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授与した学位	博 士
専攻分野の名称	理 学
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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5条第1項該当)
学位論文の題目	In situ spectroscopic study of water speciation in the depolymerized silicate melts (その場分光観察による低重合ケイ酸塩メルト中の水の溶解種平衡の研究)
論文審査委員	教授 中村 栄三 准教授 山下 茂 教授 神崎 正美 准教授 芳野 極 教授 Harald Behrens (Universitaet Hannover)

学位論文内容の要旨

The mechanism of water and silicate melts interaction has been a subject of many petrological studies. Recent development of *in situ* spectroscopic techniques made possible direct measurement of water speciation in hydrous silicate melts at simultaneous high temperatures and high pressures. Though *in situ* spectroscopic measurements on water speciation were performed in the wide temperature and pressure ranges for the polymerized rhyolitic melts, there is a lack of such data for the depolymerized silicate melts. It has been shown by previous studies that equilibrium constant for the water speciation reaction can change one order of magnitude at the temperature near the glass transition for the melts of different composition. On the other hand, compositional dependence of the water speciation equilibrium has never been evaluated at magmatic conditions. This study is the first attainment of *in situ* determination of the water speciation in the depolymerized sodium silicate melts at pressure to 1.7 GPa and temperature to 900 °C.

In situ measurements on hydrous silicate melts using hydrothermal diamond anvil cell (HDAC) technique require a thoroughly developed procedure for the determination of pressure during experiments. In the first part of my dissertation I describe the synthesis of ¹³C diamond pressure sensor suitable for the experiments in HDAC. I further examine the precision of pressure determination for this pressure sensor at simultaneous high temperatures and high pressures by cross calibration with the phase transitions of H₂O pressure medium and the pressure- and temperature-dependent Raman shift of α -quartz. Experimental results in the range of pressures to 4.2 GPa and temperatures to 500 °C showed that independent pressure and temperature calibrations of the ¹³C diamond Raman shift can be used for the determination of pressure with an accuracy better than ± 0.3 GPa inside the sample chamber of HDAC.

The second part of my dissertation is focused on the *in situ* spectroscopic measurements of water speciation in the depolymerized sodium disilicate melts. Sodium disilicate composition was chosen as a structural analog of basaltic melt in terms of the number of non-bridging oxygens per silica tetrahedron (NBO/T \approx 1.0). The pressure- and temperature-dependence of water speciation equilibrium were examined at 0.3-1.7 GPa and 800-900 °C by monitoring the change in near-infrared absorption bands of OH groups and H₂O molecules. Water speciation equilibrium in this melt was found to be independent of pressure, indicating that formation of OH groups at the expense of H₂O molecules is accompanied by a negligible volume change. The temperature dependence of equilibrium constant for the reaction between water species in the melt can be expressed by $\ln K_1 = 4.02 - 3698 / T$ (K). Compositional dependence of water speciation equilibrium at 800-900 °C is much weaker than that expected from the previously reported data for low-temperature range (200-320 °C).

論文審査結果の要旨

This study is the first attainment of direct observation of the water speciation equilibrium in depolymerized silicate melts at magmatic conditions.

Water is the first major volatile component dissolved in magma at depth, and is capable of promoting a major change in the physical properties of the melt. For understanding such a phenomenon, detailed knowledge of the water speciation in the melt is crucial. There has been demanded for experimental determination of the water speciation at magmatic conditions, but this has been obstructed by that the water speciation is not quenchable from high temperature and high pressure, particularly in depolymerized silicate melts. Chapter 1 reviews this problem and introduces *in situ* vibrational spectroscopy in an externally heated diamond anvil cell (DAC) as possible solution. Chapter 2 is devoted to enhancement of the *in situ* spectroscopy technique by improving optical pressure sensor. High quality polycrystalline ^{13}C diamond was successfully synthesized in a multi anvil apparatus, and its performance as optical pressure sensor was tested in a DAC using various pressure scales as reference. The results confirm that the ^{13}C diamond pressure sensor is reliable over a wide range of pressure and temperature with accuracy of ± 0.3 GPa. This achievement allowed to probe the water speciation in magmatic melts *in situ* as a function of pressure and temperature. Chapter 3 demonstrates results from a series of *in situ* vibrational spectroscopy/DAC experiments on the depolymerized sodium disilicate melts. The water speciation equilibrium in the melts is independent of pressure to 1.7 GPa at 800-900 °C, consistent with those previously reported in less depolymerized aluminosilicate melts. Another important finding is that the water speciation equilibrium in the melts is influenced by the silica network depolymerization, but to far less extent than that expected from the ambient glass data.

The results outlined above provide an outlook for a universal view of the water speciation equilibrium in magmatic melts with a wide coverage of pressure condition and silica network depolymerization. Chapter 2 is in press in a peer-reviewed scientific journal. Based on these observations, we, the dissertation committee, recommend that Nadezda Chertkova be awarded the degree of Doctor of Philosophy in Science.