Grain boundary water diffusion in microcrystalline quartz aggregates: high temperature in-situ infrared spectroscopy

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Diffusion of water in mineral grain boundaries and pores plays a key role in various Earth's dynamics. However, literature data on diffusion coefficients for grain boundary diffusion are limited because of the lack of appropriate methods. In this study, grain boundary water diffusion was studied by dehydration experiments of microcrystalline quartz aggregates using high temperature in-situ micro infrared (IR) spectroscopy.

The chalcedonic quartz (agate) sample was from Chayagawa, Oshamanbe, South-West Hokkaido, Japan. Under the optical polarizing microscope, the sample thin section exhibits the periodic rhythmic extinctions of fibers (Runzelbanderung) at a few micrometers intervals (i.e. length-fast chalcedony). Water contents as Si-OH and liquid-like water were determined to be 0.2 wt% of Si-OH and 0.3 wt% of H_2O by IR absorption bands around 4500 (Si-OH) and 5200 (H_2O)cm-1, respectively, using a thick sample thin section (450 um). The pore size distribution of the sample was evaluated by adsorption-desorption isotherms of nitrogen. Most of pore sizes are in the range of about 1 to 8 nm with a dominant size of about 2 nm. Doubly polished thin sections of the microcrystalline quartz were prepared with sizes of 3 x 3 mm and 130 ~240 um thick. In-situ infrared spectra of these thin sections in a heating stage were measured at constant temperatures of 350 ~500 C during 500 minutes.

The water IR bands of the microcrystalline quartz are at 3585 cm-1 and around 3425 cm-1 at room temperature (RT). These two bands are attributed to Si-OH and H_2O, respectively and shift to higher frequencies at a rate of 3.6 cm-1/100 C and 30 cm-1/100 C, respectively (Fukuda and Nakashima in press). In-situ IR spectra of the sample during the dehydration experiments at 500 C showed two additional bands at 3730 and 3660 cm-1. These bands have been considered to be due to completely isolated surface silanol and slightly hydrogen bonded isolated surface silanol, respectively, because of the loss of liquid-like water from grain boundaries and pores.

Since dominant dehydration of liquid-like water is observed at lower temperatures than 500 C with little decrease of Si-OH, changes with time in band areas around 3500 cm-1 in the in-situ IR spectra can be analyzed by kinetic models of dehydration of liquid-like water through pores and grain boundaries. A one-dimensional diffusion model of liquid-like water in the direction of thickness of the thin section was applied here to fit the 3500 cm-1 band area decrease curves. This diffusion simulation gave good fits to the experimental results yielding diffusion coefficients of ca. 10(-14)m2/sec at 350 C and ca. 10(-12)m2/sec at 500 C. By plotting these data against temperature in an Arrhenius diagram, the activation energy was obtained to be 115 + - 17 kJ/mol.

These diffusion coefficients and the activation energy are in agreement with those of grain boundary water diffusion in quartzite and calcite aggregates determined by H218O isotopic exchange experiments by Farver's group. These diffusion coefficients are much larger (about 10(-6)) than those for H in quartz single crystal with about half value of activation energy.