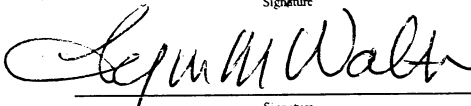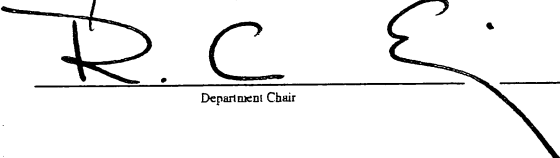Author

Ni Sun

Title

In situ Investigation of Brucite and Aqueous Fluids in the MgO-H$_2$O System

at Elevated Pressure and Temperature

submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Geology
Department of Geological Sciences
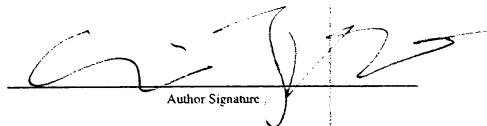The University of Michigan

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In situ Investigation of Brucite and Aqueous Fluids in the MgO-H₂O System at Elevated Pressure and Temperature

By Ni Sun

Advisor: Professor Lars P. Stixrude

Master of Science in Geology

The University of Michigan

2006

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ABSTRACT

In-situ Raman measurements in MgO-H$_2$O system are reported to 800 $^{\circ}$C and 11 kbar. Brucite Raman modes depend strongly on temperature. The shifts in frequency with temperature are fitted as the following expressions: ν(cm^{-1})=278 – 0.031T($^{\circ}$C) with R^2=0.86, ν(cm^{-1})=444 – 0.041T($^{\circ}$C) with R^2=0.97, and ν(cm^{-1})=3650 – 0.011T($^{\circ}$C) with R^2=0.84. Brucite begins to dehydrate at certain temperature between 250 $^{\circ}$C and 300 $^{\circ}$C. A new magnesium complex species is observed in the aqueous fluids by a Raman mode at 356 cm^{-1}, which is considered to be caused by Mg^{2+}-oxygen stretching.

INTRODUCTION

Fluids are primary agents of terrestrial chemical differentiation and play an essential role in geological processes as mantle metasomatism and magma generation in subduction zones. This may be most dramatically expressed in the arc environment, where the mantle is generally regarded as being fluxed, the addition of aqueous fluid being central to the genesis of magmas and presumably the formation of continents. Pre-eruptive arc magmas are thought to contain as much as 8 % water (Grove *et al.*, 2002). Recent studies indicating very rapid ascent of arc magmas (< 1000 years) also suggest extensive interaction between silicates and fluids in the arc environment (Turner *et al.*, 2001; Audetat and Keppler, 2004). Experiments show that silicate liquids and water may be completely miscible at pressure-temperature conditions typical of the mantle wedge (Shen and Keppler, 1997; Bureau and Keppler, 1999).

Understanding the chemical interaction of silicates and fluids at elevated pressure and temperature is also important for understanding the solid mantle. Even small amounts of added water can alter mantle viscosity by orders of magnitude (Hirth and Kohlstedt, 1996). Experimental studies have detected that olivine could store 0.1 wt% water (Kohlstedt *et al.* 1996); wadsleyite and ringwoodite could store several wt% water (Kohlstedt *et al.* 1996); and orthopyroxene could store 700~800 ppm wt% water (Rauch and Keppler, 2002).

We focus our efforts on the interaction of water with magnesia, the most abundant oxide component in the mantle by mole fraction. It is not known to what extent magnesium is soluble in water at elevated pressure-temperature conditions; most previous studies have focused on the interaction of water with more felsic compositions (Shen and Keppler, 1997; Bureau and Keppler, 1999). It is known that the solubility of water in magnesium-rich silicates increasing markedly with increasing pressure (Hirth and Kohlstedt, 1996), and there is some evidence that the solubility of magnesia in water also increases with increasing pressure (Stalder *et al.*, 2001). However, the nature of magnesium-bearing aqueous fluids at mantle conditions has not been clarified. In this study, we investigated the structure of aqueous fluids *in situ* in the MgO-H_2O system.

