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Ca self-diffusion in grossular garnet

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ABSTRACT

Use of a thin-film technique and an ion microprobe make it possible to conduct cation self-diffusion experiments of ^{44}Ca in near end-member grossular garnet at temperatures of 800–1000 °C. The experiments were conducted at 1 atm and under quartz + fayalite + magnetite f_{O_2} conditions. The resulting activation energy ($E_a = 155 \pm 10$ kJ/mol) and the frequency factor ($D_0 = 7.2 \times 10^{-16}$ m^2/s; log $D_0 = -15.1 \pm 0.4$) were obtained from the temperature dependence of the diffusion data. Comparison of these data with a comparable study of ^{25}Mg self-diffusion coefficients in pyrope confirmed that Ca diffuses more slowly through garnet than Mg under identical conditions.

INTRODUCTION

Petrologic modeling and the development of theoretical predictive models of cation diffusion in silicate minerals require a complete understanding of the pertinent mechanisms. Much work has been done to identify rates and mechanisms of cation diffusion through minerals such as garnet that typically exhibit compositional zoning. Cation-diffusion experiments involving garnet have typically investigated cations that occupy the eightfold-coordinated site, especially Mg and Fe diffusion in pyrope-almandine garnets (Freer 1979; Duckworth and Freer 1981; Cygan and Lasaga 1985; Elphick et al. 1985; Loomis et al. 1985; Chakraborty and Ganguly 1991, 1992; Schwandt et al. 1993, 1995).

The present investigation used the Ca end-member of garnet to understand better the mechanisms of cation diffusion by examining the garnet structure with the largest eightfold-coordinated cation (Ca^{2+}) and unit cell (Novak and Gibbs 1971). Volume diffusion of Ca in garnet is inferred to be slower than volume diffusion of Mg, Fe, and Mn because of the larger ionic size of Ca (Chakraborty and Ganguly 1991; Tracy 1992), but the rate has not been previously measured. This paper presents the results of ^{44}Ca self-diffusion experiments in nearly end-member grossular garnet annealed at 1 atm under quartz + fayalite + magnetite (QFM) f_{O_2} conditions at 800, 900, and 1000 °C. Self-diffusion is volume diffusion of an isotope along an isotopic gradient rather than a compositional gradient. Compositional end-member self-diffusion coefficients have values that are similar in order of magnitude to multicomponent diffusion coefficients (Lasaga 1979; Cygan and Lasaga 1985; Chakraborty and Ganguly 1991, 1992). More important, the end-member self-diffusion coefficients define the limits of the compositional effect on cation diffusion. Once all four end-member self-diffusion or tracer diffusion coefficients have been determined, they can be used to calculate multicomponent diffusion coefficients (Lasaga 1979; Brady 1995) based on the mineral composition.

EXPERIMENTAL APPROACH

Diffusion usually must be measured for several crystallographic directions of a mineral to define accurately the diffusion properties as represented by a 3 × 3 diagonal matrix (Nye 1957). However, because of the high symmetry of the isometric garnet structure, this matrix is reduced to a simple diagonalized matrix with equivalent components. Colorless, gem-quality grossular garnets from Lalatema, Tanzania (Table 1), were sectioned with a wafering saw into several pieces (1 × 4 × 4 mm) and then polished with diamond pastes down to 1 μm grit. The final stage of polishing utilized a 0.06 μm colloidal silica polish. The polished grossular pieces were preannealed for 24 h at experimental annealing conditions (800–1000 °C at f_{O_2} = QFM conditions) in a mixed-gas vertical-tube furnace to equilibrate the point-defect structure at experimental conditions (Schwandt et al. 1993), though other researchers have found results equivocal for a variety of preparation procedures, including physical polishing, chemical etching, and preannealing (Ryerson et al. 1989; Chakraborty et al. 1994). Electronically regulated mixtures of CO-CO$_2$ gas controlled and maintained the f_{O_2} in the 5 in. hot zone of the furnace to slightly below (about one-tenth of a log unit) that of the QFM buffer (log $f_{O_2} = -15$ to -11). A solid electrolyte cell, mounted 2 cm above the samples, monitored f_{O_2} during all annealing experiments. The QFM fugacities were selected because they are consistent with the typical oxidation conditions of natural metamorphic mineral assemblages.

