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OH Stretching Vibration Changes of Water at Water-Rock Interface under High Temperatures and Pressures: An In-Situ Study using Infrared Spectroscopy

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Abstract. In order to investigate effects of molecular behavior of interfacial water on rock surface, high temperature-pressure cell (up to 400 °C and 50 MPa) was developed to measure infrared (IR) and Raman spectra, which was attached with optical microscopy, therefore, in situ and microscopic measurements were enabled at high temperature and pressure (HT & HP) conditions. IR spectra of water on metal, interfacial water on quartz surface and synthetic quartz solution were measured. As a result of IR spectroscopic measurements of water on metal, the broad peak at ca. 3400 cm⁻¹, attributed to OH stretching vibration of water molecules, was observed at high temperature and pressure conditions. Continuous shift of the OH vibration mode was obtained from room to hydrothermal conditions. Compared with the result of IR properties of water on a metal, IR properties of water on a quartz surface exhibit different trend: the peak position shifted to higher wavenumber with increasing temperature and slightly shifted with pressure. IR property of water was changed by environmental conditions such as temperature, pressure and substrate. Molecular structure of interfacial water on the rock and rock-forming mineral at elevated temperatures and pressures were not only changes due to physical conditions such as temperature and pressure but also interaction between water and solid rock materials.

Keywords: IR spectroscopy, Water, High temperatures and pressures, Hydrothermally derived fracturing

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INTRODUCTION

We have investigated dissolution behavior of granite at sub- and supercritical hydrothermal conditions. As a result, we found occurring of granite fracture under hydrothermal conditions. In our previous fracturing experiments using granite and quartz, material failure were initiated by quartz fracturing, and both substances were well fractured at specific hydrothermal conditions such as about 350 °C - 500 °C and in relatively low pressures under dry steam conditions, which had been termed as hydrothermally derived fracturing (HDF) [1,2]. In addition, this phenomenon was also observed to occur under natural conditions [3]. Hydrothermal solution have shown great role to generate and accelerate fractures in rock and rock-forming mineral. In order to investigate effects of molecular behavior of water at interface on the rock surface for HDF, high temperature-pressure cell (up to 400 °C and 50 MPa) was developed. Using the cell and FT-IR and Raman spectrometer, which was attached with optical microscopy, therefore, in situ and microscopic spectroscopy was enabled at high temperature and pressure (HT & HP) conditions [4].

We have performed IR absorption spectroscopic measurements to investigate the state of pure water on a metal and pure water on an artificial quartz at HT & HP conditions. Additionally, in order to investigate the effects of surface dissolved quartz, IR spectra of solution of quartz were measured.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus

Micro spectroscopic measurements were performed on a Micro Infrared-Raman spectrometer (Abe et al., 2006). The spectrometer consists of microscope unit (BX51, Olympus co.), Fourier transform IR spectrometer unit (IlluminatIR., Smiths Group plc.) and Raman spectrometer unit (Hololab 5000, Kaiser Optical Systems, Inc.). Microscope unit gives visual images of the sample by reflected light. The IR unit configuration is: a ceramic light source, KBr beam splitter, MCT detector and a Cassegrainian mirror. The Raman unit configuration is: Nd:YAG laser source (Wavelength : 532 nm), grating and CCD detector.
EXPERIMENTAL RESULTS

IR Absorption Properties of Water on Metal at HT & HP Conditions

IR spectra of water on a metal at 100 °C and 400 °C are shown in Fig. 2. Broad peaks at ca. 3400 cm⁻¹ attributed to OH stretching vibration of water molecules [5,6] were detected. The peak shifted with changes in temperatures and pressures. Figure 3 shows relationship between peak position and pressure. With increasing temperature, peak position of OH stretching vibration shifted higher wavenumber. And with increasing pressure, peak position shifted lower wavenumber. It was reported that the peak attributed to OH stretching vibration shifted with changes in temperatures and pressures[7,8].

Experimental Procedure

IR absorption spectra of water on a metal and water on an artificial quartz were measured. In addition, quartz was dissolved in pure water at 350 °C and 20 MPa for 24 hours (Si concentration was 322 ppm.), and IR absorption spectra of solution of quartz were measured. IR spectroscopies were performed in the 4000 cm⁻¹ – 650 cm⁻¹ wavenumber range with 4 cm⁻¹ resolution by Fourier transformation of 70-100 accumulated interferograms.
IR Absorption Properties of Interfacial Water on Artificial Quartz at HT & HP

Figure 4 shows IR spectra of water on an artificial quartz at 100 °C and 400 °C. Figure 5 shows relationship between peak position of OH stretching vibration and pressure. Peak position shifted to higher wavenumber with increasing temperature but slightly shifted with pressure. Compared with the result of IR absorption properties of water on a metal, IR absorption properties of water on artificial quartz exhibit different trend. Therefore, surface structure of rock surface may give effects on structure of water molecules.

