spess_{4.5}$, *Alm(5)* $Alm_{77}Pyr_{12}Gr_{10}Spess_1$, *Pyr(1)* $Alm_{46.7}Pyr_{47.6}Gr_{12}Spess_1$, *Pyr(2)* $Alm_{16}Pyr_{75.7}Gr_8Spess_{0.3}$, *Pyr(3)* $Alm_{37}Pyr_{51}Gr_{11}Spess_1$, *Pyr(4)* $Alm_{26}Pyr_{60}Gr_{12}Spess_2$, *Pyr(5)* $Alm_{20}Pyr_{80}Gr_1$)

| Run no.	Diffusion couple	P (kbar)	T (°C)	Time (h)	$D(10^{15})$, cm²/s			
					Mg	Fe	Ca	Mn
R17	Alm(1)-Pyr(1)	38	1432	94.8	396.5	26.5	15.0	
DPA6	Alm(3)-Pyr(3)	38	1375	73.5	75.5	15.5		
R11	Alm(1)-Pyr(1)	40	1344	72.8	65.4	5.4		
DPA10	Alm(4)-Pyr(3)	38	1280	218	6.5	3.5		
DPA5	Alm(3)-Pyr(3)	30	1250	192	28.3	3.3		4.3
GD13	Alm(5)-Pyr(5)	20	1200	167.8	28.0	3.5	1.0	
DPA1	Alm(3)-Pyr(4)	25	1150	260	8.7	4.7	1.7	
DPA7	Alm(4)-Pyr(3)	26	1100	576	3.4	0.4		
DPA4	Alm(3)-Pyr(3)	28	1057	438	1.2	0.04		0.44

ment of diffusion profiles. A diffusion front, which appeared as a straight line in lower magnification often turned out to be wavy at higher resolution. Special care was, thus, taken to select linear domains of the interface to measure the diffusion profiles so that the measured compositional variation was truly due to diffusion *normal* to the interface. All diffusion profiles were analyzed by beam scanning, that is, by electronically stepping the microprobe beam at 1/3 or 1/4 micron steps (see Chakraborty and Ganguly 1992, for further details). The diffusion profiles analyzed by this technique were significantly shorter than the length (50 μm at 1000 × magnification) at which distortion due to deviation of the beam from vertical becomes significant. As discussed by Chakraborty and Ganguly (1992), the beam scanning procedure is preferable to moving the sample stage mechanically as it permits smaller step size, and hence better definition of the profile shapes.

The self diffusion coefficients of the major divalent cations present in the natural garnet crystals, which formed an experimental diffusion couple, were retrieved by numerical simulation of the experimental multicomponent profiles. It was assumed that the self diffusion coefficients were insensitive to compositional change within the range encompassed by a diffusion couple. The

formal concepts and numerical procedure involved in these simulations were discussed by Loomis et al. (1985) and Chakraborty and Ganguly (1991, 1992), and are, therefore, not discussed here for the sake of brevity. As discussed in these works, the uncertainty (1σ) in the retrieved value of a diffusion coefficient from modeling a specific set of multicomponent profiles is within 10% of its quoted value.

In some cases, the diffusion profiles showed a rather long segment of gentle slope before achieving a plateau value (Fig. 1a). The reason for this phenomenon is not well understood. However, it was also possible in some of these samples to find segments across the same interface where the diffusion profiles did not show this

