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論　文　目　次

Abstract

Chapter 1: Introduction

1.1. Atomic diffusion

1.1.1. Definition of atomic diffusion

1.1.2. Various factors relating to diffusion

1.2. Importance on diffusion studies in mantle minerals

1.2.1. Rheology

1.2.2. Mixing of chemical heterogeneities

1.2.3. Electrical conductivity

1.3. Previous diffusion studies in mantle minerals

1.3.1. Olivine

1.3.2. Wadsleyite

1.3.3. Ringwoodite

1.3.4. Silicate perovskite

1.4. Factors affecting depth resolution in SIMS measurements

1.5. Motivations of this study

Chapter 2: Experimental techniques

2.1. High pressure and high temperature generation

2.1.1. MAP-3000

2.1.2. MAP-1000
2.1.3. MAP-1500
2.2. Analytical techniques
2.2.1. Phase identification
2.2.2. Measurement of grain size
2.2.3. Estimation of water content
2.2.4. Analysis of diffusion profiles
2.2.5. Measurements of sputtering crater depth
Chapter 3: Si diffusion in Mg_2SiO_4 wadsleyite
3.1. Introduction
3.2. Experimental procedures
3.2.1. Starting material synthesis
3.2.2. Deposition of $^{29}SiO_2$ thin film
3.2.3. Examination of surface roughness produced by annealing
3.2.4. Reaction between wadsleyite and SiO_2 diffusing sources
3.2.5. Diffusion experiments
3.3. Results
3.3.1. Starting material synthesis
3.3.2. Thickness of $^{29}SiO_2$ thin film
3.3.3. Reaction between wadsleyite and SiO_2 diffusing sources
3.3.4. Examination of surface roughness produced by annealing
3.3.5. Diffusion experiments
3.4. Discussions
3.4.1. SIMS depth resolution
3.4.2. Temperature dependence
3.4.3. Diffusion kinetics and effective diffusivity
3.4.4. Comparison with previous work
3.5. Conclusions
Chapter 4: Si and O diffusion in (Mg,Fe) $_2SiO_4$ wadsleyite
4.1. Introduction
4.2. Experimental procedures
4.2.1. Starting material synthesis
4.2.2. Deposition of ^{29}Si and ^{18}O enriched (Mg,Fe) $_2SiO_4$
4.2.3. Diffusion experiments
4.3. Results
4.3.1. Starting material synthesis
4.3.2. Diffusion experiments
4.3.3. Measurements of roughness of surface and crater bottom
4.4. Discussions
4.4.1. SIMS depth resolution

4.4.2. Temperature dependences
4.4.3. Diffusion kinetics and effective diffusivity
4.4.4. The slowest diffusing element in wadsleyite
4.5. Conclusions
Chapter 5: Si and O diffusion in $(Mg,Fe)_2SiO_4$ ringwoodite
5.1. Introduction
5.2. Experimental procedures
5.2.1. Starting material synthesis
5.2.2. Deposition of ^{29}Si and ^{18}O enriched $(Mg,Fe)_2SiO_4$
5.2.3. Diffusion experiments
5.3. Results
5.3.1. Starting material synthesis
5.3.2. Diffusion experiments
5.4. Discussions
5.4.1. SIMS depth resolution in this study
5.4.2. Temperature dependencies
5.4.3. Diffusion kinetics and effective diffusivity
5.4.4. The slowest diffusing element in ringwoodite
5.5. Conclusions
Chapter 6: Geophysical Implications
6.1. Comparison of diffusion rates in mantle minerals
6.1.1. Si diffusion
6.1.2. O diffusion
6.2. Deformation mechanisms in the mantle transition zone
6.3. Viscosity in the mantle transition zone
6.4. Rheology of the subducting slabs
6.5. Effect of water on Si diffusivity in wadsleyite
6.6. Conclusions
Acknowledgements
References

論 文 内 容 要 旨

In this work, diffusion rates on polycrystalline wadsleyite and ringwoodite have been determined at pressures between 16 to 22 GPa and temperatures between 1400 to 1600 ℃. These conditions are relevant to the Earth's mantle transition zone. High pressure experiments were conducted using a Kawai-type multi-anvil high pressure apparatus. Pre-synthesized polycrystalline wadsleyite or ringwoodite were used as starting materials. Diffusing sources were deposited on the surface of polished synthesized wadsleyite and ringwoodite. After that, diffusion annealing experiments were conducted. The diffusion profiles were obtained by a depth

profiling mode using a secondary ion mass spectrometer (SIMS).

