LETTER

Water at high temperatures in a microcrystalline silica (chalcedony) by in-situ infrared spectroscopy: physicochemical states and dehydration behavior

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In order to study physicochemical states of water in a chalcedony, thin sections were heated from room temperature (RT) to 400 °C at 50 °C intervals under an infrared (IR) microscope. A sharp IR absorption band due to hydroxyls (Si-OH) shifts linearly from 3585 cm⁻¹ at RT to 3599 cm⁻¹ at 400 °C (1.8 cm⁻¹/50 °C). A broad band due to H₂O shifts also linearly from 3425 cm⁻¹ at RT to 3535 cm⁻¹ at 400 °C (15 cm⁻¹/50 °C). These reversible band shifts, without dehydration, of hydroxyl and H₂O can be explained by the increasing hydrogen bond distance and the decreasing coordinating numbers of water molecules, respectively.

The in-situ IR spectra of the chalcedony thin sections during the isothermal heating at 550 °C showed a decrease of the total water band area. The RT spectra quenched from 550 °C indicated the major decrease of 3585 cm⁻¹ absorbance due to Si-OH with the minor decrease of the 3425 cm⁻¹ absorbance due to H₂O. These results suggest the dominant dehydration of Si-OH species from the microcrystalline quartz and the certain stability of liquid-like H₂O against dehydration in pores and grain boundaries.

Keywords: Hydroxyl, H₂O, Dehydration, In-situ IR spectroscopy, Hydrogen bond

INTRODUCTION

In the earth's surface materials, water exists as hydroxyls in crystal structures and as H₂O in pores and grain boundaries between minerals (e.g., Farver and Yund, 1992; Hiraga et al., 2001; Ito and Nakashima, 2002). One of simple materials including these hydroxyls and H₂O is chalcedonic quartz. Chalcedony is mostly composed of microcrystalline quartz (Flörke et al., 1991). Water in chalcedony was studied by infrared (IR) spectroscopy to be present as hydroxyls (Si-OH) mainly in crystal defects and as liquid water (H₂O) (e.g., Frondel, 1982; Graetsch et al., 1985). In-situ high temperature IR spectroscopy has been conducted for studying different states of water in quartz and chalcedony (Yamagishi et al., 1997; Suzuki and Nakashima, 1999). Suzuki and Nakashima (1999) reported high temperature IR spectra of hydroxyl associated with Al³⁺ defect in quartz single crystal and showed the remarkable OH frequency change upon $\alpha \rightarrow \beta$ quartz transitions. Yamagishi et al. (1997) showed IR spectral

changes with temperature for water in chalcedony. However, these authors did not discuss quantitatively changes with temperature of physicochemical states and dehydration behavior of water.

In this study, we first conducted in-situ step heating IR experiments of a chalcedony to evaluate frequency changes of hydroxyl and H₂O absorption bands at high temperatures. Then, in-situ isothermal IR spectra and their room temperature (RT) spectra quenched from high temperature have been studied. Dehydration behavior of hydroxyl and H₂O from the microcrystalline quartz will be reported.

MATERIALS AND EXPERIMENTAL METHODS

Doubly polished thin sections were prepared from a microcrystalline chalcedony block from Chayagawa, Oshima, South-West Hokkaido, Japan (the same block as Yamagishi et al., 1997). Under a polarizing microscope, the sample thin section shows the negative elongation (length-fast) and rhythmic extinctions (Runzelbänderung) (Graetsch, 1994). From powder X-ray diffraction, the size of crystallite was estimated to be 300 Å and weak

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Figure 1. In-situ high temperature IR spectra of the chalcedony thin section (170 μm thick) from RT to 400 $^{\circ}\text{C}$. Two bands at 3585 cm^{-1} and 3425 cm^{-1} (RT) are due to hydroxyl (Si-OH) and H_2O , respectively. The solid spectra upon heating from RT to 400 $^{\circ}\text{C}$ can be recovered upon cooling (dotted spectra from 400 $^{\circ}\text{C}$ to RT) indicating the reversibility of the bands without dehydration.

moganite peaks were observed in addition to dominant quartz peaks.

The IR instrument (FT-IR 620+IRT-30) used for experiments was equipped with a ceramic IR source, a KBr beam splitter and a MCT detector. A heating stage (Linkam TS-1500) was set on the sample stage of the IR microscope. The step heating experiments were carried out using the sample thin section. IR transmission spectra of the sample were first measured at RT and from 100 $^{\circ}\text{C}$ to 400 $^{\circ}\text{C}$ at 50 $^{\circ}\text{C}$ intervals. The isothermal dehydration experiments were conducted at 550 $^{\circ}\text{C}$ and dehydration behavior was monitored in-situ until 500 minutes. Another series of IR measurement was conducted at RT after quenching from heating for 0 to 500 minutes at 550 $^{\circ}\text{C}$.

