High silicon self-diffusion coefficient in dry forsterite

Tomoo Katsura\textsuperscript{a}, Hongzhan Fei\textsuperscript{a}, Chamathni Hegoda\textsuperscript{b}, Daisuke Yamazaki\textsuperscript{b}, Michael Wiedenbeck\textsuperscript{c}, Hisayoshi Yurimoto\textsuperscript{d}, Svyatoslav Shcheka\textsuperscript{a},

\textsuperscript{a}Bayerisches Geoinstitut, University of Bayreuth, Germany
\textsuperscript{b}Institute for Study of the Earth’s Interior, Okayama University, Japan
\textsuperscript{c}Helmholtz Centre Potsdam, Germany
\textsuperscript{d}Department of Natural History Sciences, Hokkaido University, Japan

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Introduction:

$D_{Si}$ in $Fo$

**Olivine**: the main upper mantle constituent.
- ~60% in volume (Ringwood, 1991)

**Forsterite**: Mg-rich end member of olivine.
- Similar rheology properties as $Ol$ (Durham and Goetze, 1977)

**Plastic deformation**: controlled by
- Diffusion creep and dislocation creep
- controlled by diffusion (Weertman, 1999; Frost, H.J., Ashby, M.F., 1982)

**Si**: rate controlling element.
- Slowest diffuse species
  (Costa and Chakraborty, 2008; Shimojuku et al., 2009; Dobson et al., 2008)

$D_{Si}$ in $Fo$: essential for understanding the upper mantle rheology.
Introduction: previous studies

$D_{Si}$ in dry $OI$ at 1 atm

$\log D_{Si} (m^2/s)$

-22.5

$OI$ (Dohmen et al., 2002)

$Fo$ (Jaoul et al., 1981)

1600 K
1 atm
Dry
Introduction: previous studies

$D_{Si}$ in dry $Ol$ at 1 atm

Large discrepancy between measured $D_{Si}$ from diffusion experiments and estimated from deformation experiments.

--- ~ 2 -- 3 orders of magnitude
Introduction: previous studies

\( D_{Si} \) in dry \( OI \) at high \( P \)

Large discrepancy between high pressures and ambient pressure.
This study

**Determine** $D_{Si}$

**Sample**
- *Fo* single crystal
- Fine polished

**Deposition**
- $^{29}$Si enriched Mg$_2$SiO$_4$

**Annealing**
- 1 atm -- 13 GPa
- 1600 & 1800 K
- Dry ($C_{H2O} < 1$ ppm)
  
  Even 10 ppm H$_2$O largely enhances $D_{Si}$
  
  (Costa & Chakraborty, 2008)

**SIMS** (Secondary ion mass spectrometry)
- Obtain diffusion profile

**Introduction:**

- Determine $D_{Si}$
- Obtain diffusion profile
Sample

**Synthetic Fo** (Mg$_2$SiO$_4$)

--Major impurity: Ir (~80 ppm) by ICP-MS

--cored into disks

--1 mm thickness, 1 mm diameter

--normal to $b$-axis

(longest crystallographic axis)

Experimental methods

*Fo* single crystal
Experimental methods

Deposition

Thin film deposition:
-- $^{29}\text{Si}$ enriched $\text{Mg}_2\text{SiO}_4$ film
-- Thickness: $\sim 300$-$500$ nm
-- Covered by $\sim 100$ nm $\text{ZrO}_2$
-- Pulsed laser deposition technique (PLD)

Pulsed laser deposition system at Ruhr University of Bochum
Annealing

--- Multi-anvil or ambient \( P \) furnace apparatus
--- 0 - 13 GPa
--- 1600 & 1800 K
--- 0 - 41 h

(Fei et al., EPSL, 2012)
Experimental methods

SIMS analysis

Cameca IMS-6f
(Helmholtz Centre Potsdam)

Crater after SIMS analysis

Principle of SIMS

Example of diffusion profile

$$c = \frac{c_0 - c_1}{2} erf\left(\frac{x-h}{\sqrt{4Dt - L^2(\sigma)}}\right) + \frac{c_0 + c_1}{2}$$
Results

FT-IR spectrum

Absorption (cm$^{-1}$)

Wave number (cm$^{-1}$)

Without annealing, $C_{H_2O} < 1$ ppm

3 GPa, 1600 K, $C_{H_2O} < 1$ ppm

1 GPa, 1600 K, $C_{H_2O} < 1$ ppm

No determinable water by FT-IR
Results

$D_{Si} \text{ vs } P \text{ in } Fo$

- Negative $P$ dependence of $D_{Si}$.
- $\Delta V = 1.7 \pm 0.4 \text{ cm}^3/\text{mol}$. $\Delta E = 410 \pm 30 \text{ kJ/mol}$.