IR Absorption Properties of Solution of Quartz at HT & HP

IR spectra of solution of quartz at HT & HP conditions are shown Fig. 6. And Fig. 7 shows relationship between peak position and pressure. With increasing temperature, peak position shifted higher wavenumber. And with increasing pressure, peak position shifted lower wavenumber. Compared with the result of IR absorption properties of water on a metal, IR absorption properties of solution of quartz exhibit same trend. And compared with the result of IR absorption properties of water on artificial quartz, IR absorption properties of synthetic quartz solution exhibit different trend.

DISCUSSION

IR spectra of several aqueous solutions (pure water, NaCl, Na₂CO₃, and NaHCO₃) up to 100 °C have been measured, and it was reported that the OH stretching bands showed systematic change with increasing solute concentration under room temperature [9]. Slight peak shift of water on artificial quartz was considered as influence of quartz dissolution. However IR properties of solution of quartz and water on a metal exhibited the same trend; the peak position shifted with pressure, therefore slight peak shift of water on an artificial quartz was considered as influence of not dissolution of quartz but water-quartz interaction.
IR spectra were performed base-line correction, and the 3200 cm\(^{-1}\) / 3400 cm\(^{-1}\), 3650 cm\(^{-1}\) / 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\) / 3400 cm\(^{-1}\) ratios of water on a metal show at Fig. 8. The peak at 3200 cm\(^{-1}\), 3400 cm\(^{-1}\), 3650 cm\(^{-1}\) and 3700 cm\(^{-1}\) attribute to ice-like water molecules, free-water molecules, Si-OH vibration and vapor-like water molecules, respectively.

With increasing pressure, the 3200 cm\(^{-1}\) / 3400 cm\(^{-1}\) ratio shifted higher value, and the 3650 cm\(^{-1}\) / 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\) / 3400 cm\(^{-1}\) ratios shifted lower value. This indicated that vapor-like water configuration occupied at low pressure conditions, and ice-like water configuration occupied at high pressure conditions. And these ratios of water on an artificial quartz show at

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**FIGURE 8.** The 3200 cm\(^{-1}\) / 3400 cm\(^{-1}\), 3650 cm\(^{-1}\) / 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\) / 3400 cm\(^{-1}\) ratios of water on a metal.

**FIGURE 9.** The 3200 cm\(^{-1}\) / 3400 cm\(^{-1}\), 3650 cm\(^{-1}\) / 3400 cm\(^{-1}\) and 3700 cm\(^{-1}\) / 3400 cm\(^{-1}\) ratios of water on an artificial quartz.
Fig. 9. These ratio slightly shifted with increasing pressure. This indicated that quartz surface structure affect water configuration. Figure 10 shows isopleth of peak position of water on a metal on pressure-temperature (P-T) diagram. Peak position at quartz fracturing region is higher value more than 3600 cm\(^{-1}\), higher wavenumber indicate vapor like condition of water molecules. And itopleth is oblique to Vapor Saturated Curve of water. Figure 11 shows isopleth of peak position of water on artificial quartz on P-T diagram. Peak position at quartz fracturing region is lower value than water on metal. This indicates structure of quartz surface might affect water structure on quartz surface. Isopleth is approximately perpendicular to Vapor Saturated Curve of water.

As results of IR spectroscopic measurements of water on a metal and water on an artificial quartz, it can be seen that the peak of water molecules was changed by environmental conditions such as temperature, pressure and substrate.

**FIGURE 12.** Schematic illustration of possible structure model of water-quartz interface.

Surface structure of artificial quartz surface may give effects on structure of water molecules. We can consider on a possible structure of water molecules on quartz surface (Fig. 12.). Interfacial water molecules interacted via hydrogen bonding with surface silanol molecule of quartz. This water-quartz interaction might influenced water structuring on quartz surface. It was reported that the absorbed water on silicon oxide surface at room temperature forms hydrogen-bonded icelike network, and the network grows up to three layers from silicon oxide surface by ATR-IR spectroscopy [10]. Thickness of structured water layer is uncertain, however it was considered that IR spectra of structured water molecules were detected using newly developed high temperature-pressure cell.

As HDF phenomena occur, quartz reacts with structured water under hydrothermal conditions and water molecules break Si-O bonds. And then, fracturing might be occurred. It was reported by theoretical studies that water molecules Si-O bond weakening and bond breaking [11].

**CONCLUSION**

IR spectra of water above rock surface and solution of rock were measured. Molecular structure of water changed depending on temperatures, pressures and substrates. Additionally, solid surface may influence molecular behavior of water. Such water, interacted with solid surface at HT & HP conditions, is considered to accelerate HDF phenomena. Interfacial water at solid surface under HT & HP conditions should be studied to reveal the details of the change of the water molecules interacted with the surface of solid materials, and then the mechanism of dissolution and fracturing of mineral induced by water-rock interaction might be revealed. It is possible to create well fractured reservoir by HDF for Enhanced Geothermal Systems (EGS).
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