RESULTS

Step heating experiments

The in-situ IR spectra from RT to 400 $^{\circ}\text{C}$ are shown in Figure 1. At RT, a sharp band at 3585 cm^{-1} and a broad

Figure 2. The band shifts of Si-OH and H_2O for high temperatures based on the data in Figure 1. The linear shifts of Si-OH and H_2O bands are observed (1.8 $\text{cm}^{-1}/50$ $^{\circ}\text{C}$ and 15 $\text{cm}^{-1}/50$ $^{\circ}\text{C}$, respectively).

band around 3425 cm^{-1} with a shoulder at 3240 cm^{-1} are observed. The 3585 cm^{-1} band is considered to be due to stretching mode of hydroxyl of Si-OH (e.g., Graetsch et al., 1985). The broad band around 3425 cm^{-1} with a shoulder at 3240 cm^{-1} is similar to that of liquid water (H_2O) (Aines and Rossman, 1984). For increasing temperature, the H_2O band at 3425 cm^{-1} significantly shifts to higher frequencies, while the hydroxyl band at 3585 cm^{-1} shifts slightly. These changes of absorption bands with temperature are reversible between RT and 400 $^{\circ}\text{C}$ upon heating (solid spectra) and cooling (dotted spectra) (Fig. 1). The hydroxyl and H_2O bands are found to shift linearly with temperature to higher frequencies at a rate of 1.8 $\text{cm}^{-1}/50$ $^{\circ}\text{C}$ and 15 $\text{cm}^{-1}/50$ $^{\circ}\text{C}$, respectively (Fig. 2). Because of the reversibility of the absorption bands (Fig. 1), these changes are not from dehydration but from changes with temperature in physicochemical states of hydroxyl and H_2O in the microcrystalline quartz.

Isothermal dehydration experiments

In order to study dehydration behavior of the chalcedony at a higher temperature than 400 $^{\circ}\text{C}$, isothermal changes in IR spectra were measured in-situ at 550 $^{\circ}\text{C}$ (Fig. 3). The total band areas gradually decrease with time, indicating in-situ dehydration of water. However, since the Si-OH and H_2O bands are supposed to be closely overlapping (3604 cm^{-1} vs. 3583 cm^{-1} from extrapolation of the linear trends in Fig. 2), the origin of the total water band decrease is not clear.

Figure 3. Isothermal in-situ IR spectra at 550 °C for the chalcedony thin section (260 μm thick). The total band area decreased from 0 to 500 minutes showing dehydration.

Figure 5. The decreases with time of absorbance at 3425 cm^{-1} due to H_2O and 3585 cm^{-1} absorbance due to Si-OH during the isothermal heating at 550 °C in Figure 4. The remarkable decrease of Si-OH is observed within 50 minutes (30%), while the H_2O band decreases slightly (12%).

Because the two bands are well separated at RT (3585 cm^{-1} vs. 3425 cm^{-1} ; Figs. 1 and 2), IR spectra were measured at RT after quenching from 550 °C heating from 0 to 500 minutes. The 3585 cm^{-1} band due to Si-OH shows a remarkable decrease with time (Fig. 4). On the other hand, H_2O band around 3425 cm^{-1} does not show significant changes. The peak heights at 3585 cm^{-1} and 3425 cm^{-1} after baseline correction were plotted against time in Figure 5. The 3585 cm^{-1} peak height rapidly decreases from about 1.2 (absorbance unit) to about 0.85 (30% decrease) within first 50 minutes and the decrease becomes

Figure 4. IR spectra at RT quenched after heating at 550 °C from 0 to 500 minutes for the chalcedony thin section (170 μm thick).

gentle. The 3425 cm^{-1} peak height appears to decrease slightly from about 1.65 to about 1.45 (12% decrease) within first 50 minutes and it remains almost unchanged around 1.4. Therefore, the band decreases in Figure 3 (about 50% decrease for 500 minutes) may reflect the major decrease of Si-OH together with a minor contribution of H_2O decrease.

DISCUSSION

Physicochemical states of water in the chalcedony at high temperatures

The slight shift of band position of hydroxyl in the chalcedony shown in Figures 1 and 2 can be originated from the slight increase of hydrogen bond distances (Libowitzky, 1999) in quartz, through the thermal expansion of the quartz lattice (e.g., Kihara, 2001).

On the other hand, the H_2O band in the microcrystalline quartz shifted significantly to higher frequencies at higher temperatures (15 $\text{cm}^{-1}/50$ °C). It is generally accepted that at RT liquid water consists of various degrees of coordination number of hydrogen bonding (maximum number is four; two donors and two acceptors in a single H_2O molecule). The dominant coordinating number of hydrogen bonding at RT is two and three, while zero, one and four coordinating numbers are fewer (e.g., Brubach et al., 2005). The frequency of H_2O stretching shifts to higher region for decreasing coordinating number of hydrogen bond (Brubach et al., 2005). Therefore, the broad IR band of H_2O in the chalcedony around 3425 cm^{-1} at RT is dominantly due to the two and three coordinating numbers of hydrogen bonding. The increase of higher frequency

components for higher temperatures can be interpreted as the decrease of coordinating numbers of hydrogen bonding becoming less than two above the supercritical temperatures (Nakahara et al., 2001). These results indicate that H₂O in the microcrystalline quartz behaves similarly to liquid water at high temperatures despite its presence in confined pores and grain boundaries.

Dehydration behavior in the chalcedony

The isothermal heating experiments of the chalcedony suggested the dominant dehydration of Si-OH species, while H₂O showed only a slight decrease (Figs. 4 and 5). On the other hand, the remarkable decrease of H₂O band around 3425 cm⁻¹ compared with the Si-OH band around 3585 cm⁻¹ and the appearance of the additional band at 3740 cm⁻¹ due to isolated surface Si-OH were reported during the heating of chalcedonic quartz (Graetsch et al., 1985; Yamagishi et al., 1997). Despite the liquid-like states of water in pores and grain boundaries of the microcrystalline quartz, the present results indicate possible stability against dehydration at high temperatures of at least a part of liquid-like water in the microcrystalline quartz. Therefore, further systematic studies are needed to elucidate the dehydration behavior in the microcrystalline quartz in relation to the physicochemical environments of water in different textures such as grain size, pore size, grain boundary thickness etc.

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