

# Electrical conductivity measurements of brucite under crustal pressure and temperature conditions

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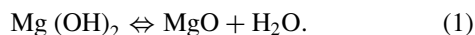
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Hydrous minerals are crucial because their occurrence is associated with seismic activity through the dehydration process that occurs in the earth's crust and/or mantle. We have developed a technique to observe the dehydration reaction of brucite using electrical conductivity variation under sealed conditions. The electrical conductivity of brucite was measured as a function of temperature. The confining pressure for the measurements was 1 GPa, which represents that of the lower crust. Two types of remarkable electrical conductivity variation were observed. During the first heating, the conductivity of the sample showed a linear variation below 700 K, as was expected from the Arrhenius equation. Once the temperature was increased to near the dehydration boundary, the sample showed a high conductivity. Even though only a small amount of H<sub>2</sub>O was formed after dehydration, bulk conductivity of the sample varied greatly, presumably caused by a combination of the presence of coexisting solid and fluid phases and a mixed electronic and ionic conduction mechanism operating in the sample.

**Key words:** Brucite, electrical conductivity, X-ray diffraction.

## 1. Introduction

A large number of researchers have investigated the physical properties of hydrous minerals and observed their reactions with fluid and mineral. Hydrous minerals, which occur throughout the lower crust and/or mantle, often dehydrate markedly during seismic activity. Brucite is a particularly good example of a hydrous mineral because of the simplicity of its chemistry. Brucite dehydrates as follows:



Schramke *et al.* (1982) employed volumetric methods to study the dehydration reaction of brucite at 8.1 kbar and 806°C and found that the results were in agreement with an equilibrium P-T curve derived from thermo-chemical data. Kanzaki (1991) adopted the differential thermal analysis (DTA) technique to study the dehydration reaction of brucite at 4–6 GPa and 1030–1120°C. Their data were used to estimate the dehydration boundary of brucite by means of thermodynamic calculations to evaluate its stability in the upper mantle. More recently, Fukui *et al.* (2005) carried out in-situ X-ray diffraction and ex-situ textural observation and thermodynamic calculations to confirm phase relations in the system MgO–H<sub>2</sub>O under high P-T conditions. These studies verified incongruent melting and precise dehydration processes for brucite.

The measurement of changes in electrical conductivity can be used to detect the phase transition of hydrous minerals. When brucite dehydrates to form periclase and H<sub>2</sub>O

under crust-like P-T conditions, a remarkable variation in conductivity can be observed. However, as noted by Johnson and Walker (1993), measuring the electrical conductivity variation associated with phase change in brucite is not without problems.

To detect dehydration in brucite, we have attempted to observe electrical conductivity changes associated with the dehydration reaction process. To this end, a technique of measuring electrical conductivity in the sample under sealed conditions was developed. Specifically, a sapphire single-crystal sample case was used. This sample case provides an ideal closed system in which the sample is not affected by physical and chemical alterations. The electrical conductivity of brucite was measured as a function of temperature while the confining pressure was fixed at 1 GPa. The recovered sample was inspected by X-ray diffraction pattern and electron probe microanalysis (EPMA). In this paper, we report the electrical properties of brucite as they relate to its dehydration process under sealed conditions.

## 2. Experimental Procedures

### 2.1 Sample preparation and high-pressure experiments

Single-crystal brucite was obtained from Ethei Mine, Zimbabwe. The crystal structure and properties of such brucite have been studied by Shinoda and Aikawa (1998). The sample was homogeneously ground to a fine grained powder, and a new cubic pressure cell for the electrical conductivity measurements was developed to seal the dehydrated brucite and prevent it from reacting with surrounding materials. This cell is shown in Fig. 1.

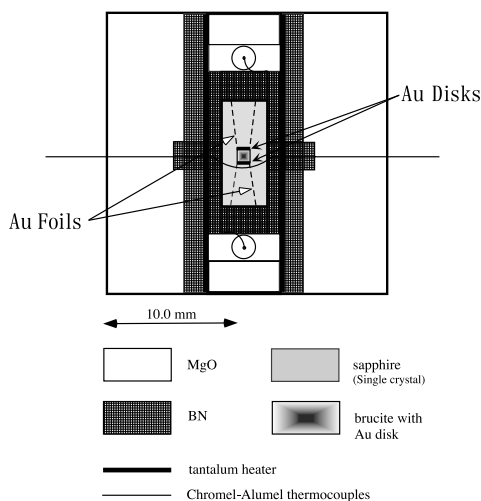


Fig. 1. Schematic cross section showing a detailed view of the cubic pressure cell. A single-crystal sapphire capsule was settled in the center of the cell and the sample was injected and sealed.

