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授与した学位	博士		
専攻分野の名称	学 術		
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学位授与の要件	自然科学研究科 地球惑星物質科学 専攻 (学位規則第4条第1項該当)		
学位論文の題目	Electrical conductivity and redox kinetics of nominally anhydrous minerals (NAMs) in the upper mantle (上部マントル無水鉱物の電気伝導度と酸化還元カイネティクス)		
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<b>学位論文内容の要旨</b>			
<p>Electrical conductivity is a powerful tool to investigate and quantify the influence of water and oxygen fugacity (<math>fO_2</math>) on nominally anhydrous minerals (NAMs). In this study, electrical conductivity of San Carlos clinopyroxene aggregates with various water contents were measured. The results showed that the conductivity increases with increasing water content in clinopyroxene. Two groups of activation enthalpies were identified, i.e. Low H Group of 0.70-0.75 eV and High H Group of 1.23-1.37 eV. Contrary to previous view that all hydrogens contribute to increasing conductivity equally, only a limited amount (20%-40%) of hydrogen was found to act as effective charge carrier in clinopyroxene at high temperatures.</p> <p>To clarify the contribution of hydrogen associated with different sites, electrical conductivity of pre-sintered hydrous forsterite aggregate under different buffered conditions (1 wt% MgO added or 1 wt% SiO<sub>2</sub> added) was measured. The result showed that higher electrical conductivity and activation enthalpy was observed in SiO<sub>2</sub> buffered forsterite when assuming a same water content. And the difference in their IR spectra showed that hydrogen in Mg site and Si site do have different contribution to conduction. However, hydrogen incorporation mechanism in SiO<sub>2</sub> buffered forsterite changed at higher pressure (8 GPa) and that pressure effect outweighed the effect of buffer. The fraction of hydrogen contributing to electrical conduction is reduced. Therefore, in real Earth case (SiO<sub>2</sub> buffered condition), electrical conductivity of hydrous forsterite might reach a maximum value at around 4 GPa and then decreases with depth.</p> <p>To know the iron effect on electrical conductivity, conductivity of synthesized hydrous olivine with different water contents at NNO or IW buffered condition was measured. The result shows high activation enthalpy of ~ 1.2 eV for either NNO or IW buffered olivine, which is much higher than previous studies of &lt; 1.0 eV. The conductivity of reduced olivine is higher than that of oxidized one and with increasing water content, its difference is likely to be smaller.</p> <p>To know the redox kinetics in olivine, diffusion experiments were performed using diffusion couple method in dry system. The change of <math>fO_2</math> can be quantified as a diffusion process. Diffusion coefficient in oxidized olivine showed strong composition dependence while that for reduced sample is near constant, indicating that redox mechanism at different redox state is different. The diffusivity is on the order of <math>10^{-11}</math> to <math>10^{-13}</math> with an activation energy of ~ 235 kJ/mol. In this case, the full homogenization of subducted slab is impossible even assuming the entire Earth age. So the oxidized subducted slab can supply oxygen to the core-mantle boundary, if it keeps dry state.</p>			

## 論文審査結果の要旨

Chengcheng Zhao has studied electrical conductivity and redox kinetics of nominally anhydrous minerals in the upper mantle during intensive 5-years PhD course. Electrical conductivity of nominally anhydrous mantle minerals has been thought to be sensitive to water in their crystal structure. Combining the electromagnetic observations, it can allow us to estimate water content. However, laboratory measurements investigating effect of water on electrical conductivity of olivine have shown a large discrepancy. To solve this problem, she has studied effect of water on electrical conductivity of mantle minerals at various well-controlled buffered conditions.

This thesis is composed of 4 parts as follows: 1) Electrical conductivity of clinopyroxene aggregates with various water contents. 2) Electrical conductivity of MgO- and SiO<sub>2</sub> buffered forsterite aggregates. 3) Electrical conductivity of olivine aggregates at different oxygen fugacity. 4) Redox kinetics of olivine aggregates.

A series of experiments gave new insights on site-specific hydrogen mobility in mantle minerals. The mobility of hydrogen entering into Si site shows low activation energy related to proton conduction, whereas that in Mg site shows high activation energy related to  $[V]_{Mg}$ . The conductivity of reduced olivine is higher than that of oxidized one and with increasing water content. Thus, this study suggested that inconsistency of the previous studies is caused by disequilibrium of hydrogen-related defect in their measured samples. To evaluate the time to reach equilibrium, the redox kinetics experiments in olivine aggregates were performed using diffusion couple method. The diffusivity is on the order of  $10^{-11}$  to  $10^{-13}$  with an activation energy of  $\sim 235$  kJ/mol. This result suggests that the annealing time for synthesis of sample in the most of previous studies is not sufficient to reach the defect equilibrium. In addition, the full homogenization of subducted slab is impossible even assuming the entire Earth age. The oxidized subducted slab can supply oxygen to the core-mantle boundary.

Ph D. defense for Chengcheng Zhao was held on 13th February. We considered that this thesis includes the new insights on site occupancy and mobility of hydrogen in olivine and contributes to the Earth science. Therefore, we judged that this thesis is suitable to be accepted as a dissertation of Doctor of Philosophy in Okayama University.