

学位論文の要旨

Abstract of Thesis

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学位論文題目 Title of Thesis (学位論文題目が英語の場合は和訳を付記)

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ンेटィクス

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Water is known to affect physical and chemical properties of mantle materials significantly, such as deformation, diffusion, melting temperature and so on. Electrical conductivity is a powerful tool to investigate and quantify the water influence on nominally anhydrous minerals (NAMs), and to infer water budget in the Earth's interior when combined with magnetotelluric data. Water incorporation and hydrogen self-diffusion mechanisms in NAMs can be constrained by electrical conductivity measurement when combined with IR spectra. We can infer the hydrogen migration mechanism whether a certain site or jump is caused by water or the existence of fluid or melt due to their different responses to impedance spectroscopy. The importance of oxygen fugacity in the Earth's interior has been overlooked, despite it covers as large as 7 log units. Iron and other multi-valence elements exist in NAMs in different valences, depending on the redox state of the minerals at their formation time. With continuous subduction of oxidized slab, mantle is continuously altered, and the redox state of minerals is changed to some extent which might result in a different property. Investigating the influence of oxygen fugacity on physical and chemical properties and understanding the redox kinetics operate behind them thus becomes important.

The origin of the high conductive region (60-120 km) observed from magnetotelluric data near the East Pacific Rise remains unsolved. Conductivity enhanced by hydrous olivine and orthopyroxene was insufficient to account for this anomaly. Clinopyroxene could be a possible candidate because water tends to partition into it rather than olivine and orthopyroxene ($D_{\text{cpx/ol}} = 12.5-88$). So, the electrical conductivity of San Carlos clinopyroxene aggregates with various water contents were measured under Ni-NiO buffer at 1.5 GPa and

600-1200 K in a DIA-type apparatus. The conductivity increases with increasing water content in clinopyroxene, but it still cannot account for the high conductive regions. 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.

This finding raised the possibility of site-dependent hydrogen diffusion and conduction. 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% SiO₂ added) was measured at 500-900 K, 4 GPa and 8 GPa, using multi-anvil apparatus. The result showed that though MgO buffered forsterite could incorporate 10 times more water content at 4 GPa, higher electrical conductivity and activation enthalpy was observed in SiO₂ buffered forsterite when assuming a same water content. Since the IR spectra of MgO buffered forsterite showed sharp typical peaks at high wavenumbers, while SiO₂ buffered one showed broad peaks across high and low wavenumbers, it is possible that hydrogen in Mg site and Si site do have different contribution to conduction with the former slower. However, at higher pressure (8 GPa), the IR spectra of MgO buffered forsterite remained the same while IR spectra of SiO₂ buffered sample became similar to that of MgO buffered one, regardless of the amount of SiO₂ buffer. It suggests that the hydrogen incorporation mechanism in SiO₂ buffered forsterite changed and that pressure effect outweighed the effect of buffer. The activation energy and electrical conductivity decreased when compared with SiO₂ buffered one, which means that the fraction of hydrogen contributing to the electrical conduction is reduced. Therefore, in real Earth case (Si buffered condition), electrical conductivity of hydrous forsterite might reach a maximum value at around 4 GPa and then decreases with depth.

Since in the upper mantle, oxygen fugacity varies from +5 to -2 Δ IW, up to 7 orders, its possible effects on conductivity of iron-bearing olivine cannot be neglected. On the other hand, when comparing the conductivity of hydrous forsterite and olivine buffered at Ni-NiO condition with a same water content, it was found that the contribution from iron is negligible, which raised a doubt about the influence of iron on electrical conductivity of olivine. Therefore, electrical conductivity of synthesized hydrous olivine with different water contents at NNO or IW buffered condition was measured at 4 GPa, 500-1000 K, using a Kawai-type multi-anvil apparatus. Electrical conductivity of San Carlos olivine (SCO) with doped water at different duration and NNO buffered condition was also measured. The result shows high activation enthalpy of \sim 1.2 eV for either NNO or IW

buffered olivine, which is much higher than previous studies of < 1.0 eV. The conductivity of SCO with intermediate water content which annealed for long time shows a same high activation enthalpy. However, the SCO with much shorter annealing time showed smaller activation enthalpy of ~ 0.8 eV, consistent with previous studies, indicating that the smaller activation enthalpy might be due to local hydrogen equilibrium because of short doping time. The conductivity of reduced olivine is higher than that of oxidized one and with increasing water content, its difference is likely to be small.

The opposite-to-expectation result calls for detailed investigation on the redox kinetic of olivine. On the other hand, redox budget of subducting slab bringing into mantle and the time scale needed for homogenization could help us understanding coevolution process between the oxidized slab and the surrounding reduced mantle. Therefore, diffusion experiments were performed using diffusion couple method which containing two pieces of reduced and oxidized samples at 1 GPa, 1100-1300 °C using piston-cylinder apparatus. The change of oxygen fugacity in dry olivine 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 10^{-11} to 10^{-13} 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. However, during subduction, speed of redox process is expected to operate faster in oxidized slab and with increasing homogenization, it slows down. The oxidized subducted slab can supply oxygen to the core-mantle boundary, if it keeps dry state.