Combined experimental and computer simulation studies of cation diffusion in silicate garnets

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Introduction

Garnet is an important petrological indicator in crustal and mantle metamorphic rocks. The persistence of compositional zoning, often in the form of bell-shaped profiles for Mn, Fe and Mg has long been recognised e.g. Hollister (1966), Anderson and Olympio (1977), Dempster (1985), and demonstrates the slow diffusion rates of cations during geological time. Knowledge of diffusion rates of the relevant cations should enable bounds to be placed on the cooling history of the host rocks. Similarly, the ubiquity of garnets in many types of rocks has given them increased importance as indicators of metamorphic reactions; these are of considerable use in geothermometers and geobarometers, e.g. Essene (1989). Again diffusion data are needed to calibrate such mineral reaction thermometers and barometers.

The behaviour of Ca zoning in garnet is often different to that of other elements (Crawford 1977) in part reflecting the availability of Ca in the surrounding rock and exchange reactions. There is now a growing body of experimental diffusion data for interdiffusion and tracer diffusion of Fe, Mn and Mg in garnet (Freer, 1979; Elphick *et al,* 1985; Chakraborty and Ganguly, 1992; Cygan and Lasaga, 1985) but as yet there is little direct information on the transport properties of Ca. The present study was undertaken to examine Ca-Fe exchange between grossular and almandine single crystals as a function of temperature, pressure and buffering conditions. Interdiffusion experiments were performed in piston-cylinder apparatus.

Complementary modelling studies were performed to determine the energies required to form defects and move ions through the garnet structure. Activation energies were determined for the major divalent cations in grossular and almandine; the results have been used to interpret the experimental diffusion data and help to infer the diffusion mechanism.

Experimental

Starting materials were 'grossular' and 'almandine' single crystals. From each crystal slices 3mm thick were cut. Cores of 3mm diameter were cut from the slices; contact faces were polished down to 1lm diamond paste. After cleaning, pairs of samples (grossular and almandine) were placed face-to-face and wrapped in Pt foil to form a diffusion couple. Outer capsules were formed from 4mm diameter Pt tubing. The inner capsule, containing the crystals, was sealed with a buffer (Fe/FeO or Quartz/magnetite/fayalite) in the outer capsule.

High pressure diffusion experimental runs were performed in a conventional piston-cylinder apparatus; at 900°C to 1100°C and 30 kbar, to define an activation energy, and at 1000°C and a range of pressures, 15 kbar–32.5 kbar, to define an activation volume. At the end of the experiments samples were recovered, mounted, polished and analysed by electron microprobe in a direction perpendicular to the original interface to define the diffusion profiles for the major cations. Interdiffusion coefficients were determined from Ca and (Mg + Fe) profiles using the standard Boltzmann-Matano method (Matano, 1933).

Computer simulation methods

Atomistic simulation techniques, based on the Born model using interatomic potentials to describe the total energy of the system in terms of atomic positions, were employed (Catlow and Macrodt, 1982). Potential parameters for cation-cation and cation-oxygen interactions were transferred from those derived for simple oxides (e.g. Lewis, 1983). To determine the properties of defects in garnet, a two region strategy was employed (Mott and Littleton, 1938). Full details are given in Edwards (1991).

The CASCADE code was used to define the lattice energy of individual garnet compositions. Energies required to generate vacancies at various lattice sites and to form interstitial species were calculated. Saddle point energies between pairs of lattice sites (or interstitial sites) enabled the migration energies to be defined. Activation volumes were obtained by performing calcula-

tions with unit cells having a range of lattice-parameters, i.e. as a function of pressure.

Results and discussion

Experimental studies. Twenty one interdiffusion experiments were performed at a range of temperatures and pressures. Elemental profiles for Fe, Ca, Mg and Al varied from 15 μm to 80 μm, depending upon temperature, pressure and buffering conditions. For example, a profile of 35 μm in length was obtained in 112.25 hours at 1100°C, whilst a run of 1441 hours at 900°C yielded a profile of less than 25 μm. The effect of pressure on profile length was less than that of temperature. Interdiffusion profiles followed the standard sigmoidal shape with Ca exchanging for (Fe + Mg).