$D_{Si} = A_0 \exp\left(-\frac{\Delta E + P\Delta V}{RT}\right)$
Compare with previous $D_{Si}$

$D_{Si}$: 2--3 orders of magnitude higher than previous $D_{Si}$.

- **No ZrO$_2$** film was used in Jaoul (1981) and Dohmen (2002).
- **Large deformation of isotopically enriched film.**

**Without ZrO$_2$ film**
Horizontal shrink

**With ZrO$_2$ film**
Normal surface
Normal surface With ZrO$_2$, 1 atm, 1600 K

No ZrO$_2$, 1 atm, 1600 K

Isotopically enriched films horizontally shrank.
Profiles of \textit{none-ZrO}_2 \& \textit{with-ZrO}_2 \textit{samples}

\begin{itemize}
\item No ZrO\textsubscript{2}, horizontal move
\item 1 atm, 1600 K, \textbf{12} hours
\item With ZrO\textsubscript{2}, normal sample
\item 1 atm, 1600 K, \textbf{13} hours
\end{itemize}

(Fei et al., EPSL, 2012)
Role of ZrO$_2$

Profiles at 1 atm:
without ZrO$_2$ $<<$ with ZrO$_2$

Profiles at high $P$:
without ZrO$_2$ $\approx$ with ZrO$_2$

Large difference is caused by:
Shrink of isotopically enriched thin film, not by presence of ZrO$_2$.
ZrO$_2$ prevents the horizontal shrink.

(Fei et al., EPSL, 2012)
Discussion ---2

\[ D_{si} \text{ well explains creep rate} \]

- [O\text{I} (Estimated from deformation)] (Goetze & Kohlstedt, 1973)
- [O\text{I} (Dohmen et al. 2002)]
- \[ F\text{o} \text{ (Jaoul et al. 1981)} \]

1600 K
1 atm
Dry
Discussion ---2

$D_{si}$ well explains creep rate

- 2--3 orders of magnitude higher than previous studies of $D_{si}$ at ambient $P$.
- Explains the high creep rate.
Discussion ---3

**$D_{si}$ in Fo, Wd, and Rw**

- Linear relationship of $D_{si}$ in Fo, Wd, and Rw.
- Effect of iron, water, and structural difference of (Mg,Fe)$_2$SiO$_4$ on $D_{si}$ is small.

**Figure:**

- Fo (This study)
- Wd (S2009)
- Rw (S2009)

S2009: Shimojuku et al. (2009)
Iron and water bearing Wd and Rw.

(Fei et al., EPSL, 2012)
Discussion ---4

$D_{si}$ and viscosity in the upper mantle

- Positive $T$ dependence. Negative $P$ dependence.
- $D_{si}$ slightly increases with depth.
- $\eta$ slightly decreases with depth.

(assuming inversely proportional to $D_{si}$)

Based on adiabatic geothermal $T$ from Katsura et al. (2010)
$D_{si}$ in wadsleyite from Shimojuku et al. (2009)
Effect of water

$D_{Si}$ in olivine
1473 K

"Dry", 1 atm

2 GPa

(Costa and Chakraborty, 2008)

(Dohmen et al., 2002)

Costa & Chakraborty (2008):
Large $C_{H_2O}$ dependence of $D_{Si}$.
45 ppm H$_2$O => 3 log $D_{Si}$. 

Discussion ---5
Effect of water

$D_{Si} \propto (C_{H_2O})^{0.32 \pm 0.07} \approx (C_{H_2O})^{1/3}$

1000 ppm H$_2$O $\Rightarrow$ 1 log $D_{Si}$. Small $C_{H_2O}$ dependence.

Discussion ---5

$D_{Si} = A_0 C_{H_2O}^r \exp(-\Delta H/RT)$

(Fei et al., Manuscript submitted)
Summary

1. **Negative $P$ dependence** of $D_{Si}$ in dry $Fo$ (1 atm--13 GPa)
   - $\Delta V = 1.7 \pm 0.4 \text{cm}^3/\text{mol}$
   - $\Delta E = 410 \pm 30 \text{kJ/mol}$

2. $D_{Si}$ **much higher** than previous studies at 1 atm
   - 2—3 orders of magnitude higher
   - Large deformation of coated film

3. **$D_{Si}$ at 1 atm**
   - Explains the high creep rates in deformation studies

4. **$D_{Si}$ and viscosity in the upper mantle:**
   - $D_{Si}$ slightly increases with depth
   - $\eta$ slightly decreases with depth

5. **Effect of $H_2O$ on $D_{Si}$ is very small:**
   - $1000 \mu g/g H_2O => 1 \log D_{Si} << 45 \text{ ppm} H_2O => 3 \log D_{Si}$
   - Effect of water on upper mantle rheology is very small based on Si self-diffusion coefficients.