After preannealing, the samples were coated with a thin film (~2000 Å) of ^{44}CaO formed by high-vacuum thermal evaporation of an enriched ^{44}CaO powder, in which ^{44}Ca was enriched to 97% of the total Ca (Schwandt et al. 1993). The diffusion couples were then annealed at the

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TABLE 1. Representative composition of grossular garnets determined by electron microprobe analysis

SiO_2	38.49 ± 0.48
TiO_2	0.43 ± 0.06
Al_2O_3	23.41 ± 0.74
MgO	0.37 ± 0.02
FeO	0.16 ± 0.06
MnO	0.19 ± 0.06
CaO	37.12 ± 0.44

Note: From mean of 40 electron microprobe analyses. Uncertainties are two estimated standard deviations.

experimental temperature and f_{O_2} for periods of a few days to three months depending on the temperature. After annealing, the $Ca(OH)_2$ films were removed from the garnet surfaces by soaking the samples in deionized water at 40–45 °C for 24 h, resulting in dissolution of the thin film and reexposure of the polished grossular surfaces. Trace amounts of insoluble components, silica and tungsten oxide from the polishing and the evaporation process, remained after removal of the thin film. These nonsoluble materials are uniformly distributed on the polished grossular surface and produce only minor surface topography (50–100 Å).

Annealed garnet samples were analyzed to determine the diffusional penetration profile using a Cameca IMS 4F ion microprobe with a 10 kV, 100 nA primary beam of O^- ions. Additional parameters for analyzing positive secondary ions included a ±10 eV energy window, a 50 V sample bias offset, a 750 μm field aperture, a 50 μm contrast aperture, and a 200 × 200 μm primary-beam raster. These conditions produced a linear sputter rate of 0.90 ± 0.05 Å/s through the grossular as measured by contact profilometry of test craters.

Intensities of secondary ions resulting from the action of the primary O^- beam interacting with the garnet sample were measured as a function of time. The ^{24}Mg, ^{27}Al, ^{28}Si, ^{40}Ca, ^{44}Ca, ^{47}Ti, ^{55}Mn, and ^{56}Fe were monitored during the sputtering process. The values of interest for the diffusion experiments are the $^{44}Ca/(^{40}Ca + {}^{44}Ca)$ intensity fractions as a function of depth into the garnet. These data were used in an error-function diffusion model to derive the diffusion coefficient. The major element components of garnet were analyzed to ensure that no breakdown reactions occurred during the experiment. The samples remain optically isotropic after the experiments, confirming the absence of garnet breakdown. Unlike the thin film in our pyrope experiments (Schwandt et al. 1995), in which we measured the $^{25}Mg/^{28}Si$ intensity fractions because of the presence of an insoluble ^{25}MgO thin film, the ^{44}CaO thin film is removable. Revealing the original garnet surface makes analysis and interpretation of the diffusion profile a simple and convenient process.

