論文題目 　　　　Diffusion of noble gas in forsterite

(フォルステライト中の希ガスの拡散)

氏 名 　　　小 泉 　早 苗

Introduction

　　Despite the widespread use of noble gases as tracers of mantle processes and as geological chronometers, many fundamental aspects on their geochemical behavior remain poorly understood. Noble gas diffusion in mantle minerals is generally considered very fast based on their chemical inertness and incompatibility to mantle minerals as the basic assumption in previous studies.

Diffusive concentration of impurities to grain boundaries has been well documented not only in synthetic materials and ceramics but also in geological materials more recently. Because the intergranular transport medium within a rock is of paramount importance for the transport and/or storage of elements which are incompatible to the rock-forming minerals. But no studies have evaluated the behavior of the large, uncharged, noble gas in this regard. Here, we address an important characteristic of noble gas geochemistry about which no data and little understanding exist: to what extent do grain boundaries diffusion of noble gases involved. The phenomenon has not commonly been considered, yet if significant, it would have important implications for several fields in geochemistry, including studies on evolution of chemical/isotopic heterogeneity in the Earth's mantle and noble gas geochronology.

Synthesis of highly dense and fine-grained aggregates of mantle composites by vacuum sintering of nano-sized mineral powders

Synthesized mineral powders with particle size of < 100 nm are vacuum sintered to obtain highly dense and fine-grained polycrystalline mantle composites: single phase aggregates of forsterite (Mg_2SiO_4), olivine ($Mg_{1.8}Fe_{0.2}SiO_4$), diopside ($CaMgSi_2O_6$), and enstatite ($MgSiO_3$); two phase composites of forsterite + spinel ($MgAl_2O_4$) and forsterite + periclase (MgO); and, three phase composites of forsterite + enstatite + diopside. Nano-sized powders of colloidal SiO_2 (Fig.1**A**) and highly dispersed $Mg(OH)_2$ with particle size of $\leq$ 50 nm are used as chemical sources for MgO and SiO_2, which are common components for all of the aggregates. These powders are mixed with powders of $CaCO_3$, $MgAl_2O_4$, and $Fe(CO_2CH_3)$ to introduce mineral phases of diopside, spinel, and olivine to the aggregates, respectively. To synthesize highly dense composites through pressureless sintering, we find that calcined powders should be composed of particles that have: (i) fully reacted to the desired minerals, (ii) a size of < 100 nm, and (iii) less propensity to coalesce. Such calcined powders are compressed by using cold isostatic pressing and then vacuum sintered. The temperature and duration of the sintering process are tuned to achieve a balance between high density and fine grain size. Highly dense (i.e. porosity $\leq$ 1 vol%) polycrystalline mantle mineral composites with grain size of 0.3-1.1 μm are successfully synthesized with this method.

In such materials, the volume fraction of the grain boundaries is 10^{-2}~10^{-3} (Fig. 2**B**) which is desirable, particularly for experimental studies of diffusion. The apparent diffusion coefficient in polycrystalline body is described as a sum of the diffusion coefficient of grain boundary and crystal lattice (Fig. 2**A**). ($D_i^{bulk} = sD_i^l + (1-s)D_i^{gb}$, where $s \cong 3\delta/d$, δ is grain boundary width (ca. 1×10^{-9} m, Hiraga et al., 2004), d is grain size) Thus, I expect to detect chemical components from grain boundaries using conventional whole rock chemical analysis.
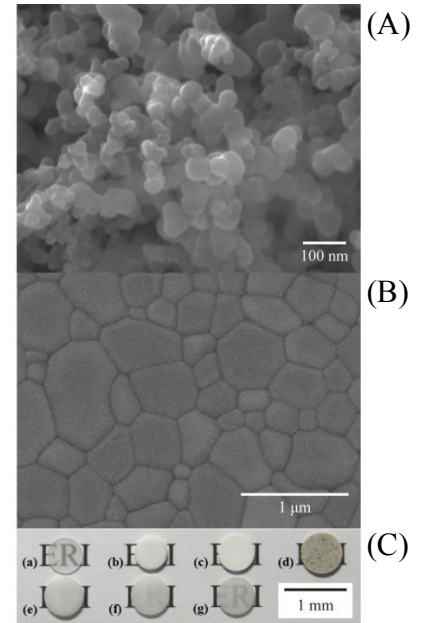

(A)

(B)

(C)

Fig.1 (A) SEM images of the Nano-sized powders of colloidal SiO_2. (B) SEM images of forsterite (Fo_{100}) aggregate, sintered at constant conditions of 1310 °C for 3 h. (C) Comparisons of light transparency of the aggregates of **a** forsterite, **b** enstatite, **c** diopside, **d** olivine, **e** forsterite + periclase, **f** forsterite + spinel and **g** forsterite + enstatite + diopside. All sample thicknesses were fixed at 0.5 mm.