All experiments were performed in an externally heated Bassett-type diamond-anvil cell, which allows us to investigate aqueous fluids *in situ* up to 1200 K and 5 GPa and observe the samples visually and by Raman spectroscopy. The ability to observe the sample *in situ* avoids problems associated with quenched hydrous samples. We have also investigated the Raman spectrum of brucite as a function of temperature in order to gain further insight into the nature of hydrogen bonding in this sytem.

EXPERIMENTAL

Starting Material

Starting material for all experiments were samples of natural brucite ($Mg(OH)_2$) crystals from Ward's Natural Sciences. To investigate MgO-H_2O system, brucite crystals and de-ionized water were added in hydrothermal diamond anvil cell chamber. Depending on the conditions of pressure and temperature, additional water may be released by the dehydration of brucite according to the reaaction $Mg(OH)_2 \Leftrightarrow MgO + H_2O$.

High Pressure Experiments

In our experiments, we used a Bassett-type externally heated diamond anvil cell (Figure 1, Basset et al. 1993 a, b). In this cell, a rhenium gasket with a thickness of 250 microns and a 500 micron drillhole was used as the sample chamber. The cell was loaded with natural brucite and excess water.

Temperature was measured by K-type thermocouples which are surrounding the diamonds. The high thermal conductivity of the diamonds and their WC seats (tungsten carbide seats) is expected to keep the entire sample region nearly isothermal. The temperature controller allows us to control the temperature to ±1 °C. Maximum temperatures are limited by the stability of the diamonds and the mechanical competence

of the WC seats. A mixture of Argon and Hydrogen were flowing to the diamonds and the Re gaskets to prevent them from oxidizing.

The diamond interface was used as the pressure calibrant (Davis *et al.*, 2003). Diamond has a primary Raman line at 1332.15 cm^{-1}, which shifts with temperature and pressure. The effects of temperature and pressure are independent of one another so that an independent measurement of temperature (with thermocouples) together with the measured Raman shift determines the pressure (Davis *et al.*, 2003; Davis, 2005). The primary Raman line of diamond shifts with respect to temperature and pressure according to the following equation:

$$\Delta v_S (P,T) = 1.86(10) + 1.34(9)P - 0.0051(3)T - 4.00(6) \times 10^{-5}T^2 + 1.9(1) \times 10^{-8}T^3$$

Where *T* is temperature in Kelvin, P is the pressure in kbar and $\Delta v_S(P,T)$ is the shift of the primary Raman line of diamond with pressure.

Raman Spectroscopy

Raman spectra of MgO-H_2O system were recorded with a single-pass spectrometer, equipped with 600 and 2400 g/mm holographic gratings and a liquid nitrogen cooled CCD detector. A single monochromater is combined with notch filters to maximize the signal of the scattered radiation. The signal is stronger than in alternative designs (triple-

pass) with the disadvantage that we are not able to probe very small frequency shifts. Even so, our equipment is able to detect bands with frequency shifts as low as 100 cm^{-1}.

The 514.5 nm line of an Ar$^+$ laser was used as exitation source at 2500 mW power. Radiation from an Ar$^+$ laser is directed down the axis of a Mitatuyo long-working distance lens via a beamsplitter. At 514.5 nm wavelength, the lens is capable of focusing the laser to a spot size of 2 microns on the sample within the HDAC. Raman-shifted, backscattered radiation is then collected with the same objective lens and directed either to a microscope equipped with a CCD video (for alignment and focusing) or to the spectrometer (for data collection). The radiation going to the spectrometer is first passed through confocal optics that serves as a spatial filter, limiting the sampling depth within the sample to several microns. The radiation is then focused onto the slit of the spectrometer. Accumulation times varied from 60 sections to several minutes at different temperatures.

