

Cation diffusion in chromian spinel: analyses based on evaporation method

Kazuhito Ozawa[1], Hiroko Nagahara[2]

[1] Univ. Tokyo, EPS, [2] Dept. Earth Planet. Sci., Univ. Tokyo

1. Introduction

Diffusivity of elements in rock forming minerals is important in understanding pressure-temperature-deformation history that rocks and minerals had experienced before they were exposed on the earth's surface. There are various ways to determine the diffusivity such as diffusion couple method for interdiffusion coefficients and thin film method for tracer or selfdiffusion coefficients. We have developed a vacuum evaporation method and applied it to determine the Mg-Fe interdiffusion and Ni tracer diffusion coefficients in olivine (Ozawa and Nagahara, 2000).

In this paper, we applied the evaporation method to chromian spinel to understand diffusion processes in the complex spinel solid solution. Chromian spinel is one of important minerals in peridotites, basalts, and meteorites. Although the abundance is usually minor, it is a good indicator for thermal history (e.g., Ozawa, 1984; 1989) and petrogenesis of peridotites (Ozawa, 1997). The diffusivity of important elements in spinel has not yet determined except for a few literatures (e.g., Freer and O'Reilly, 1980).

The evaporation method is benefited in its experimental simplicity. What we need is a homogeneous crystal as a starting material, which is heated in vacuum at a given temperature for desired time. Another important advantage is that diffusion anisotropy can be determined easily and accurately. We sacrificed cumbersome of data processing to the experimental simplicity. There are, however, some disadvantages. The higher activation energy for evaporation as compared with that of diffusion inhibits experiments at low temperature. Heating in vacuum may cause the defect density (vacancy or interstitial atoms) significantly different from that at atmospheric or higher pressures.

2. Experimental method

Octahedral chromite grains with {111} natural surfaces sampled from Horokanai ophiolite, the Kamuikotan metamorphic belt, Hokkaido were used. Experiments were performed in a W mesh heater constructed in a vacuum chamber with 25cm diameter and 30 cm height. The samples were heated at 1300, 1400, and 1500C for 7 - 100 hours.

3. Experimental results

After the experiments, remarkable zoning with the width of 10 ~ 80 mm was developed in all samples. The width depends on temperature and duration. The zoning is characterized by enrichment of Al, Cr, and Mg and depletion of Fe (Fe²⁺ and Fe³⁺) near the surface. The outer part is either flat in all elements or zoned in Al and Cr, depending on experimental conditions. When Al and Cr are zoned, Al shows marked uphill diffusion, which is more common in the low temperature experiments. The inner limit of zoning is marked by abrupt increase of Fe³⁺ content from nearly zero to the initial value, which is most plausibly explained by reduction of Fe³⁺ to Fe²⁺ in the spinel lattice.

Because Fe²⁺ decreases in the similar manner when Fe³⁺ becomes nearly negligible, the net reaction is evaporation of magnetite component. By assuming parabolic rate law for the development of reaction zone, the activation energy is estimated to be 200 kJ/mol. The value is within a range of activation energy for cation diffusion in silicate minerals, but the diffusivities of Al are comparable to those of Mg and Fe²⁺, suggesting involvement of defects formed by the reduction. A plausible reaction processes are as follows. Electrons, which are formed on the surface of chromian spinel by selective evaporation of Fe and O₂ leaving Al³⁺ and Cr³⁺, migrate into the crystal and cause reduction of Fe³⁺ to Fe²⁺. The reduction reaction gives rise to octahedral site vacancies, which migrate to the surface with counterdiffusion of Al³⁺ and Cr³⁺ into the crystal. The uphill diffusion of Al can be explained by the large contrast of selfdiffusion coefficient between Al and Cr. The very slow diffusivity of Cr is consistent with the deformation-induced Al-Cr zoning in chromian spinel from mantle peridotites formed at low temperatures (Ozawa, 1989).