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In Situ FT-IR Observations on NaCl-H₂O-D₂O Fluids at Temperatures up to 850° C Using Hydrothermal Diamond Anvil Cell

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1 Introduction

NaCl-H₂O is the main composition of the earth crust and mantle fluids. Aqueous fluids play a fundamental role in the geochemical evolution of the earth. But, knowledge for molecular nature of such fluids at temperatures approaching and exceeding the critical temperature of water, however, is more limited, thus may not accurately understand the behaviors of the fluids in the depths and their fundamental role in the geochemical evolution of the earth. Recently, many high temperature and pressure experiments combined with theoretical prediction (involving molecule dynamic calculations) indicated that given the huge range of P-T-x regimes in crust and mantle, aqueous fluids at high temperatures and pressures are strongly variable in molecular structure, phase transition, and exhibit specific physical and chemical properties. Previously, most investigators focus on high pressure water, i.e., ice. Water and aqueous solutions were in situ examined using diamond anvil cell (DAC) at super-high pressure and room temperature, using XRD, FT-IR, and Raman spectrometers, with synchrotron radiation light source (Aoki et al., 1996; Goncharov et al., 1999). Recently, in situ high pressure temperature Raman spectroscopy and synchrotron x-ray diffraction have been used to examine the phase diagram of H₂O (Lin et al., 2005). But a few experiments using DAC on water and NaCl-H₂O connected with FT-IR spectrometer are performed at high temperatures and very high pressures. We use hydrothermal diamond anvil cell connected with FT-IR spectrometric microscope to examine phase transitions and molecule structure of aqueous solutions at high temperatures and pressures.

2 Experimental Design

The hydrothermal diamond anvil cell, HDAC were modified with a wide-angle window to allow FT-IR beam pass through the sample. The HDAC can be connected to both an optical microscope and infrared microscope. A computer is used to control the analysis of the spectrum data from the FT-IR instrument, Bio-Rad 6000. In our experimental setup, the HDAC is put in the IR microscope path (Bio-Rad, UMA 500) and connected to an image system: for direct observation of the sample and recording of temperature indicator and time, superimposed and recorded on computer simultaneously.

Through the window, we have observed the phase transitions and measure the infrared spectra for NaCl-H₂O-D₂O solutions with different salinities at high temperatures (850° C) and pressures (3GPa). Pressure could be determined by using molecular spectrum of quartz (Hu et al., 2000; Zhang and Hu, 2004). FT-IR measurements were performed with the combination of MCT detector and KBr beam splitter operating at a spectral resolution of 4 cm⁻¹. And interferograms from 256 (or 512) scans were averaged to obtain one spectrum. The HDAC was used to observe NaCl-H₂O at temperatures from 20 to 500° C, and at pressure up to 3 to 10 GPa using XRD and EXAFS, while applied the Synchrotron X ray diffraction. The HDAC was also used to examine the FT-IR spectra of the fluids (or other materials) at room temperature and pressures from 1 to 10 GPa.

3 Results: NaCl-H₂O-D₂O System at High Temperatures

As we examined aqueous solutions at high temperatures using FT-IR spectrometric microscope, the strong absorbance of water appeared at about 3500cm⁻¹, which is not easily and perfectly capable of distinguishing the real frequency from a large absorbance band. So that, we prepared a proportional H₂O and D₂O solution. For NaCl-H₂O-D₂O system, as increasing temperature, phase

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transitions can be divided in to three paths: H(halite)+L (liquid)+V(vapor) \rightarrow L+V \rightarrow L(or supercritical fluids, SCF); H+L+V \rightarrow L; H+L+V \rightarrow H+L \rightarrow L.

Temperature effect on IR spectra of NaCl-H₂O- D₂O

For the phase transition (H+L+V \rightarrow L+V \rightarrow L) of NaCl-H₂O (39 wt% NaCl), the IR spectra were examined (Hu et al., 2000; Zhang and Hu, 2004). When the temperature increases from 29 to 650° C, the L+V immiscibility field becomes unstable at temperature > 330° C. With continued heating, there remains one liquid phase as T>467° C. A NaCl solution with salinity of 25-31wt% was observed along an isochore: V+L+H \rightarrow L+H \rightarrow L sequence.