Raman scattering has many advantages to investigate MgO-H$_2$O system compared with Infrared. First, by using the 514.5 nm laser line for excitation (which is green), interference from black-body emission at high temperature can be reduced. Second, by working with visible light as an excitation source, the laser line can be focused to a very small spatial cross-section, approximately 2 microns (diffraction limited). Third, the use of confocal optics increases the signal-to-noise ratio by rejecting light not near the focal point of the laser (Sharma *et al.*, 1996). The ability to spatially resolve small regions is very useful for work in the diamond cell. Fourth, Raman is more sensitive than infrared

to structural adjustments in silicate melt structures that are induced by the addition of water (McMillan *et al.*, 1983; McMillan and Remmele, 1986).

In situ Raman spectra were collected from 100-4000 cm^{-1}, especially the vibrational modes of aqueous magnesium species at 100-1000 cm^{-1}, O-H stretching modes at 3000-4000 cm^{-1}, and the modes of brucite.

RESULTS AND DISCUSSION

Brucite Dehydration

Brucite crystals were studied at ambient pressure. Two brucite crystal chips were put into the HDAC chamber and the screws of HDAC were kept loose, which ensured ambient pressure was performed in the whole experiment. The HDAC cell was heated gradually (temperature was increased 50°C per step) and the Raman spectra of brucite were recorded (Figure 2 and Figure 3). At ambient conditions, we found three strong Raman modes at frequencies of 278 cm^{-1}, 443 cm^{-1}, and 3650 cm^{-1}, and a weaker mode at ~725 cm^{-1} in agreement with previous studies (Dawson *et al.*, 1973). By comparison with other $Mg(OH)_2$ compounds and with deuterated samples, these modes have been assigned as follows: octahedral bend (278 cm^{-1}) octahedral stretch (443 cm^{-1}), OH libration (725 cm^{-1}) and OH stretch (3650 cm^{-1}) (Lutz *et al.*, 1994).

Brucite became visibly darker with increasing temperature due to the scattering of light as dehydration (disruption of brucite lattice) produced interfaces within the crystal (Bassett *et al.*, 1993a). It is totally black at 300 °C. This is the same temperature at which we find that the Raman spectrum disappears. The solid dehydration product (periclase) has no Raman active modes. Darkening and loss of Raman signal therefore indicate dehydration of brucite between 250 °C and 300 °C, in agreement with the previous result (271 °C, Aranovich and Newton, 1996).

Temperature Dependence of Brucite Modes

Raman spectra of brucite crystals were recorded at ambient pressure and elevated temperature. The brucite crystals were gradually heated until the Raman signal could no longer be detected and then were cooled to room temperature. The three strongest modes have obviously negative linear relation with temperature (Figure 4, Figure 5, and Figure 6). The weakest mode at 725 cm^{-1} was not resolvable at elevated temperature.

The data were fitted with the expression $\Delta v = aT + v_0$, where Δv is the frequency at elevated temperature in cm^{-1}; v_0 is the frequency at ambient conditions; T is temperature in °C, and a is a constant. The results of the fits are given in figure captions. The decrease in frequency with temperature of the lattice modes is expected and may be attributed to thermal expansion. The decrease in the hydroxyl stretching frequency with increasing temperature is inconsistent with behavior expected of the hydrogen bond. As the lattice expands we might anticipate weakened hydrogen bonding and an increase in the hydroxyl stretching frequency. Our results therefore indicate that brucite does not in fact contain hydrogen bonding in agreement with previous studies (Chakoumakos *et al.*, 1997; Mookherjee and Stixrude, 2006).

Aqueous Species

In order to investigate the structure of aqueous Mg species, brucite crystal chips and deionized water were added into the HDAC chamber and the screws of HDAC were tightened carefully. The cell were heated 50 °C every step, then cooled down gradually. In our experiment, the sample chamber remains approximately isochoric, so that pressure and temperature increase together at a rate determined largely by the equation of state of water.