Fig. 1a, b Measured (*irregular lines*) and simulated (*smooth lines*) diffusion profiles across the interface of a pyrope-almandine diffusion couple. **a** Fe and Mg concentration profiles show an extended domain of gentle concentration gradients (*shoulders*) in the Fe-rich side of the couple. **b** Another set of diffusion profiles along a different traverse across the same interface. Note the absence of shoulders on the Fe-rich side. The *hump* in the Mg-rich side coincides with a fracture. The profiles in both figures are fitted by the same set of diffusion coefficients (*Fe* 1×10^{-15}, *Mg* 4×10^{-15}, *Ca* 4×10^{-16}, *Mn* 2×10^{-15} cm²/s). The diffusion couple was annealed for 576 h at 26 kbar, 1100 °C in a graphite capsule
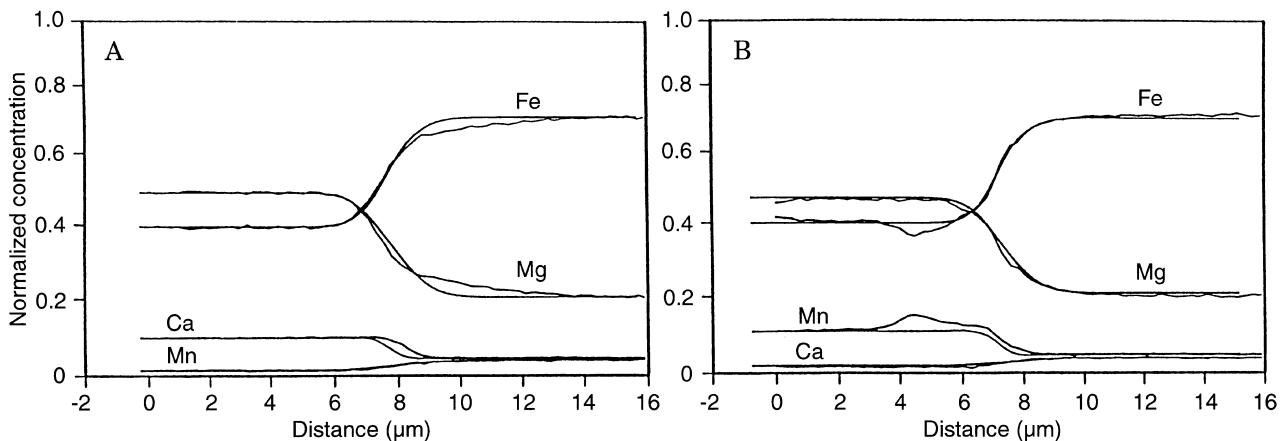
feature (Fig. 1b). The latter profiles were used to retrieve the diffusion coefficients. The segment of gentle slope could imply localized concentrations of dislocations, which might have resulted from the coherency or misfit strain near the interface (Ganguly et al. 1996). Interestingly, however, these segments were always on the Fe-rich side of the diffusion couples, and we did not observe similar features in earlier experiments (Loomis et al. 1985; Chakraborty and Ganguly 1991) using spessartine-almandine diffusion couples.

Deconvolution of diffusion coefficients

The spatial averaging effect in the microprobe spot analysis results in a convolution of the true concentration profile. Assuming that the excitation intensity of the sample volume had a Gaussian distribution with radial symmetry about the beam axis, Ganguly et al. (1988; Eq. 20) showed that the diffusion coefficient (D_C) retrieved from the measured (or convolved) concentration profile is related to the true diffusion coefficient, D, according to

$$D = D_C - \frac{\varepsilon^2}{2t} \tag{1}$$

where t is the time, and ε is the error standard deviation of the intensity distribution of X-rays resulting from the spatial averaging effect of the microprobe beam. They also showed that the convolution effect decreases rapidly with increasing length of the concentration profile, and becomes insignificant for profile length ≥ 10 μm measured in a modern electron microprobe using a step size ≤ 0.5 μm.

From analysis of the convolution of a "stepped" profile across the interface of a specially prepared garnet-aluminum couple (which was not affected by any significant diffusion), measured in the same microprobe as used in this work and using the same step size (1/3 μm), Ganguly et al. (1996) estimated $\varepsilon = 0.54$ μm. Since, however, the excitation of the sample volume near the garnet-aluminum interface is not exactly the same as that near the interface of a garnet-garnet diffusion couple, we seek a new estimate of ε for the latter case as follows.

Ganguly et al. (1996) measured the diffusion profile across the interface of a natural garnet-garnet diffusion couple by spot analysis in both electron microprobe and analytical TEM (ATEM). The convolution effect in ATEM was vanishingly small because of the extremely small size of the excited analytical volume, which was not only due to the very small beam size and rastering area, but also due to the thinness of the sample to electron transparency. Thus, the Dt value retrieved by modeling the profiles measured by ATEM, which was 7.5×10^{-12} cm^2, can be treated as the true Dt value. In comparison, the convolved $(Dt)_C$ value retrieved from modeling the concentration profiles measured in the microprobe was 1.16×10^{-19} cm^2. Thus, from Eq. (2) we obtain $\varepsilon = 0.48$ μm for the convolution of the diffusion profiles measured by our microprobe under the operating condition of 15 kV accelerating voltage, 50 nA beam current and ~ 1 μm nominal beam size. Ganguly et al. (1988), however, showed that the value of ε was not significantly affected by the variation of beam current between 10 and 50 nA, and of accelerating voltage between 11 and 20 kV.