In nominally dry Mg_2SiO_4 wadsleyite, Si diffusion rates were examined at the conditions of 18 GPa and 1450－1600 ℃ using the ^{29}Si enriched SiO_2 thin film as a diffusing source. In the $^{29}SiO_2$ deposition, a high vacuum evaporation system was utilized using a rhenium as a heating generator. An oxide activity was controlled by adding SiO_2 powder.

In nominally dry $(Mg,Fe)_2SiO_4$ wadsleyite and ringwoodite, temperature dependencies on Si and O diffusion rates were determined using the ^{29}Si and ^{18}O enriched $(Mg,Fe)_2SiO_4$ thin film as a diffusing source at the conditions of 1400－1600 ℃ and at 16 GPa and 22 GPa. In depositing the ^{29}Si and ^{18}O enriched $(Mg,Fe)_2SiO_4$, Pulsed Laser Deposition (PLD) were employed in order to ensure the deposition of stoichiometric thin films. An oxygen fugacity and an oxide activity were controlled by putting Ni－NiO and SiO_2 powder, respectively.

All of the diffusion profiles obtained were composed of volume diffusion and grain-boundary diffusion regimes. Therefore, temperature dependencies in volume diffusion and grain-boundary diffusion rates have been determined simultaneously.

Their diffusion rates are characterized as follows:

In Mg_2SiO_4 wadsleyite with ~69 wt. ppm H_2O,

$$D^{l}_{Wd_Si\ i} = 6.71\times10^{-11}\ [m^2s^{-1}]\ \exp(-323\ [kJ\ mol^{-1}]/RT)$$

$$\delta D^{GB}_{Wd_Si} = 6.91\times10^{-20}\ [m^3s^{-1}]\ \exp(-186\ [kJ\ mol^{-1}]/RT)$$

In $(Mg,Fe)_2SiO_4$ wadsleyite with ~79 wt. ppm H_2O,

$$D^{l}_{FeWd_Si} = 1.51\times10^{-6}\ [m^2s^{-1}]\ \exp(-442\ [kJ\ mol^{-1}]/RT)$$

$$\delta D^{GB}_{FeWd_Si} = 5.56\times10^{-14}\ [m^3s^{-1}]\ \exp(-346\ [kJ\ mol^{-1}]/RT)$$

$$D^{l}_{FeWd_O} = 4.97\times10^{-10}\ [m^2s^{-1}]\ \exp(-301\ [kJ\ mol^{-1}]/RT)$$

$$\delta D^{GB}_{FeWd_O} = 6.89\times10^{-16}\ [m^3s^{-1}]\ \exp(-264\ [kJ\ mol^{-1}]/RT)$$

In $(Mg,Fe)_2SiO_4$ ringwoodite with ~220 wt. ppm H_2O,

$$D^{l}_{FeRw_Si} = 6.55\times10^{-7}\ [m^2s^{-1}]\ \exp(-439\ [kJ\ mol^{-1}]/RT)$$

$$\delta D^{GB}_{FeRw_Si} = 7.63\times10^{-16}\ [m^3s^{-1}]\ \exp(-311\ [kJ\ mol^{-1}]/RT)$$

$$D^{l}_{FeRw_O} = 3.45\times10^{-7}\ [m^2s^{-1}]\ \exp(-416\ (\pm96)\ [kJ\ mol^{-1}]/RT)$$

$$\delta D^{GB}_{FeRw_O} = 2.03\times10^{-15}\ [m^3s^{-1}]\ \exp(-306\ (\pm108)\ [kJ\ mol^{-1}]/RT)$$

Si diffusion rates in Mg_2SiO_4 wadsleyite with ~69 wt. ppm H_2O is about three times slower than those with ~507 wt. ppm H_2O [*Shimojuku et al.*, 2004].