The sample was continuously heated to 800 °C (11kbar), then gradually cooled down to room temperature. The crystal was observed to decrease in size, indicating significant increase in the amount of Mg^{2+} in solution at these conditions. A new Raman mode at $356\ cm^{-1}$ is observed at 700 °C and 10.9 kbar (Figure 7). The frequency of this mode is essentially identical to the strongest Raman mode observed in Mg chloride aqueous solutions at ambient conditions. This mode has been assigned to the symmetric stretch of the hexaquamagnesium (II) ion $Mg(OH)_6^{2+}$ on the basis of quantum mechanical calculations, polarized Raman studies and isotopic substitution (Pye and Rudolph, 1998; Rudolph et al., 2003). Our observation of this mode in an $MgO-H_2O$ solution confirms previous interpretations that association in Mg chloride solutions is minor.

We were unable to resolve this new mode at other pressure and temperature conditions because of its low intensity. We believe that our observation should serve as the basis for further study of the structure of Mg^{2+} in high pressure-temperature aqueous solutions, in

particular investigations of the dependence of the new mode on pressure and temperature. Such studies would require longer collection times or different chemistry in order to increase the amount of Mg^{2+} in solution.

CONCLUSIONS

The present study demonstrates that Raman spectroscopy in externally heated hydrothermal diamond anvil cells allows the identification of the major species in MgO-H_2O system. The main modes of brucite show strong temperature dependence. The frequencies all decrease with temperature. This is expected in the case of the lattice modes, but does not agree with the notion that brucite is hydrogen bonded. Previous studies have also concluded that hydrogen bonding in brucite is absent and that the layers are bound instead by point-dipole interactions (Mookherjee and Stixrude, 2006). We find that brucite begins to dehydrate at certain temperature between 250 $^{\circ}$C and 300 $^{\circ}$C at one bar, as evidenced by the loss of the Raman spectrum. This is consistent with previous studies and confirms the utility of Raman spectroscopy in the quantifaction of phase equilibria. We find for the first time evidence of a hexaquamagneium ion in MgO-H_2O solutions, which had previously only been seen in chloride and sulfate solutions. The observed Raman mode at 356 cm^{-1}, is caused by symmetric stretching of the ion.
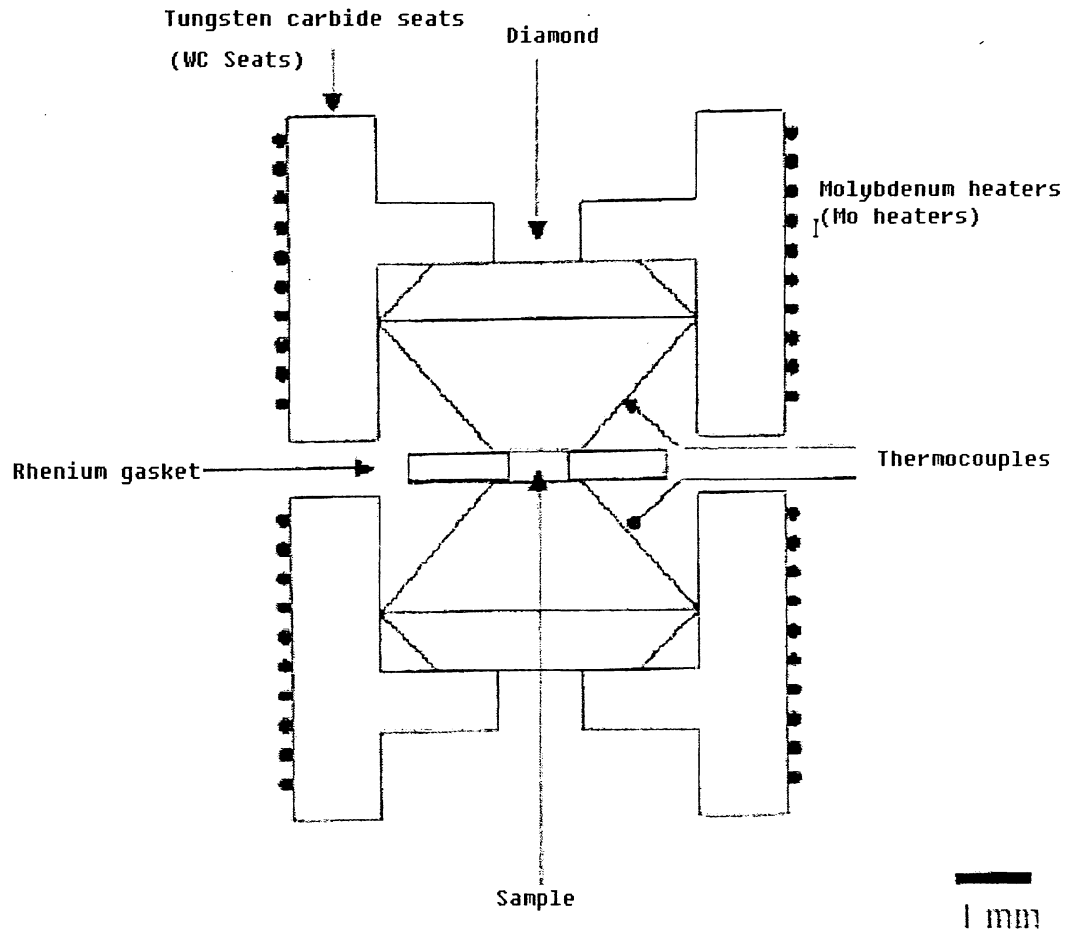
Figure 1. Sketch of hydrothermal diamond anvil cell (HDAC). The upper and lower