The brucite was loaded into a single crystal sapphire cylinder that was sealed using a horn-shaped sapphire and Au foil. This shape was effective for sealing decomposed periclase and  $H_2O$ . The capsule was also designed to seal a sample at the desired pressure and temperature conditions. Au foils play the dual roles of gasket in the sapphire assembly and electrodes for the conductivity measurement. The sample was 1.0 mm in diameter and 1.0 mm in length.

High pressure was generated by a DIA-type cubic anvil press (UHP-2000/20, Sumitomo Heavy Industry, Ltd., Tokyo, Japan). To guarantee a high degree of insulation, each assembly consisted primarily of MgO and BN. A MgO cube with a 21-mm edge length was used as the pressure medium. The edge length of the anvil truncation was 15.0 mm. A gasket 3.0 mm thickness pyrophyllite was used. Confining pressure for the measurement was 1 GPa, which is representative of the pressure of the lower crust. However, the actual sample pressure would be expected to be greatly different to the confining pressure because of the hard sapphire capsule. In this study, we estimate the sample pressure from the temperature by assuming that the sample P-T conditions are on the known dehydration curve of brucite (e.g., Schramke *et al.*, 1982). We consider that this is the case at the highest temperature at each heating cycle, but not during cooling because of the supposed disequilibrium. Because of the large thermal expansion coefficient of water, the sample pressure during cooling must be much lower than that at the highest temperature. As mentioned later in this article, dehydration started at about 700 K, which suggests that the sample pressure was extremely low when the dehydration began. The sample pressure was expected to reach 0.5 GPa at the highest temperature used in this study, namely, 1027 K.

The sample was heated using a 20- $\mu$ m tantalum foil heater. A pair of Chromel-alumel thermocouples, 0.10 mm in diameter, was placed around the sample case. Another pair of wired thermocouples was connected by the Au foil that wrapped around the horn-shaped sapphire. The Au disks (diameter: 1 mm) above and below the sample that

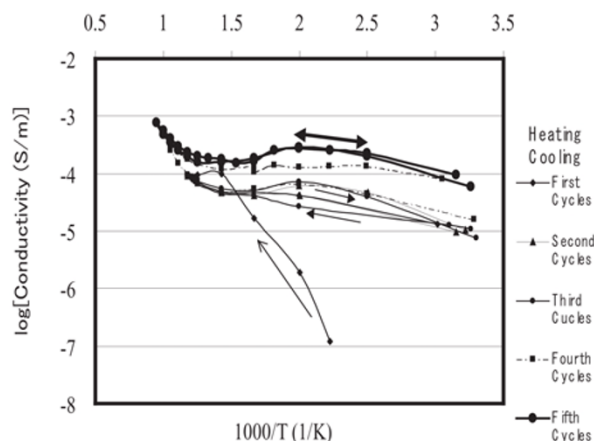


Fig. 2. Electrical conductivity of brucite at a confining pressure at 1 GPa. The conductivity data was obtained at various temperatures during the heating/cooling cycles.

acted as electrodes did not react with anything in the sample case. As the side anvils were made of conductive WC (tungsten carbide), alumina sleeves were used to cover the measurement wires for insulation outside of the cubic assembly.

## 2.2 Electrical conductivity measurements

The conductivity of the sample was carefully measured while the temperature was raised from room temperature up to 1050 K. The sample was connected to a function generator and reference resistance. A sinusoidal signal with an amplitude of 1 Vp-p was applied to the circuit. Two different electrical circuits were used, depending on the expected resistance to be measured. Where the sample resistance was comparable to or smaller than the reference resistance, the voltage applied to the sample was monitored using a digital multi-meter. If the resistance of the sample is very high, electrical noise seriously impairs the ability to measure the voltage on the sample. In this case, the voltage generated by the function generator was monitored and considered to be the same as that applied on the sample. The electrical conductivity measurements were made at 10 mHz in order to avoid significant noise from frequencies higher than 60 Hz stemming from the commercial power supply. Results on insulation tests and detailed measurement procedure are described in Fuji-ta *et al.* (2004).

## 3. Results

Many preparatory experiments have been performed to confirm the effect of moisture and water content around the pressure medium (Fuji-ta *et al.*, 2004). To exclude moisture around the pressure medium, we heated a cubic assembly up to about 500 K and kept it at this temperature for 0.5 h in advance. This procedure was essential to purge the moisture prior to the conductivity measurements. Following the preparatory heating of the sample, conductivity data and corresponding temperature were acquired. Electrical conductivity measurements were made at intervals (50 K) of increasing temperature in the high temperature range in order to monitor variations in conductivity in detail, while conductivity data were acquired every 100 K in the low temperature range to provide a rough trend in conductivity.