Phase transition H+L+V \rightarrow L+V \rightarrow L: The maximum concentration of the symmetric O-H stretch was obtained in the conditions at temperatures from 300 to 330° C, just near the critical point of water. At 330° C, a sharp peak of OH stretching vibration was attained at 3623, while the HOH bend at 1600 weakens. In the temperature range from 29 to 300° C, a wide band from 3200 to 3700 reflects a deconvoluted spectrum of O-H stretching vibrations corresponding to the hydrogen bond (HB) and the non-hydrogen bond (NHB), and accompanying the H-O-H bend vibration. The sharp and strong O-H stretching vibration near the critical point of water (300 to 330° C, 400° C) proves the breakdown of the hydrogen bonding network of water molecules (Hu et al., 2000; Zhang and Hu, 2004).

Those studies indicate that the OH stretching frequency changes with temperature (Zhang and Hu, 2004). These experimental results indicated that temperature effect on the molecular spectrum is different from the pressure

effects. Previous studies have already shown that some frequencies for O-H stretching vibration decreases with increasing pressures.

It is well known that the density of liquid phase or vapor phase in the L+V immiscibility field will vary distinctly with temperature. At temperature above 330° C, the O-H symmetric stretch vibration (corresponded to NHB) predominates due to lowering density and dielectric constant of water. The OH stretching vibration varies from 3623 to 3659 with increasing temperature from 29 to 502° C, which probably consists of stretch vibration. Because of the high absorbency, some of the vibration spectra of low frequency have a qualitative significance. But it is obvious that the combined OH stretch and HOH bend frequencies appear at the range 5158 to 5269, which increases with increasing temperature from 29 to 605° C (Zhang and Hu, 2004).

Phase transition H+L+V \rightarrow H+L \rightarrow L: As observed NaCl (25-31wt%) -D₂O-H₂O, and increasing from 25° C to 585° C, vapor phase disappeared at 88° C, and thus H+L+V \rightarrow H+L. At 176° C, solid (H) disappeared, H+L \rightarrow L. At 498° C, L \rightarrow L+V. The IR spectra during the phase transition (H+L+V \rightarrow H+L \rightarrow L) are examined, and found that the frequency of the maximum intensity of the stretching vibration of water in NaCl - D₂O (17%) - H₂O(83%) system vary with temperature. The wavenumber increases with increasing temperature and shows a continuous change. In this case, the non-hydrogen bonding (NHB) group becomes progressively predominant at high temperatures. See Fig.1

It is also obvious that the combined OH stretch and HOH bend frequencies, $\nu_{1,3} + \nu_2$ (H₂O) increases with increasing temperature, which appear at the range 5146 to

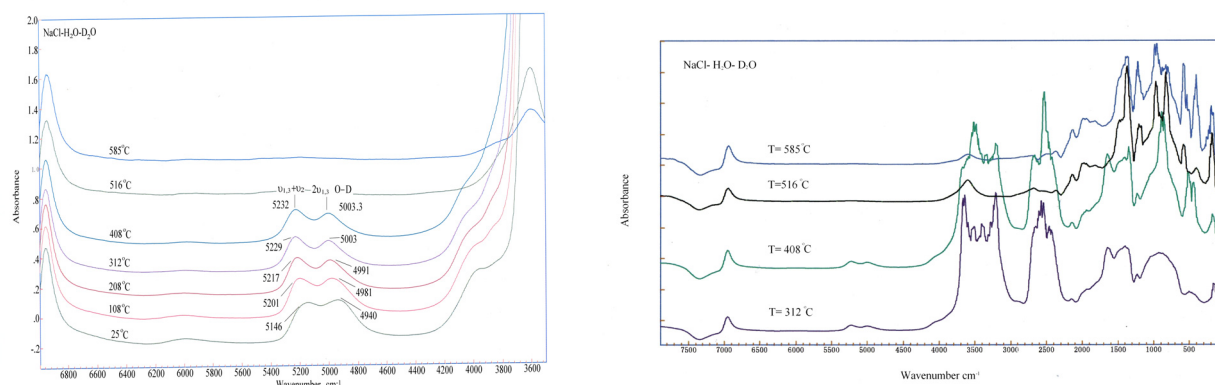


Fig 1. Infrared spectra of NaCl - mixture solution of D₂O and H₂O solution at temperatures from 25 to 585°C, and pressure at about at 3GPa.