diamonds are surrounded by Mo-resistance heaters that wrap around the WC supports.

The confining gasket is made of Re (the thickness is not to scale). The fluid sample

resides in a hole in the gasket and can be observed through the diamonds. Two chromel-

alumel thermocouples permit accurate temperature measurement. These are in contact

with the diamonds, which are in turn in contact with the sample. As the thermocouples

are at ambient pressure, no pressure correction is needed. (After Snyder, 1998)
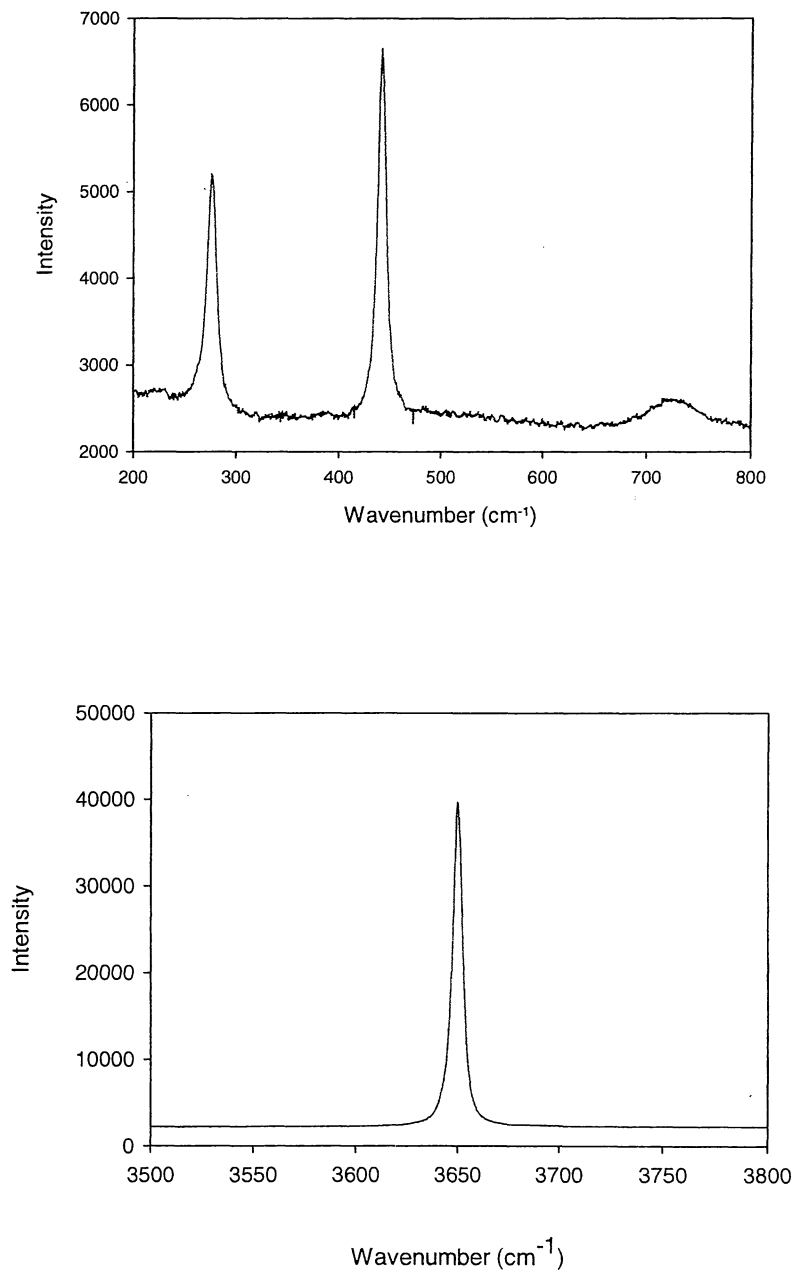
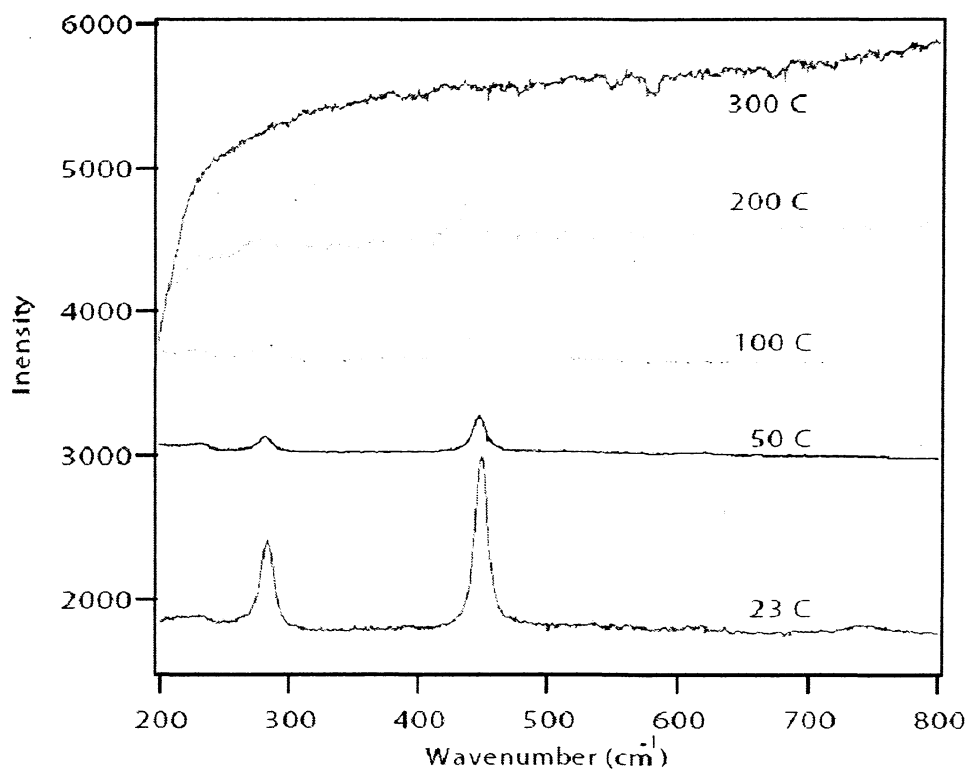**Figure 2.** Brucite Raman Spectra at ambient pressure and room temperature.