(A)

(B)
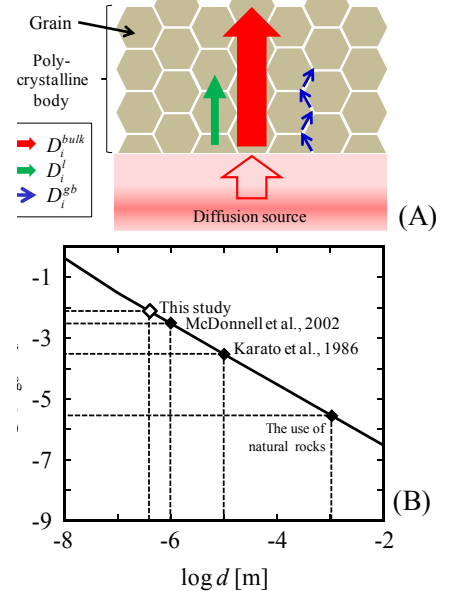
Fig.2 (A) Schematic drawing the apparent diffusion coefficient (D_i^{bulk}, red arrow) in polycrystalline body. The apparent diffusion coefficientred is the sum of the diffusion coefficient of grain boundary (D_i^{gb}, blue arrow) and that of crystal lattice (D_i^l, green arrow). (B) contribution to D^{gb} of D^{bulk} with respect to grain size, d.

Diffusion of argon into forsterite

Argon diffusion experiments were performed on the gem quality clear forsterite sample (Myanmar) and synthetic polycrystalline forsterite with grain size of 500 nm and porosity ≤ 0.06 vol%. The samples were placed on a platinum plate, and then put in an electric tube furnace. Samples surface were directly exposed to the Ar gas pressure of 0.15 MPa at 1280 ºC for 10, 100 and 133 hours. Argon atoms are expected to diffuse into the crystals from their surface resulting in formation of concentration gradients at near-surface. Total amounts of diffused Ar were determined by in-vacuo heating extraction and noble gas mass spectrometry (Fig. 3). Depth concentration profiles of ^{40}Ar started from the near-surface were calculated to reproduce the total amounts of Ar incorporated into the synthetic polycrystalline forsterite with several uptake durations (Fig. 4). The calculated diffusion distance by follow equation was < 100 nm even after diffusion anneal of 133 hours, indicating very slow Ar diffusion with a diffusion coefficient (D) of 1.44×10^{-21} m^2/s at 1280 °C. Amount of Ar released from the single natural forsterite crystal was several orders of magnitude lower than those from the synthetic polycrystalline forsterite, indicating a significant uptake of Ar at grain boundaries. This result is consistent with the result by Thomas et al. (2008).
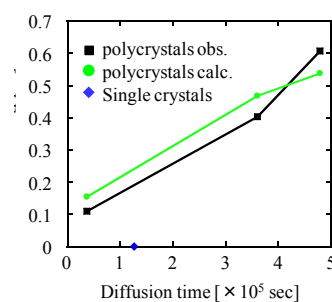
Fig. 3 The amount of released Ar in isothermal experiments of single crystal and synthetic polycrystalline forsterite. The diffusion experiment were performed at 1280 °C.
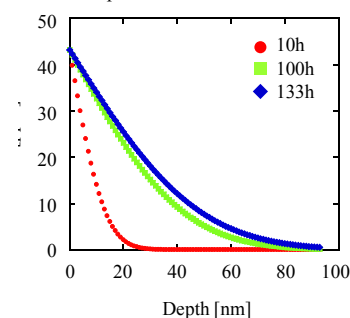
Fig. 4 Diffusion profiles for Ar diffusion in forsterite (Mg$_2$SiO$_4$). Diffusion profiles were determined by high precision stepped heating and noble gas mass spectrometry. Measured concentration gradients were fitted with complementary error-function curves.

Diffusion of neutron induced ^4He, ^{21}Ne and ^{37}Ar in forsterite

In order to introduce controlled amounts of the noble gases homogeneously into natural single forsterite crystals and synthesized polycrystalline forsterite, they were irradiated by neutrons in a nuclear reactor. The key reaction we exploit is $^{40}Ca(n,\alpha)^{37}Ar$, whereby ^{37}Ar is in situ produced in the forsterite (Mg$_2$SiO$_4$) doped with minor amount (~3wt%) of diopside (CaMgSi$_2$O$_6$). ^{38}Ar was produced by $^{37}Cl(n,\gamma)^{38}Cl(\beta^-)^{38}Ar$ from trace amount of Cl involved as impurity in the sample. Nuclear reaction of major elements associated with α-emission produces ^4He. Neon isotopes are produced by (n,α) reactions of Mg. Temperature dependent diffusive release of the in-situ produced noble gas nuclides were then determined simultaneously by high precision stepped heating in vacuum and noble gas mass spectrometry. In stepwise heating, the sample to be analyzed was dropped into the crucible and then heated at a given temperature (400 ºC to 1900 ºC) for a given time (15 to 60 minute), and after extracted gases were measured, the same sample was heated again at a higher temperature to release gases from higher retentive sites of the sample. Because the noble gas components even in the same sample shows different origins (e.g. crystal lattice, grain boundary, inclusion and crystal surface), they will have different release patterns during stepwise heating. The determined diffusivities exhibit the Arrhenius behavior at a