RESULTS AND DISCUSSION

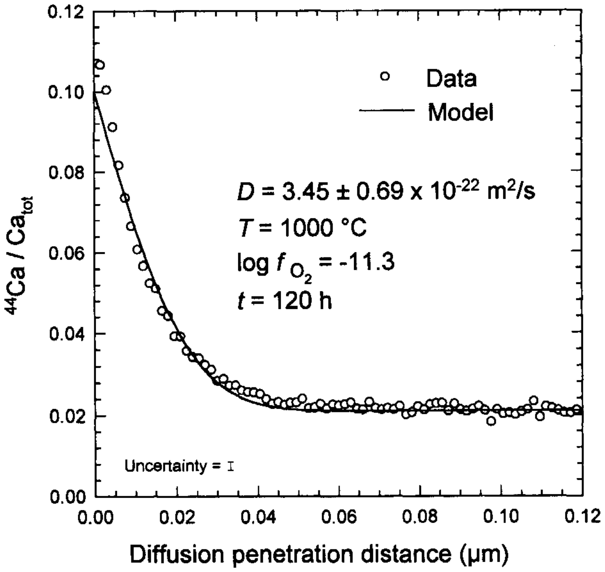

FIGURE 1. Diffusion profile for Ca in grossular garnet obtained at 1000 °C, log $f_{O_2} = -11.3$, and annealed for 120 h. The greatest misfit between the model and the data occurs closest to the interface, or garnet surface where the compositional gradient is large, but the fit is otherwise excellent.

The $^{44}Ca/(^{40}Ca + {}^{44}Ca)$ diffusion profiles were modeled with a nonlinear curve-fitting algorithm using the following modified equation from Crank (1975) for a semi-infinite medium:

$$C_x = C_s + (C_b - C_s)\mathrm{erf}\left(\frac{x}{\sqrt{4Dt}}\right) \qquad (1)$$

where C_x is the fraction of ^{44}Ca at a distance x from the interface; C_b is the fraction of ^{44}Ca in the bulk sample, which, in this case, is equivalent to the natural abundance of ^{44}Ca (2.086%); C_s is the fraction of ^{44}Ca at the interface; D is the self-diffusion coefficient; and t is the anneal time. The measured profiles were fitted to Equation 1 to determine the optimum value of the self-diffusion coefficient, D (Fig. 1). Determinations of D for individual curve fits have an uncertainty of about 3% (relative). Replicate ion microprobe analyses provide an uncertainty of about 20% (relative).

Figure 2 presents the log D values of the annealed garnet at 800, 900, and 1000 °C and 1 atm as a function of the inverse of the absolute temperature, which demonstrates the Arrhenius relationship of diffusion with temperature. Experiments at 1000 °C were conducted for several durations to ensure that the diffusion coefficient values are independent of time. Although the thin-film technique imposes a minor artificial time dependence on the D values (see 1000 °C values obtained at log $f_{O_2} = -11.3$ in Table 2), this behavior is entirely analytical, resulting from the insoluble remnants on the garnet surface (see Schwandt et al. 1993, 1995). To avoid this problem, we ensured that the diffusion annealing experiments were sufficiently long in duration to produce significant diffusional penetration. The slope of the Arrhenius line (Fig. 2)

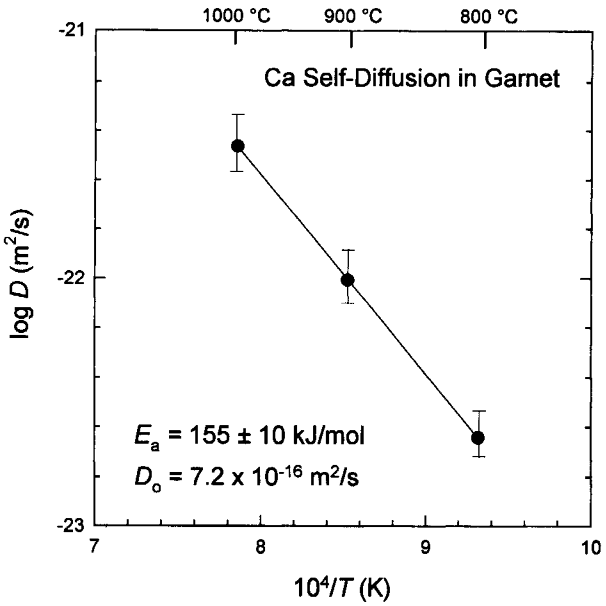

Figure 2. Arrhenius plot of the Ca self-diffusion data. The correlation coefficient for this Arrhenius relation is 0.99. Error bars represent estimated relative error (20%).