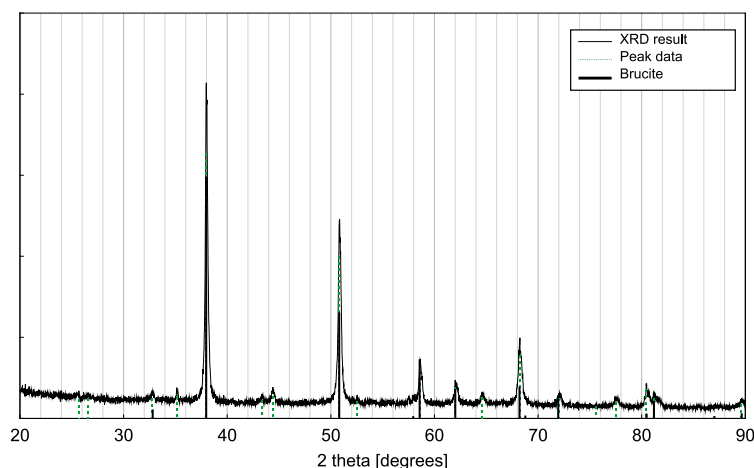


Fig. 3. X-ray diffraction patterns obtained from the recovered sample. Two peaks of brucite ( $\text{Mg}(\text{OH})_2$ ) and periclase ( $\text{MgO}$ ) were searched. The minor peaks are due to identified fragments of Au foils and Au disks in the sealed sapphire capsule.

Conductivity was plotted logarithmically against reciprocal temperature, as shown in Fig. 2.

The electrical conductivity showed a linear variation between 450 and 700 K; as such, it is in agreement with the Arrhenius law and can be fitted to a linear trend. Similar conductivity variations were observed during the measurements of crustal rocks (e.g., Fuji-ta *et al.*, 2004; Fuji-ta *et al.*, in press).

At temperatures over roughly 700 K, electrical conductivity variation was different to that observed in the low temperature range. As the temperature increased the conductivity of the sample did not change linearly. The conductivity path gradually increased during the four heating and cooling cycles, as shown in Fig. 2. Absolute conductivity varied from  $2.7 \times 10^{-5}$  to  $2.9 \times 10^{-4}$  S/m at 500 K.

As mentioned above, there are two remarkable variations in conductivity that correspond to different conductivity mechanisms. In the first heating, the conductivity changes linearly below 700 K; in the second to fifth cycles, the conductivity variation is non-linear. However, in the high temperature range up to 1050 K, the conductivity is once again linear and shows a steep gradient. The non-linear variation is similar to the change in conductivity of the electrolytes (Nesbitt, 1993).

The sample from the experimental run was decompressed and gradually cooled. The single-crystal sapphire case was recovered from the cubic assembly and examined. Although the inside of the sample case was fracture-free, micro-cracks were observed in the outside of the case, which led us to reconfirm that the sample had not been contaminated nor had it reacted with other materials in a sealed condition—which it had not. The sample enclosed in the sapphire capsule was mounted in epoxy and polished for analysis. To observe structural change of the recovered bulk powder sample, a micro-focused X-ray diffractometer was used. A  $\text{CuK}\alpha$  line generated from a rotating anode X-ray source with 40 kV and 200 mA was collimated and focused on a polished specimen. Experiments were carried out using monochromatic radiation ( $\lambda=1.54056$ ). Two diffraction patterns of brucite and periclase were studied. Only the brucite phase was detected, as shown in Fig. 3. The decom-

pressed and gradually cooled sample did not include periclase. As Johnson and Walker (1993) report, difficulty with quenching is a well-recognized phenomenon. The kinetics of dehydration and rehydration are so rapid that periclase and  $\text{H}_2\text{O}$  tend to re-form to brucite upon cooling from high temperature and pressure.

The sample was also examined by EPMA and observed using backscattered electron image (BEI). Neither cracks nor fractures were observed in the sample and the grains were uniform. Quantitative analysis indicated that the recovered sample was of a high purity  $\text{MgO}$  (99.8 wt%).

#### 4. Discussion

As shown in Fig. 2, two distinct types of temperature/electrical conductivity dependences were observed. Electrical conductivity increased linearly from 450 to 700 K, and activation energy was obtained from this linear increase—about 0.30 eV—which is unique to solid brucite. Below 700 K, the conduction mechanism operating in the solid sample involves unpolarizable and immobile charge carriers (Freund, 2003).