Reduction of polythermal diffusion data to isothermal condition

In a talc-glass pressure cell, the power required to maintain a constant thermocouple emf in a run of several days' duration always varies with time. The typical nature of this variation consists of an initial period of power drop followed by progressive increase of power with intermittent fluctuations. In the earlier phase of our work, we interpreted this progressive power increase to be the result of decalibration of thermocouple by chemical reaction with the surrounding material (alumina, BN, graphite) inside the pressure cells. Consequently, during the course of an experiment, we switched from emf to power control mode whenever the power continued to drift in the same direction for a long time. This procedure was followed for one of the experiments reported here (R17), which was conducted by Elphick et al. (1985). However, the interpretation of thermocouple decalibration was found to be erroneous since no significant power change was observed when the outer bushing of talc-glass was replaced by CsCl (Elphick et al. 1985). Thus, the temperature during the experiment R17 varied considerably. In addition, the temperature of the experiment DPA7 varied between 1040 and 1100 °C due to a technical problem with the temperature controller.

The polythermal diffusion data in each of the above experiments were converted to isothermal diffusion data as follows (see, for example, Shewmon 1963). Since D is a function of temperature through the Arrhenian relation [$D = D_0 \exp(-Q/RT)$, where Q is the activation energy], one can express D as a function of time (t) from the recorded T versus t relation during an experiment. It is then possible to find an isothermal D, denoted below as D_T, by satisfying the relation

$$\int_0^{t'} D(t)\,dt = (D_T)t' \tag{2}$$

where t' is the total time or duration of an experiment. The temperature corresponding to D_T will henceforth be referred as the characteristic temperature, T_{Ch}.

For each polythermal experiment, we guessed a value of T_{Ch} within the range of temperature of the experiment. These data were then treated along with the isothermal data to retrieve the D_0 and Q values (by regressing $\ln D$ vs $1/T$). Using these values, D_T was evaluated from Eq. (1), and the corresponding T_{Ch} was calculated from the Arrhenian relation. The new D_T and T_{Ch} data for each polythermal experiment were again treated along with the isothermal diffusion data to obtain new values of the Arrhenian parameters, which

were then used to retrieve a second set of D_T values from Eq. (1), and the corresponding T_{Ch} values from the new Arrhenian relation. The process was repeated until the value of the retrieved T_{Ch} converged to a constant value. The D(Mg) and D(Fe) data were treated separately, and for each polythermal experiment, the two sets of diffusion data yielded the same T_{Ch}.

Pressure dependence of diffusion coefficients

Since a diffusion coefficient in an iron bearing system is a function of f_{O_2}, the variation of diffusivity as a function of pressure along an oxygen fugacity buffer has two components, namely: (1) the effect of pressure at constant f_{O_2}; (2) the effect of variation of f_{O_2} defined by the oxygen fugacity buffer as a function of pressure. Thus, the activation volumes reported by Chakraborty and Ganguly (1992) to account for the pressure dependence of the self diffusion coefficients of Fe, Mg and Mn in garnet at f_{O_2} defined by graphite-O_2 buffer represent "effective" activation volumes which can be used to account for the pressure effect on D as long as f_{O_2} is defined by the same buffer.

The true activation volume that accounts for the pressure dependence of diffusivity at constant f_{O_2} can be retrieved as follows. At constant temperature,

$$(\partial \ln D)_T = \left(\frac{\partial \ln D}{\partial P}\right)_{f_{O_2},T} (\partial P)_T + \left(\frac{\partial \ln D}{\partial \ln f_{O_2}}\right)_{P,T} (\partial \ln f_{O_2})_T \quad (3)$$

Thus, if the variation of f_{O_2} at a constant temperature is controlled by the pressure dependence of the graphite buffer, then

$$(\partial \ln D)_T = \frac{\Delta V^+}{RT}(\partial P)_T + \left(\frac{\partial \ln D}{\partial \ln f_{O_2}}\right)_{P,T} \left(\frac{\partial \ln f_{O_2}}{\partial P}\right)_{C,T} (\partial P)_T \quad (4)$$

where ΔV^+ is the activation volume at constant f_{O_2} and the subscript C stands for the graphite buffer.

Thermodynamic analysis of the effect of variation of f_{O_2} on the point defect concentration [through the equilibrium $3(Fe^{2+})_{Fe} + \frac{1}{2}O_2(gas) = FeO + 2(Fe^{3+})_{Fe} + V_{Fe}$, where the subscript Fe denotes iron site] suggests that D should vary as 1/6th power of f_{O_2} at constant P-T condition (e.g., Buening and Buseck 1973; Morioka and Nagasawa 1991). Calculation of the $\ln f_{O_2}$ versus P slope defined by the graphite buffer using the fluid property of Belonoshko and Saxena (1992a,b; SK Saxena, personal communication) yields an average value of $2.5 \times 10^{-4}/$bar. Thus, the last term in Eq. (4) reduces to $(1/6) \times (2.5 \times 10^{-4}/\text{bar})\text{d}P$, so that the Eq. (4) can be written as

$$\left(\frac{\partial \ln D}{\partial P}\right)_{T,C} = -\frac{[\Delta V^+ - 4 \times 10^{-5}RT]}{RT} \quad (5)$$