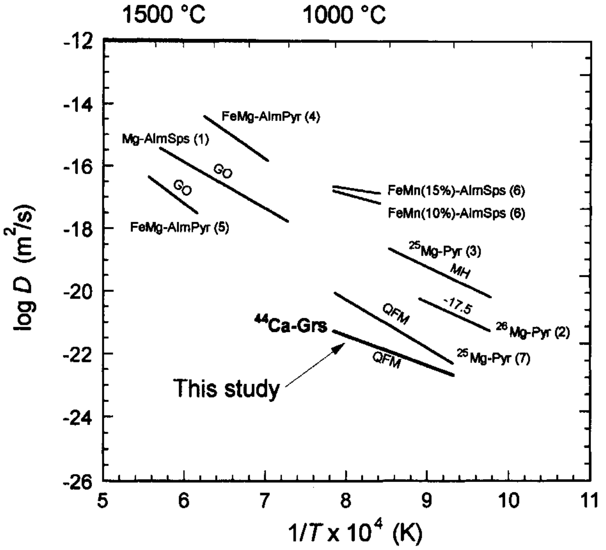

Figure 3. Arrhenius compilation of the experimental data for Mg, Fe, Mn, and Ca diffusion in garnet: 1 = Chakraborty and Ganguly (1992), 2 = Chakraborty et al. (1992) and Chakraborty (personal communication), 3 = Cygan and Lasaga (1985), 4 = Duckworth and Freer (1981), 5 = Elphick et al. (1985), 6 = Freer (1979), and 7 = Schwandt et al. (1995). No corrections were made for differences in composition, pressure, or f_{O_2}. Experimental f_{O_2} conditions (solid-state buffer assemblages or log values) are noted for each line when reported in the original study.

represents the activation energy for Ca self-diffusion in grossular, and a value of E_a = 155 ± 10 kJ/mol is obtained. The zero intercept, at infinite temperature, is known as the frequency factor D_0 and is 7.2 × 10^{-16} m²/s (log D_0 = −15.1 ± 0.4). The Ca diffusion coefficients are slower by approximately a factor of 5 than those obtained for Mg self-diffusion under identical experimental conditions (Schwandt et al. 1995). These results are consistent with the expectation that Ca would diffuse more slowly than Mg through garnet because of its larger ionic size (Chakraborty and Ganguly 1991; Tracy 1992). These Ca data provide the minimum diffusion coefficients relative to the compositional end-members of garnet and along with our Mg self-diffusion in pyrope data (Schwandt et al. 1995) represent one-half of the end-member information necessary to define completely the compositional dependence of eightfold-coordinated cation diffusion in garnet. These self-diffusion or tracer diffusion values can then be incorporated into binary or multicomponent diffusion expressions for ionic systems to obtain the necessary diffusion coefficients for application to a natural system (Brady 1995). The Ca self-diffusion coefficients are a couple of orders of magnitude smaller than the extrapolated data for Mg, Fe, and Mn diffusion in Fe-rich garnets of Chakraborty and Ganguly (1991, 1992; see Fig. 3).

Table 2. Self-diffusion coefficients for ^{44}Ca in grossular garnet

Anneal		Self-diffusion coefficients (m²/s)		
t (h)	log f_{O_2}	1000 °C	900 °C	800 °C
24	−11.3	1.60 × 10^{-21}		
72	−6.0	5.90 × 10^{-22}		
72	−9.0	4.00 × 10^{-22}		
72	−11.3	4.70 × 10^{-22}		
72	−16.0	6.40 × 10^{-22}		
120	−11.3	3.45 × 10^{-22}		
789	−13.0		9.84 × 10^{-23}	
2208	−15.3			2.28 × 10^{-23}

Note: Uncertainties are approximately 20% (relative).