After the first heating over 700 K, the conductivity of the sample did not depend on temperature. Non-linear conductivity variations from room temperature to 1050 K were observed during the second to fifth cycles, as indicated by the arrows in Fig. 2. Although absolute values of conductivity were different, Nesbitt (1993) depicted variations in the conductivity of electrolytes with increasing temperature. The similarities in conductivity imply that the sample includes a fluid phase. Once conductivity had reached  $1.0 \times 10^{-5}$  S/m, the conductivity was consistently high. After this point, the conductivity gradually increased from  $2.7 \times 10^{-5}$  to  $2.9 \times 10^{-4}$  S/m at 500 K during the second to fifth heating-cooling cycles. This increase in conductivity occurs after the sample has been subjected to a peak temperature of around 1000 K.

The experimental data successfully detected electrical conductivity variations of four orders of magnitude between data obtained in the initial stage and that obtained during the following five heating and cooling cycles. Once the temperature had been increased to around the dehydration

boundary, the sample showed a high conductivity due to the sensitivity of the electrical conductivity to dehydration; therefore, small phase changes or reactions can be detected.

Even though dehydration is not significant and only a small amount of H<sub>2</sub>O is formed, the total conductivity of the sample was high after the second round of cycles. Consequently, it can be concluded that mixed charge carriers of periclase and H<sub>2</sub>O existed in the sample near the phase boundary conditions. In fact, in the experiments conducted, the brucite did not completely dehydrate and did not produce much periclase, most likely due to the conversion of periclase to brucite during decompression and quenching, as reported by Johnson and Walker (1993). Kanzaki (1991) also pointed out that previous studies revealed that periclase tends to react with H<sub>2</sub>O to form brucite during quenching. This explains the X-ray diffraction patterns that showed only brucite peaks in the recovered sample (Fig. 3).

Dehydration often takes place in the earth's crust and upper mantle. Hydrous mineral dehydration correlates to deep focus earthquakes (e.g., Meade and Jeanloz, 1991). Electromagnetic (EM) soundings have revealed a high/low conductivity contrast under mid- to lower crustal conditions (e.g., Jones, 1992). Conductive zones have been attributed to fluids released from subducting slabs (Young and Kitchen, 1989). Our experiment can account for the formation of fluid in the crust and/or mantle under arbitrary P-T conditions. If brucite dehydrates under lower crustal P-T conditions, a fluid phase will be achieved near the phase boundary. Even if a small amount of fluid phase exists, bulk conductivity of the sample is high. In a similar manner, fluids in the crust and/or mantle can serve to enhance conductivity. The experimental data on brucite clearly displays the electrical properties of hydrous minerals at a confining pressure 1 GPa and temperatures up to 1050 K.

This is our first trial designed to observe the dehydration process from the point of view of electrical conductivity variation. Further experiments are required with the aim of observing dehydration as caused by variations in electrical conductivity variation in more detail. This will also require a theoretical understanding of conductivity network mechanisms between dehydrated minerals and their fluid phases.

## 5. Conclusions

Brucite is one of the key hydrous minerals in the earth's crust and/or mantle. In this article we have reported the reaction of brucite to dehydration using electrical conductivity measurements "in situ". Specifically, a single-crystal sapphire case was used to provide sealed conditions for the measurement of electrical conductivity.

During the first heating of the sample below 700 K, electrical conductivity changed linearly with increasing temperature. This variation is usually observed for dry samples, such as dry rocks. After heating to 700 K, electrical conductivity of the sample changed non-linearly. The conductivity was high and gradually increased during each heating-cooling cycle. This characteristic phenomenon implies that the sample includes fluid phases. Even if the sample does not dehydrate adequately, a small amount of H<sub>2</sub>O drastically enhances the conductivity and maintains high conductivity values.

The sample from the experimental run was decompressed and gradually cooled. The recovered sample had not reacted with the surrounding material and sealed conditions had been maintained. Results from X-ray diffraction analysis revealed that only a brucite phase was detected. As many previous studies have suggested, the back reaction from periclase to brucite was observed.

We were able to demonstrate that the electrical conductivity variation of brucite has two distinct stages when subjected to heating-cooling cycles at a fixed confining pressure. Near the dehydration boundary, a small amount of H<sub>2</sub>O is formed that drastically enhances the conductivity of the sample. Brucite, periclase, and an aqueous phase coexist, and mixed electronic and ionic conduction operate in the sample. Consequently, variations in the electrical conductivity of the sample show variations characteristic of electrolytes.

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