SIT03-03 会場:106 時間:5 月 25 日 14:45-15:00

Defect chemistry and diffusion in hydrous forsterite
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FEI, Hongzhan[1*] ; KATSURA, Tomoo[2]
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[1]Institute for Study of the Earth Interior, Okayama University, Misasa, Tottori, 682-0193, Japan, [2]Bayerisches Geoinstitut, University of Bayreuth, 95447, Bayreuth, Germany
[1]Institute for Study of the Earth Interior, Okayama University, Misasa, Tottori, 682-0193, Japan, [2]Bayerisches Geoinstitut, University of Bayreuth, 95447, Bayreuth, Germany

The mass transport of olivine, which reflects the flow in the Earth's upper mantle, is controlled by the diffusion of structural elements. On the other hand, the diffusivity of an ion in the crystal is dominated by the motion of point defects of the corresponding sites. It is thus necessary to know the diffusivities of elements in olivine in the view of defect chemistry so as to investigate the behaviors in the upper mantle conditions.

Fei et al. (2013, 2014) systematically measured silicon and oxygen self-diffusion coefficients (D_{Si} and D_O, respectively) in iron-free forsterite as functions of water contents, showing that $D_{Si} \propto C_{H2O}^{0.32(7)}$, $D_O \propto C_{H2O}^{0.05(6)}$. These water-content exponents are much smaller than that expected on the basis of the assumption that self-diffusion coefficient of a chemical species is simply proportional to its defect density. Therefore, a new defect chemistry model is required to explain the above relationships.

Silicon diffusion:

The D_{Si} should be proportional to the density of silicon defects, namely, $D_{Si} \propto [\mathrm{V}_{Si}'''']$. On the other hand, Si^{4+} is tightly surrounded by four-coordinated O^{2-}, and therefore, migration of Si^{4+} should be enhanced if a surrounding O^{2-} is missing. We can expect that a certain proportion of V_{Si}'''' is associated with V_O •• due to their excess charges with the opposite signs. As a result, Si migration is probably dominated by V_O •• -associated V_{Si}''''. D_{Si} is thus also proportional to $[\mathrm{V}_O \bullet\bullet]$ and we have,

$D_{Si} \propto [\mathrm{V}_{Si}''''] \times [\mathrm{V}_O \bullet\bullet]$.

Under the charge neutrality condition of $[(OH)_O \bullet] = 2[\mathrm{V}_{Mg}'']$ in hydrous forsterite, we have $[\mathrm{V}_{Si}''''] \propto (f_{H2O})^{2/3}$ and $[\mathrm{V}_O \bullet\bullet] \propto (f_{H2O})^{-1/3}$. Therefore,

$D_{Si} \propto [\mathrm{V}_{Si}''''] \times [\mathrm{V}_O \bullet\bullet] \propto (f_{H2O})^{1/3}$,

which agrees well with the experimental results: $D_{Si} \propto (C_{H2O})^{0.32(7)}$ (Fei et al., 2013).

Oxygen diffusion:

In hydrous olivine/forsterite, hydrogen exists as hydroxyl, $(OH)^-$. Oxygen ions could diffuse either by hopping of O^{2-} without H^+ or by hopping of O in $(OH)^-$. Because H+-associated O has a lower Coulomb force due to the excess charge by H^+, the hopping probability of $(OH)^-$ should be higher than that of O^{2-}. Thus, the O diffusion should be dominated by O^{2-} of $(OH)^-$. As a result, we have,

$D_O \propto [\mathrm{V}_O] \times ([O^{2-}]^{hopping} + [(OH)^-]^{hopping}) \approx [\mathrm{V}_O \bullet\bullet] \times [(OH)^-]^{hopping}$.

There are mainly three types of (OH)- in hydrous olivine/forsterite: (a) $(OH)_O \bullet$ associated with V_{Mg}''; (b) $(OH)_O \bullet$ associated with V_{Si}''''; (c) $(OH)_O \bullet$ un-associated with any cation vacancies. The un-associated $(OH)_O \bullet$ should have much higher mobility than V_{Si}'''' or V_{Mg}'' associated ones due to the Coulomb force and therefore the O diffusion is probably dominated by un-associated $(OH)_O \bullet$. Thus,

$D_O \propto [\mathrm{V}_O \bullet\bullet] \times [(OH)^-]^{hopping} \approx [\mathrm{V}_O \bullet\bullet] \times [(OH)_O \bullet]^{un-associated}$.

Under the charge neutrality condition of $[(OH)_O \bullet] = 2[\mathrm{V}_{Mg}'']$, we have $[\mathrm{V}_O \bullet\bullet] \propto (f_{H2O})^{-1/3}$ and $[(OH)_O \bullet]^{un-associated} \propto (f_{H2O})^{1/3}$. Therefore,

$D_O \propto [\mathrm{V}_O \bullet\bullet] \times [(OH)_O \bullet]^{un-associated} \propto (f_{H2O})^0$.

This model suggests that D_O is independent from C_{H2O}, which agrees well with the experimental results, $D_O \propto C_{H2O}^{0.05(6)}$ (Fei et al., 2014).

Fei et al. (2013), *Nature* **498**, 213-215.
Fei et al. (2014), *JGR* **119**, 7598-7606.

キーワード: defect chemistry, self-diffusion coefficient, silicon, oxygen, water content, forsterite
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