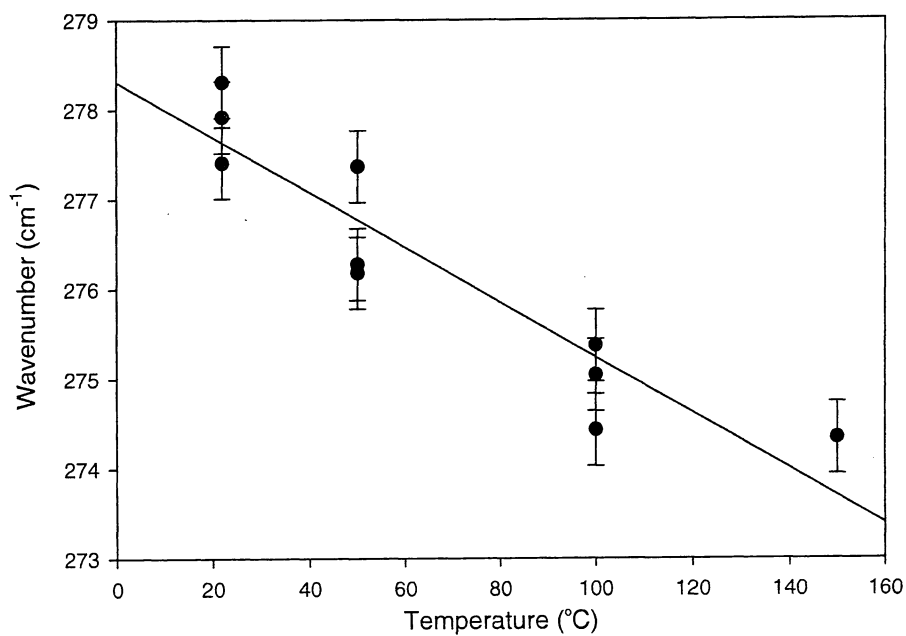**Figure 3**. Brucite Raman Spectra at ambient pressure and elevated temperature.

Figure 4. Temperature dependence of the 278 cm^{-1} mode of brucite at 1 bar. The shift has a linear relation with temperature: $\nu(\text{cm}^{-1})=278 - 0.031T(^{\circ}\text{C})$ with $R^2=0.86$.
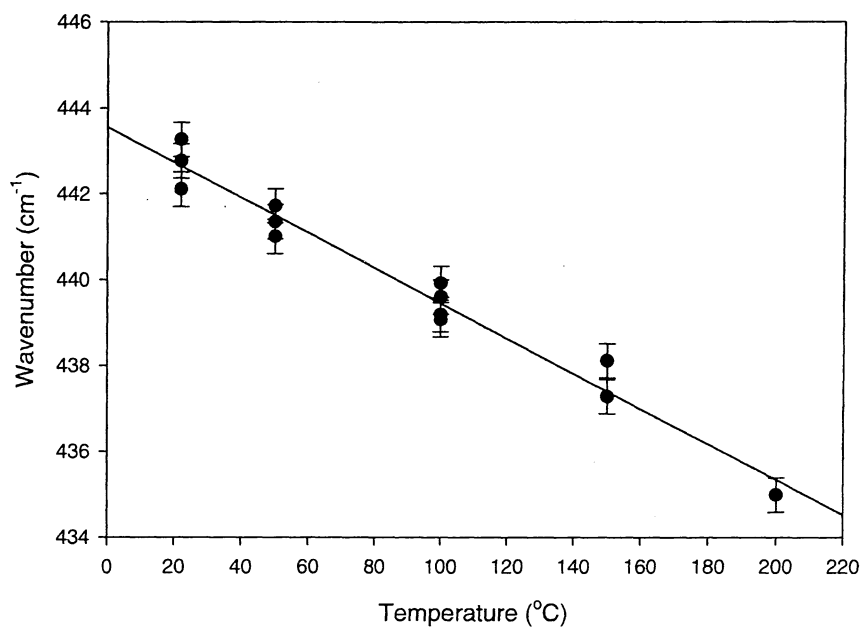
Figure 5. Temperature dependence of the 443 cm^{-1} mode of brucite at 1 bar. The shift has a linear relation with temperature: ν(cm^{-1})=444 − 0.041T(°C) with R^2=0.97.
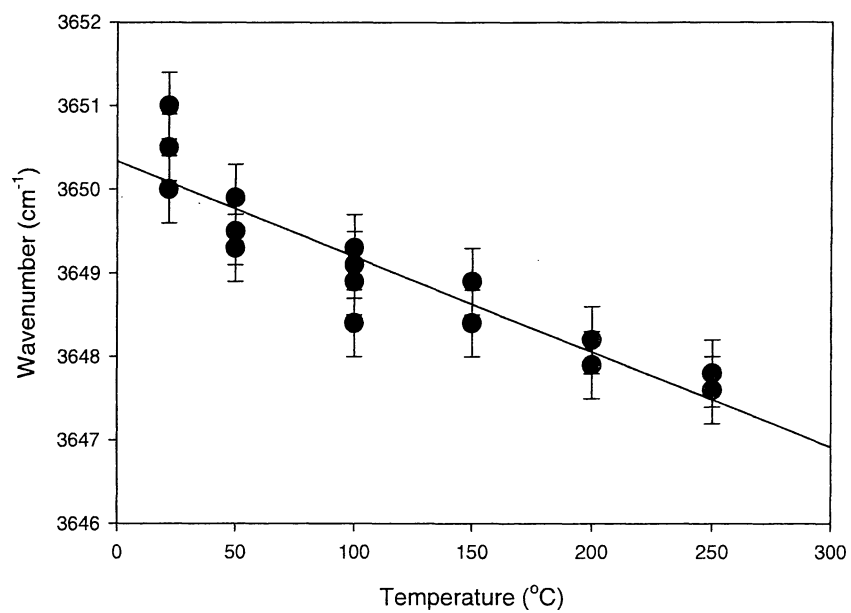
Figure 6. Temperature dependence of the 3650 cm^{-1} mode of brucite at 1 bar. The shift