Oxygen fugacity is expected to have a significant effect on pyrope-almandine systems, especially at low temperatures, because in the extrinsic region the oxidation state of Fe, or any other multivalent cation, affects the point-defect structure of the mineral (Lasaga 1981). Therefore, additional grossular diffusion couples were annealed for 72 h at 1000 °C under different f_{O_2} to check for any dependence of diffusion on f_{O_2}, but none was observed (Table 2) even though this grossular composition contains only minor concentrations of Fe and Mn.

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REFERENCES CITED

Brady, J.B. (1995) Diffusion data for silicate minerals, glasses, and liquids. In T.J. Ahrens, Ed., Mineral physics and crystallography: A handbook of physical constants, p. 269–290. American Geophysical Union, Washington, DC.

Chakraborty, S., and Ganguly, J. (1991) Compositional zoning and cation diffusion in garnets. In J. Ganguly, Ed., Diffusion, atomic ordering and mass transport, p. 120–175. Springer-Verlag, New York.

——— (1992) Cation diffusion in aluminosilicate garnets: Experimental determination in spessartine-almandine diffusion couples, evaluation of effective binary diffusion coefficients, and applications. Contributions to Mineralogy and Petrology, 111, 74–86.

Chakraborty, S., Rubie, D.C., and Elphick, S.C. (1992) Mg tracer diffusion in aluminosilicate garnets at 800 °C, 1 atm. and 1300 °C, 8.5 GPa. Eos, 73, 567.

Chakraborty, S., Farver, J.R., Yund, R.A., and Rubie, D.C. (1994) Mg tracer diffusion in synthetic forsterite and San Carlos olivine as a function of P, T and f_{O_2}. Physics and Chemistry of Minerals, 21, 489–500.

Crank, J. (1975) The mathematics of diffusion, 414 p. Oxford University Press, Oxford, U.K.

Cygan, R.T., and Lasaga, A.C. (1985) Self-diffusion of magnesium in garnet at 750 to 900 °C. American Journal of Science, 285, 328–350.

Duckworth, S., and Freer, R. (1981) Cation diffusion studies in garnet-garnet and garnet-pyroxene couples at high temperatures and pressures. Fifth Progress Report of Research Supported by Natural Environment Research Council (1978–1980), 18, 36–39.

Elphick, S.C., Ganguly, J., and Loomis, T.P. (1985) Experimental determination of cation diffusivities in aluminosilicate garnets: I. Experimental methods and interdiffusion data. Contributions to Mineralogy and Petrology, 90, 36–44.

Freer, R. (1979) An experimental measurement of cation diffusion in almandine garnet. Nature, 280, 220–222.

Lasaga, A.C. (1979) Multicomponent exchange and diffusion in silicates. Geochimica et Cosmochimica Acta, 43, 455–469.

——— (1981) The atomistic basis of kinetics: Defects in minerals. In Mineralogical Society of America Reviews in Mineralogy, 8, 216–319.

Loomis, T.P., Ganguly, J., and Elphick, S.C. (1985) Experimental determination of cation diffusivities in aluminosilicate garnets: II. Multicomponent simulation and tracer diffusion coefficients. Contributions to Mineralogy and Petrology, 90, 45–51.

Novak, G.A., and Gibbs, G.V. (1971) The crystal chemistry of the silicate garnets. American Mineralogist, 56, 791–825.

Nye, J.F. (1957) Physical properties of crystals, 322 p. Clarendon Press, Oxford, U.K.

Ryerson, F.J., Durham, W.B., Cherniak, D.J., and Lanford, W.A. (1989) Oxygen diffusion in olivine: Effect of oxygen fugacity and implications for creep. Journal of Geophysical Research, 94(B4), 4105–4118.

Schwandt, C.S., Cygan, R.T., and Westrich, H.R. (1993) A thin film approach for producing mineral diffusion couples. Pure and Applied Geophysics, 141, 631–642.

——— (1995) Mg self-diffusion in pyrope garnet. American Mineralogist, 80, 483–490.

Tracy, R. (1992) Documentation of diffusional modification of garnet growth zoning in amphibolite facies garnets. Geological Society of America Abstracts with Programs, 24(7), A219.

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