The quantity within the square brackets is the "effective" activation volume of diffusion deduced by Chakraborty and Ganguly (1992) to account for the effect of change of pressure at f_{O_2} defined by the graphite buffer. The true activation volume of diffusion (ΔV^+) at

constant temperature and f_{O_2} can be calculated from their data by adding the quantity $4 \times 10^{-5}RT$, which equals ~4.9 cm^3/mol at the average temperature of ~1473 K of their experiments. This exercise yields $\Delta V^+(\text{Mg}) = 10.2(\pm3.0)$ cm^3, $\Delta V^+(\text{Fe}) = 10.5(\pm2.9)$ cm^3, $\Delta V^+(\text{Mn}) = 10.9(\pm2.9)$ cm^3 per mol at constant f_{O_2}, where the uncertainties represent $\pm1\sigma$ errors determined by Chakraborty and Ganguly (1992) for the effective activation volumes.

Experimental results and discussion

Kinetic parameters

The conditions and results of selected experiments are summarized in the table. Two of these experiments, R11 and R17, were conducted by Elphick et al. (1985), and R17 was also modeled by Loomis et al. (1985) to retrieve the tracer diffusion coefficients. The diffusion profiles of both of these experiments were, however, re-analyzed on freshly exposed surfaces and modeled in this work. The results for R17 are essentially the same as those in Loomis et al. (1985).

In principle, both Q and ΔV^+ can be retrieved from our experimental data through by-variate statistical regression of $\log D$ versus $1/T$ and P/T (Chakraborty and Ganguly 1992). However, this procedure yields unusually large effective ΔV^+ (~15 cm^3/mol; associated Q ~65 kcal/mol), compared to those of Chakraborty and Ganguly (1992), which are ~5 cm^3/mol. The problem lies in the fact that of the nine experiments listed in the table, seven are clustered within two restricted pressure intervals (four at 38–40 kbar, and three at 25–28 kbar). Thus, the distribution of the experimental pressures is inadequate to lead to a reliable estimate of ΔV^+. In comparison, the experimental data used by Chakraborty and Ganguly (1992) were spread more evenly over a much larger pressure interval (14–44 kbar). We, therefore, felt it more appropriate to use the present data set to extract the kinetic parameters in conjunction with the ΔV^+ values from Chakraborty and Ganguly (1992).

The polybaric self diffusion coefficients of the two principal divalent cations, Fe and Mg, have been normalized to 10 kbar at f_{O_2} defined by the graphite-O_2 buffer, using the effective activation volumes of Chakraborty and Ganguly (1992), and illustrated in Fig. 2 in the form of an Arrhenius plot. The range of temperature variation in the experiments R17 and DPA4, which are discussed above, is indicated by horizontal bars. The relevant kinetic parameters that describe the temperature and pressure dependence of the diffusion coefficient *at f_{O_2} defined by graphite buffer* are summarized below:

Fe : Q(1 bar) = 65,532 ± 10,111 cal/mol;

$D_0 = 3.50(\pm2.30) \times 10^{-5}$ cm^2/s, $\Delta V^+ = 5.6 \pm 2.9$ cm^3/mol

Mg : Q(1 bar) = 60,760 ± 8,257 cal/mol,

$D_0 = 4.66(\pm2.48) \times 10^{-5}$ cm^2/s, $\Delta V^+ = 5.3 \pm 3.0$ cm^3/mol.
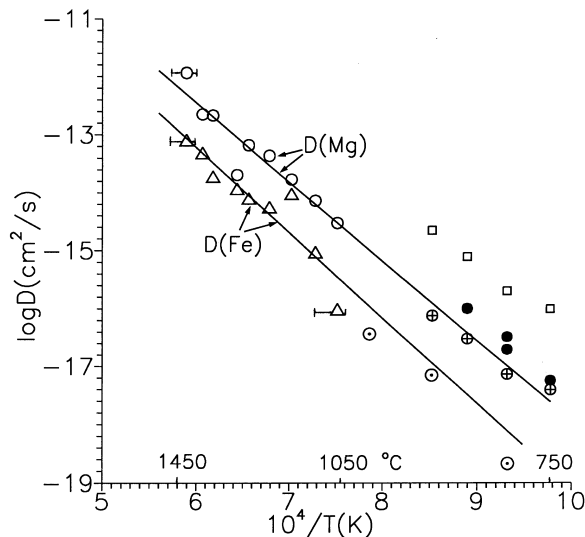
176