temperature range from 900 to 1300 °C. Although $D(^4\text{He})$ is about one order of magnitude higher than $D(^{21}\text{Ne})$, $D(^{37}\text{Ar})$ and $D(^{38}\text{Ar})$, activation energies (Ea) fall in a range from 30 to 130 kJ/mol for all noble gas isotopes. No systematic difference in diffusivities for single crystal- and polycrystalline-forsterite was observed. This suggests that a role of grain boundaries for transporting the gases is negligible when noble gases are already incorporated in mineral lattice and then they diffuse out from the samples.
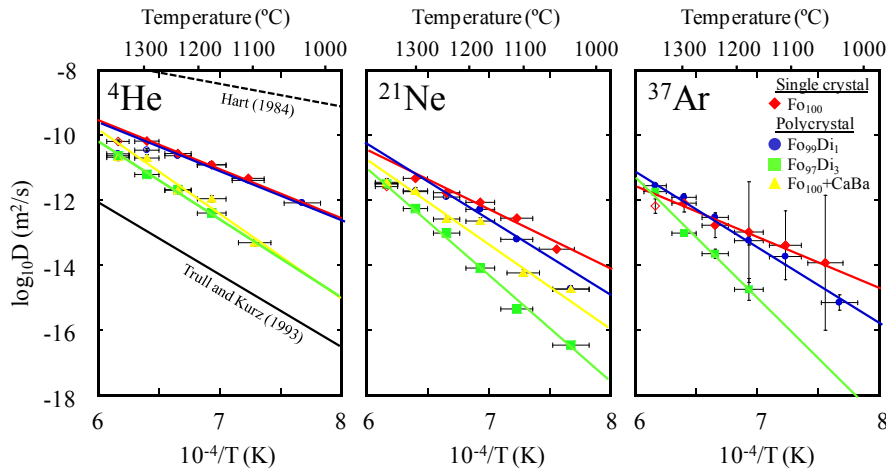

Fig.5 Arrhenius plot for apparent (a). ^{4}He (b). ^{21}Ne and (c). ^{37}Ar and ^{38}Ar diffusivity in natural and synthetic forsterite (Mg_2SiO_4), calculated for plane slab geometry. Black solid and dotted lines indicate previous measurements in olivine by Trull and Kurz (1993) and Hart (1984) respectively.

Implications for noble gas behavior in the Earth

In this study we performed two different diffusion experiments. The result from diffusive uptake of Ar shows between 10^{-9} and 10^{-11} times lower diffusivity than diffusion of neutron induced of ^{4}He, ^{21}Ne and ^{37}Ar. The geological phenomenon is more like the diffusion of neutron induced of ^{4}He, ^{21}Ne and ^{37}Ar experiment. Assuming time scale for diffusion from the values of D obtained in this study, which is the order of a few cm year^{-1}. Result from the Arrhenius plot shows the grain boundary in forsterite is no effective pathway for diffusion of noble gases. The values of noble gases diffusion coefficient are a 10^9 times higher than that of Mg^{2+} of forsterite. Rather those values were closer to the value of interstitial diffusion pathway. These suggest that noble gases were not use neighbor vacancy like the atoms sited in between normal lattice sites. Due to its inert nature, the diffusion of noble gases maybe a special case in which its intralattice migration is effectively controlled by distortion of crystal lattice to allow passage of the noble gas atoms into a new site.

It is well known that grain boundary act as an effective pathway for diffusion of elements those are incompatible to rock-forming minerals (i.e., $D_{gb} >> D_l$). Although noble gases are highly incompatible to forsterite, a major constituent of the Earth's mantle, the observation that their D_{gb} is negligible implies that mechanism in grain boundary diffusion for noble gases are quite different. The results of this study suggest that behavior of radiogenic noble gas isotopes, such as ^{4}He, ^{21}Ne and ^{40}Ar, in the mantle decouple from their parent element such as U, Th and K. This will give a new constraint for the evolution of noble gas isotope ratios of radiogenic / primordial noble gas isotope ratio (^{4}He/^{3}He, ^{21}Ne/^{22}Ne, and ^{40}Ar/^{36}Ar) over geologic timescales and scale length of several domains in the convecting mantle.