Interdiffusion coefficients, calculated by the Boltzmann-Matano method, showed little dependence on composition; results from the Ca or (Mg + Fe) profiles were very similar. Data will be described in terms of interdiffusion coefficients D(Ca-Fe) as a matter of convenience.

Over the temperature range 900–1100°C at 30 kbar, grossular-almandine couples yield interdiffusion coefficients varying by approximately two orders of magnitude: $\sim 1 \times 10^{14} cm^2 s^{-1}$ at 900°C to $\sim 1 \times 10^{12} cm^2 s^{-1}$ at 1100°C. The results may be conveniently described in terms of an Arrheinus equation of the form D = 3 × 10^{-2} exp (−67 kcal/RT) $cm^2 s^{-1}$. Faster diffusion ratios were obtained when buffers were not used.

The interdiffusion coefficients obtained in this study are high compared to those reported by Elphick *et al*(1985) for Mg−Fe and Mn−Fe interdiffusion in garnet, but in good agreement with the data of Cygan and Lasaga (1985) for Mg tracer diffusion in garnet. More recent high temperature data obtained by Chakraborty and Ganguly (1991) for Mg* diffusion in garnet (derived from interdiffusion experiments) are in agreement with Cygan and Lasaga when the data are corrected for pressure and oxygen fugacity. Activation energies obtained by other authors for tracer or interdiffusion in garnet (involving Fe, Mn, Mg) are typically 53–57 kcal mol^{-1}. This is slightly less than the value of 67 kcal mol^{-1} determined in the present study for Ca–Fe interdiffusion. The difference is not surprising, since intuitively it would be expected that the larger Ca ion would require more energy to migrate through the lattice. In view of the comparatively low temperature at which the experiments were performed and the relatively impure nature of the crystals, it is likely that the data reflects extrinsic diffusion behaviour for the garnet.

The variation of interdiffusion coefficient with pressure was relatively small. At 1000°C and 15 kbar, D = 4.4 × $10^{-13} cm^2 s^{-1}$, whilst at 1000°C and 32.5 kbar, D = 6.7 × $10^{-14} cm^2 s^{-1}$. This represents a reduction in D by about one order of magnitude as the pressure was increased by 17.5 kbar. The pressure dependence of the diffusion coefficient D, at constant temperature, is described by an equation of the form

$$\left(\frac{\delta logD}{\delta P}\right)_T = \frac{-\Delta V}{RT}$$

where P is pressure, T absolute temperature, ΔV the activation volume and R the gas constant. The activation volume was determined to be 5.05 $cm^3 mol^{-1}$. This is comparable with that obtained by Misener (1974) for cation diffusion in olivine (5.5 $cm^3 mol^{-1}$), and Elphick *et al*(1985) for interdiffusion in garnet (4.7 $cm^3 mol^{-1}$).

Modelling studies

Simulation of physical properties (e.g. dielectric and elastic constants) were generally good. Data were obtained for a number of end member garnet compositions, including grossular and almandine.

A wide variety of defect formation and migration arrangements were examined in all the end-member garnets. In general, the energies required to form Schottky (vacancy) and Frenkel (interstitial) defects are large, typically 4–5 eV. In all the silicate systems the lowest energy defect is the divalent cation Schottky, followed by Frenkel defects for divalent cations (about 0.5 eV larger). Schottky defects for trivalent cations are higher, between 4.5–6.0 eV. The magnitude of the defect energies leads to the conclusion that except at very high temperature, disorder in silicate garnets would be dominated by extrinsic factors.

Migration pathways were examined between various lattice and interstitial sites to help define activation energies. For example, the energy barriers for divalent cations in almandine are typically 50 kcal mol^{-1} and for divalent cations in grossular approximately 78 kcal. These data suggest that the experimentally-determined activation energy for D(Ca-Fe) represents diffusion via a vacancy mechanism under extrinsic conditions.

Conclusions

Combining experimental and modelling studies of cation diffusion in silicate garnets provides insight into mechanisms and help to interpret the experimental data.