Fig. 2 Experimentally determined self and tracer diffusion coefficients of Mg and Fe in garnet. All data represented by *circles* and *triangles* have been normalized to $P = 10$ kbar and f_{O_2} corresponding to those defined by graphite in the system C-O. *Circles* represent the Mg diffusion data. [*Open circles* self diffusion data determined in this work; the *horizontal bars* on the two data at the *highest* (R17) and the *lowest* (DPA4) temperatures indicate the range of temperature variation in these experiments (see text), *filled circles* ^{26}Mg tracer diffusion data by Chakraborty and Rubie (1996) in natural almandine $(Alm_{73}Pyr_{21}Gr_5Sp_1)$ and pyrope $(Alm_{38}Pyr_{50}Gr_{10}Sp_2)$ garnets, the latter being the *upper* of the two data at 800 °C, *circles with inscribed crosses* ^{25}Mg tracer diffusion data in natural pyrope garnet $(Alm_{15}Pyr_{74}Gr_{10}Uv_1)$ by Cygan and Lasaga (1985); their original data at 2 kbar and f_{O_2} corresponding to those defined by hematite-magnetite buffer are shown by *squares*, *centered circles* ^{25}Mg tracer diffusion data in natural pyrope garnets (same composition as in Cygan and Lasaga, 1985) by Schwandt et al. (1995)]

In the regression analysis, equal weight was assigned to all data. The uncertainties in the kinetic parameters are essentially due to the scatter of the data in the *P-T* space. The uncertainties of the D^* values retrieved from modeling the multicomponent profiles [$1\sigma(D^*) \approx 10\%$ of D^*, which translates into $1\sigma(\log D^*) \approx 0.04$] have virtually no effect on those of the regressed kinetic parameters. At constant f_{O_2}, the Q value is ~9 kcal/mol lower (Chakraborty and Ganguly 1992), and ΔV^+ values are ~4.9 cm^3/mol larger, as deduced above. The diffusion coefficient of Fe incorporates that of trace quantity of Fe^{3+} that must be present in equilibrium with the f_{O_2} condition imposed by the graphite buffer.

We did not carry out time series studies, such as normally done in the conventional tracer diffusion experiments (e.g., Ryerson et al. 1989), to check if the retrieved values of the diffusion coefficients at a fixed P, T, f_{O_2} condition is independent of time in order to ensure that the diffusion process was not affected by surface damage during polishing or any other artifact. It was impractical to do so because of the risk of expensive mechanical failures in runs of sufficiently longer duration at the conditions of the experiments (doubling the time causes only ~20% change of the length of the profiles). Sufficiently shorter runs, on the other hand,

would have led to diffusion profiles that had too much convolution effect in the microprobe analyses. However, we did not find any time dependence of D^* even in much shorter tracer diffusion profiles of ^{149}Sm and ^{145}Nd (~1000–2000 Å) measured in an ion probe on samples for which the surfaces were prepared exactly in the same way (Ganguly et al. 1997, and Ganguly J, Tirone M, Hervig R in preparation). Thus, it is safe to conclude that there was no significant effect of surface artifacts in the diffusion profiles modeled in this work, which were several tens of thousand angstroms (Fig. 1). Further, the diffusion profiles were visible across the interface (unlike in the tracer diffusion experiments), and the data were discarded if they appeared anomalous indicating development of fractures at or near the interface. Finally, the internal consistency of the data in the sense that they can be described well by an Arrhenian relation supports the view that the diffusion data are time independent.

Comparison with other data and the problem of change of diffusion mechanism

Chakraborty and Rubie (1996) measured the ^{26}Mg tracer diffusion coefficient in natural almandine $(Alm_{73}Pyr_{21}Gr_5Sp_1)$ and pyrope $(Alm_{38}Pyr_{50}Gr_{10}Sp_2)$ garnets between 750 and 851 °C at 1 bar and $\log f_{O_2}$(bars) $= -17.25$ to -17.5. The almandine garnet crystals were selected from the same stock of material as Alm(4) in the table. These data have been normalized to 10 kbar and f_{O_2} corresponding to that of the graphite buffer in the system C-O, and compared with the present high *P-T* diffusion data in Fig. 2. The normalization procedure accounted for the effects of changing the f_{O_2} to that defined by the graphite buffer at 10 kbar, T and the effect of changing pressure from 1 bar to 10 kbar at constant f_{O_2}, using the "true" activation volumes recovered above from the data of Chakraborty and Ganguly (1992). The normalized data of Chakraborty and Rubie (1996) are ~0.3 log unit greater than those predicted by the linear Arrhenian extrapolation of the present data. Considering the large extrapolation of the data in the P-T-f_{O_2} space required for this comparison, the agreement between the two sets of data is quite satisfactory.