has a linear relation with temperature: $\nu(\text{cm}^{-1})=3650 - 0.011T(^{\circ}C)$ with $R^2=0.84$.

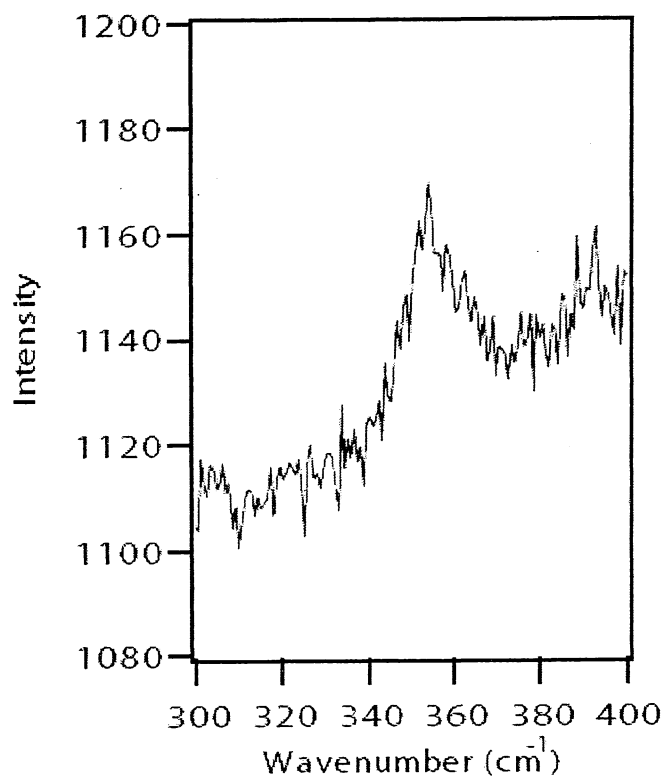**Figure 7.** Raman spectra of magnesium complex at 700 °C and 10.9kbar. The 356 cm^{-1} mode is considered to be caused by Mg^{2+}-oxygen symmetric stretching mode.

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