(a)IR spectra in a large wavenumber range at 312°C, 408°C, 516°C and 585°C at 3GPa;

(b)IR spectra in wavenumber from 3500 to 6900 cm⁻¹: O-D stretch frequency of D₂O, $2\nu_{1,3}$ (D₂O) increases with increasing temperature from 25 to 408°C.

5232, shown in Fig.1. Also, O-D stretch frequency of D_2O , $2\nu_{1,3}(D_{2O})$ increases with increasing temperature from 20 to 401° C, which is present in the range from 4941 to 5003. D-O-D bend frequency varies from 1227 to 1212 during increasing temperature from 20 to 401° C. D-O-D bend frequency decreases with increasing temperature.

Salinity effect on IR spectra of NaCl-H₂O-D₂O

The hydration of anions in aqueous solution and its water molecule spectra were studied recently, because the hydration of dissolved species in aqueous solution affects water IR spectra of the solutions. We have examined the stretching vibration frequencies of water molecules in NaCl aqueous solution, and found they vary with salinity at a constant temperature. For instance, combined OH stretch and HOH bend vibration frequencies $\nu_1+\nu_3$ vary from 3410 to 3460 cm^{-1} , as salinity increases from 0% to 36 wt% at 20° C. Simultaneously, $\nu_{1,3}+\nu_2$ vary from about 5084 to 5211 cm^{-1} . For NaCl-H₂O-D₂O system at 300° C, the combined OH stretch and HOH bend frequencies appear at the range from 5229 to 5265, while the solution salinity varies from 30 to 40 wt% (Zhang and Hu, 2004).

Pressure effect on IR spectra of NaCl-H₂O-D₂O

Observation of NaCl-H₂O using synchrotron radiation light source at temperatures from 20° C-500° C and pressure at 1 to 10 GPa, which were performed at synchrotron radiation light source, New York. As pressure increases from 1 to 10 GPa, the frequency for $\nu_{1,3}+\nu_2$ combined decreases from 5250 cm^{-1} to 4850 cm^{-1} . Simultaneously, the $2\nu_{1,3}$ decreases from 7100 cm^{-1} to 6600 cm^{-1} . These experimental results are similar with previous studies about water at high pressures (Aoki et al., 1999; Goncharov et al., 1999).

And, some metal bearing solutions at high temperature and pressures were examined using HDAC connected to FT-IR spectrometric microscope or EXAFS from synchrotron light source.

4 Discussion and conclusion

Only increasing pressure caused decreasing frequencies of $\nu_{1,3}$ of H₂O and NaCl-H₂O-D₂O. But, increasing temperature at high pressures lead increasing the frequencies of $\nu_{1,3}$ of H₂O and NaCl-H₂O-D₂O.

The observations for NaCl-H₂O-D₂O found that a sharp

peak of O-H stretching vibration was reached at 3623.2 at temperature range from 300 to 400° C, i.e., within the critical state temperature of water, which proves the breakdown of the hydrogen bonding network. Results demonstrated that decreasing water density and dielectric constant with increasing temperature from 20° C to 600° C results in weakening hydrogen bond of water molecules. Water with NHB is going to dominate progressively due to increasing temperature within the critical region, thus water tends to form large water cluster bearing metals and electrolytes, and large radii hydrate around the metal clusters. Thus effect of salinity is similar with temperature effect on the water molecule spectrum, due to probably large cluster forming, e.g. $Cl^{-} \times nH_2O$, or $NaCl$, $Na_2^{+}Cl$, $NaCl_2^{-}$, Na_2Cl_2 , ... Those phenomena, fluids would occur in the earth depth, where high temperature and high salinity fluids are present.

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Key words: hydrothermal diamond anvil cell, NaCl-H₂O, high temperatures, FT-IR, vibration frequency.

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