Cygan and Lasaga (1985) and Schwandt et al. (1995) determined the ^{25}Mg tracer diffusion coefficient in more Mg-rich pyrope garnets at 2 kbar, 750–900 °C, and f_{O_2} corresponding approximately to that defined by the hematite-magnetite (HM) buffer, and at 1 bar, 750–900 °C, $f_{O_2} = 10^{-11}$–10^{-15} bars (slightly lower than those defined by the quartz-fayalite-magnetite buffer), respectively. The compositions of garnet used by these workers were similar, varying within the restricted range $Alm_{15-18}Pyr_{66-72}Gr_{10-14}$ with 0–2 mol% of spessartine plus uvarovite components. When normalized to a pressure of 10 kbar, and f_{O_2} defined by graphite buffer in the C-O system following the procedure described above (Eq. 4, using $\Delta V^+ = 10.2$ cm^3/mol), the data of

Cygan and Lasaga (1985) are in excellent agreement with the extrapolation of our results to lower temperature, but those of Schwandt et al. (1995) are lower by ~1.5 log unit (Fig. 2). Although Chakraborty and Rubie (1996) discussed the possibility of extreme compositional dependence of the Mg tracer diffusivity in Mg-rich garnet, the reason for this discrepancy remains unclear, especially in view of the excellent agreement of the data of Cygan and Lasaga (1985) (which are of similar composition to that of garnet crystals used by Schwandt et al., 1995), with our data.

The agreement between the extrapolated values of the high P-T D(Mg) data determined in this work and the low P-T ^{25}Mg and ^{26}Mg tracer diffusion data determined by Cygan and Lasaga (1985) and Chakraborty and Rubie (1996), respectively, reinforces the conclusion of Chakraborty and Ganguly (1991) that there is *no change of volume diffusion mechanism in garnet in the temperature interval 750–1450 °C*. A similar conclusion was also reached by Chakraborty et al. (1996) and Chakraborty (1997) about the Mg tracer diffusion and Fe-Mg interdiffusion in olivine between 980 and 1300 °C. In addition, these agreements also provide at least a permissive support for the theoretical model that D varies as approximately 1/6 power of f_{O_2}.

The diffusion coefficients of divalent cations retrieved by modeling multicomponent diffusion profiles in spessartine-almandine (Chakraborty and Ganguly 1992) and pyrope-almandine diffusion couples (this study) are summarized in Fig. 3. Also shown are a few data for D(Ca) and D(Mn) which we were able to retrieve from the experimental diffusion profiles in the pyrope-almandine couples. For Ca, we assumed the same ΔV^+ as that for Mn since the ionic radius of Ca (1.12 Å) is closer to Mn (0.93 Å) than to other divalent cations (Shannon and Prewitt 1969) for which ΔV^+ data are available. Although, in principle, each experiment with pyrope-almandine diffusion couple should yield D(Ca) and D(Mn), along with D(Fe) and D(Mg), the diffusion data for Ca and Mn retrieved from couples other than those illustrated in Fig. 3 were not reliable because of the low contrast in the concentration of these components between two sides of a couple. The data summarized in Fig. 3 show that: (1) the self diffusion coefficients of Fe and Mn are quite sensitive to compositional changes, increasing by ~one and two orders of magnitude, respectively, from the pyrope-almandine to spessartine-almandine couples (i.e., enhanced by increasing Mn/Mg ratio), reflecting an overall expansion of the structure near the interface; (2) in primarily ferromagnesian garnets, Ca and Mn have similar diffusivities as Fe.