In both $(Mg,Fe)_2SiO_4$ wadsleyite and ringwoodite, it was found that Si diffusion rate is slower than O diffusion. Si is the slowest diffusing element in both $(Mg,Fe)_2SiO_4$ wadsleyite and ringwoodite compared with previously reported Mg－Fe interdiffusion rates. Therefore, Si may be rate-controlling species in high－temperature creep processes involving diffusion creep and climb-controlled dislocation creep. Compared with previously reported Si diffusion rates in olivine and perovskite, differences of Si diffusion rates in mantle minerals are characterized as follows: olivine < ringwoodite < wadsleyite < perovskite.

In both diffusion creep and dislocation creep regimes, the viscosities calculated from Si diffusion data of high-pressure phases obtained in this study are much lower than those from previously reported creep law parameters constructed based on deformation data of analogous spinel (Ni_2GeO_4) at lower pressures. Compared with mantle viscosity inferred from geophysical observations and the viscosities in diffusion and dislocation creep estimated from diffusion data, the mantle viscosity is explained by a grain size of 1－10 mm in

diffusion creep regime and a stress of 1−10 MPa in dislocation creep regime. Consequently, plausible grain size and stress in the mantle transition zone may be 1−10 mm and 1−10 MPa. The deformation mechanism dominant in the mantle transition zone is likely to be either diffusion creep or dislocation creep.

If a grain size of ringwoodite decreases to be less than 100 μm as a consequence of grain size reduction after olivine-ringwoodite transformation in cold subducting slabs, the ringwoodite is likely to be deformed by the diffusion creep. Some portions in cold subducting slabs may become softer than the surrounding mantle when the grain size of ringwoodite decreases to be below 1 μm after the olivine-ringwoodite transformation.

論文審査の結果の要旨

下宿彰提出の論文は，マントル遷移層の主要構成鉱物であるウォズレアイトとリングウッダイト中の原子の拡散速度を明らかにし，マントル遷移層と沈み込むスラブの流動特性を考察したしたものである。本研究においては川井型高圧発生装置を用い，拡散プロファイルの測定には二次イオン質量分析計を用いた。Mg_2SiO_4 ウォズレアイト多結晶体を用いて，$^{29}SiO_2$ を拡散源とし，Si の拡散速度を 18 GPa，1450-1600 ℃の条件下で測定した。また，$(Mg,Fe)_2SiO_4$ ウォズレアイトとリングウッダイト多結晶体を用いて，^{29}Si と ^{18}O に富む $(Mg,Fe)_2SiO_4$ を拡散源とし，Si と O の拡散速度をそれぞれ 16 GPa，1400-1600 ℃，22 GPa，1400-1600 ℃で測定した。

実験結果の詳細は以下のようにまとめられる。本研究において，含水量が～69 wt. ppm の Mg_2SiO_4 ウォズレアイト中の Si の拡散速度は，Shimojuku et al. (2004) によって得られた含水量が～507 wt. ppm のウォズレアイトよりも約 0.5 桁遅い。また，$(Mg,Fe)_2SiO_4$ ウォズレアイトとリングウッダイトにおいて，どちらも Si の拡散速度は O の拡散速度よりも遅く，Si が結晶中の変形を律速していることが明らかになった。

地球物理学的観測によるマントルの粘性率と，Si の拡散速度から計算された粘性率を比較すると，マントル遷移層は，拡散クリープと転位クリープの境界領域に当たり，温度・応力・歪速度・粒径によって，いずれかの変形機構も卓越し得る。マントル遷移層の粒径が 1-10 mm の場合には，拡散クリープで，また，応力が 1-10MPa のときには転位クリープによる変形で観測された粘性値を説明することが出来る。低温の沈み込むスラブ内では，オリビン-リングウッダイト相転移に伴い粒径が，100 μm 以下まで減少したときには拡散クリープによる変形が支配的になり，さらに粒径が 1 μm 以下まで減少すれば周りのマントルよりも柔らかくなる可能性があり，マントル遷移層に沈み込んだスラブが大変形する原因となっている可能性があることが明らかになった。

以上の研究は，下宿彰が自立して研究活動を行うに必要な高度の研究能力と学識を有することを示している。したがって，下宿彰提出の博士論文は，博士（理学）の学位論文として合格と認める。