Schwandt et al. (1996) determined ^{44}Ca tracer diffusion in near end-member grossular garnets at 1 bar, 800–1000 °C and f_{O_2} corresponding to that defined by quartz-fayalite-magnetite (QFM) buffer. After accounting for the potential effects of pressure and f_{O_2}, the results of Schwandt et al. (1996), $D_0 = 7.2 \times 10^{-12}$ cm^2/s, $Q = 37,046$ cal/mol [which leads to $\log D(Ca) = -18.5$ cm^2/s], are a few orders of magnitude lower than D(Ca) retrieved in this study from the pyrope-almandine diffusion couples if we assume that the activation energy for the diffusion of Ca in these diffusion couples is similar to those of other divalent cations in garnet. Ganguly et al. (1996) modeled a natural garnet-garnet diffusion couple, which consisted essentially of Fe, Mn and Ca components, with X_{Ca} varying between 0.38 and 0.04. They concluded that in these garnets $D(Ca) \sim 0.06 D(Mn) = 9.72 \times 10^{-27}$ cm^2/s at ~343 °C, if one accepts that the self diffusion coefficients determined for Fe and Mn by Chakraborty and Ganguly (1992) in spessartine-almandine diffusion couples are also valid for these samples. This result seems to be compatible with the D(Ca) derived in the present study, especially given the fact that the self diffusion coefficients seem to be enhanced with the dilution of Mg in the garnet composition.
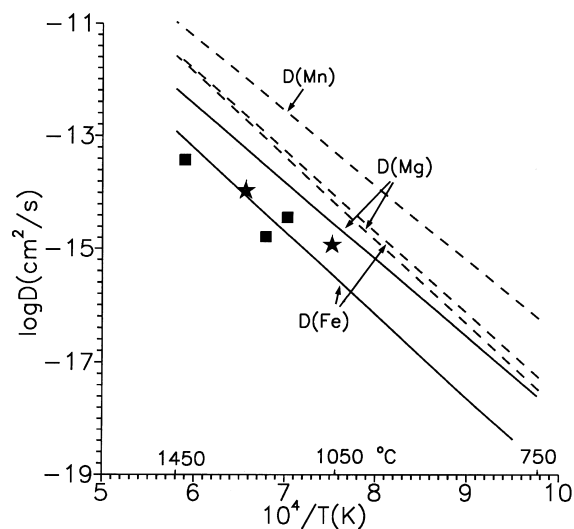
Note on the application of self diffusion data to natural samples

Prograde and retrograde metamorphism

The geological problems concerning diffusion in garnet involve the diffusion of two or more components. Thus, the evolution of the concentration profile of a component in garnet cannot be modeled only by its self diffusion data, but any such modeling must account for the effect of diffusion of other components. In some cases, such as in the problem of retrograde exchange of components between garnet and biotite leading to the development of

Fig. 3 Summary of the self diffusion data of Fe, Mg, Mn and Ca determined by modeling multicomponent diffusion profiles in diffusion couples annealed at high P-T conditions in graphite capsules. All data are normalized to 10 kbar pressure. [*Solid lines* D(Mg) and D(Fe) in pyrope-almandine diffusion couples (this study), *dashed lines* D(Mg), D(Fe) and D(Mn) in spessartine-almandine diffusion couples (Chakraborty and Ganguly 1992, which also incorporate the data of Loomis et al. 1985), *Squares and Stars* D(Ca) and D(Mn), respectively in pyrope-almandine diffusion couples (this study)]

compositional zoning in garnet (e.g., Lindstrom et al. 1991; Spear and Parrish 1996), the problem reduces effectively to a binary diffusion problem because biotite does not significantly exchange any component other than Fe and Mg. In these relatively simple cases, the diffusion coefficient to use in the solution of the diffusion equation is the interdiffusion coefficient, D(Fe-Mg), which can be calculated from D(Fe) and D(Mg) according to (e.g., Barrer et al. 1963; Manning 1968)

$$D(\text{FeMg}) = \frac{D(\text{Fe})D(\text{Mg})}{X_{\text{Fe}}D(\text{Fe}) + X_{\text{Mg}}D(\text{Mg})}\left(1 + \frac{\partial \ln \gamma_i}{\delta \ln X_i}\right) \quad (6)$$

where the quantity within the last parentheses accounts for the thermodynamic effect on the diffusion coefficient (Darken 1948; Manning 1968), γ_i being the activity coefficient of either component.

For the retrograde compositional zoning in garnet in granulites, the appropriate self diffusion data to use are those derived from experiments with pyrope-almandine diffusion couples. However, by the nature of Eq. 6, an interdiffusion coefficient becomes weighted towards the self diffusion coefficient of the dilute component $[X_i \rightarrow 0, D(i-j) \rightarrow D(i)]$ Consequently, since the concentration of Mg is usually much smaller than that of Fe in granulite facies garnets, it should be evident from the data summarized in Fig. 3 that D(Fe-Mg) calculated from the self diffusion data in the pyrope-almandine couple at regional metamorphic conditions may not differ greatly from that calculated from the self diffusion data in the spessartine-almandine couple in many cases. Thus, earlier modeling results (e.g., Chakraborty and Ganguly 1992; Okudaira 1996; Spear and Parrish 1996; Weyer et al. 1996) using the self diffusion data of Fe and Mg in the spessartine-almandine couple of Chakraborty and Ganguly (1992) would usually remain valid or need small readjustment.

For diffusion affected by exchange of more than two major components, the problem should be treated as a multicomponent diffusion problem, in which the self diffusion coefficients are to be used for the calculation of the elements of the matrix of diffusion coefficients (commonly referred to as the **D** matrix). Ganguly et al. (1996) used the **D** matrix formalism to calculate the time scale of metamorphism during Acadian orogeny by modeling diffusion zoning of Fe, Mn and Ca across the interface of a garnet-garnet diffusion couple.

As compared to metamorphic garnets which show retrograde zoning, garnets showing growth zoning during low–medium grade metamorphism are richer in Mn component. For these garnets the appropriate self diffusion data should be taken from those retrieved from spessartine-almandine couple. The self diffusion coefficients would change as a function of metamorphic grade as the garnet composition evolves from Mn-rich at low grade to Mn-poor at high grade. A general formulation of relaxation of growth zoning as a function of the dimensionless variable $\pi^2 Dt/a^2$, where a is the radius of a garnet crystal, has been presented by Chakraborty and Ganguly (1991).

Diffusion data from different sources: compatibility and pitfalls

Currently, the problem of diffusion in garnet has been modeled (e.g. Florence and Spear 1991, 1992; Okudaira 1996; Spear and Parrish 1996; Lang 1996) on the basis of the self diffusion data of Elphick et al. (1981), Loomis et al. (1985), Cygan and Lasaga (1985), Chakrabory and Ganguly (1991, 1992) and Ganguly et al. (1995). It should be noted that the Arrhenian relations for the self diffusion of Mn, Fe and Mg in spessartine-almandine diffusion couples presented by Loomis et al. (1985) are superseded by those of Chakraborty and Ganguly (1992). The latter represents the continuation of the experimental program that was initiated by Loomis et al. (1985), and the data of Loomis et al. (1985) constitute a subset of the data used by Chakraborty and Ganguly (1992) to derive the Arrhenian relations. The two sets of relations differ somewhat because of the different number of data used in each. It seems to have been overlooked (Lang 1996) that Loomis et al. (1985) and Chakraborty and Ganguly (1992) do not constitute independent sets of Arrhenian relations. Further, the self diffusion data in pyrope-almandine diffusion couples presented in this work supersedes those in Elphick et al. (1981) and Ganguly et al. (1995), which constitute progress reports (in the form of meeting abstracts) of a continued program culminating in the present publication.

As discussed above, the data of Cygan and Lasaga (1985) are at 1 bar and f_{O_2} near that defined by the hematite-magnetite (HM) buffer. Nominally, the Mg self diffusion data determined by them are $\sim$2–3 orders of magnitude faster than those of Chakraborty and Ganguly (1992), but this difference seems to be completely accountable by the difference in pressure and f_{O_2} (Fig. 2). Since f_{O_2} of natural assemblages are almost always much lower than that defined by HM buffer and the pressure is several kilobars, the use of the *nominal* D(Mg) from Cygan and Lasaga (1985) would usually yield orders of magnitude faster cooling rate than what they should be, as seems to have been reflected in the recent comparison between the cooling rates derived from geochronological data and retrograde compositional zoning in garnet (Spear and Parrish 1996).

Effects of oxygen fugacity and water

To ensure that it is not overlooked, we emphasize that our data (Figs. 2 and 3) are at f_{O_2} defined by graphite in the system C-O. These data must be adjusted if the f_{O_2} of a natural sample to which the diffusion data are applied is different. The theoretical model relating D and f_{O_2} $[D \alpha (f_{O_2})^{1/6}]$ has worked well in reconciling diverse diffusion data sets obtained under different f_{O_2} conditions (Fig. 2), and, thus, should be used for correcting the experimental diffusion data until results from a systematic experimental study on the effect of f_{O_2} on cation diffusion in garnet become available.

So far, all diffusion data were collected under dry condition, except that the nominally anhydrous natural garnets used in the experiments probably had trace quantities of water (cf., Aines and Rossman 1991). On the basis of zoning and inclusion patterns in polymetamorphic garnets, it was suggested by Erambert and Austrheim (1993) that water might significantly enhance the diffusion process. If so, then the application of the available diffusion data would yield an upper limit of the time scale over which diffusion process was effective. Interestingly, however, the application of dry diffusion data of Chakraborty and Ganguly (1992) yields results which are compatible with the thermal constraints imposed by independent thermal modeling (Okudaira 1996) and geochronological data (Weyer et al. 1996; Spear and Parrish 1996). This encouraging agreement notwithstanding, one should be alert about the potential effect of water when modeling natural diffusion process in garnet.

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