Proton migration in portlandite inferred from activation energy of self-diffusion and potential energy curve of OH bond

(自己拡散の活性化エネルギーと OH ポテンシャルエネルギー曲線から推測されるポートランドサイトのプロトン輸送機構)

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The aim of the study is to investigate the fundamental mechanism of hydrogen's self-diffusion in the proton (H⁺) layer of portlandite, Ca(OH)₂, on the atomic level. For this purpose, hydrogen–deuterium (H–D), ¹⁶O–¹⁸O exchange diffusion experiments and optical absorption measurements, were conducted for portlandite. The diffusion experiments were carried out using synthetic single crystals of portlandite, and the diffusion coefficient of D and that of ¹⁸O perpendicular to the e axis were determined. The diffusion coefficients of D and that of ¹⁸O are ~10⁻¹⁵ m²/s and ~10⁻¹⁷ m²/s at 450 °C and 150 MPa, respectively. The large difference between their diffusion coefficients indicates the hydrogen diffuses not as a H₂O molecule or a H₃O⁺ ion but as a single proton. Arrhenius parameters for the proton diffusion perpendicular to the e axis, which were determined from the temperature dependency of the diffusion coefficient of D, gave a frequency factor of 1.0×10⁻¹⁰ m²/s and an activation energy of 0.61 eV (58.5 kJ/mol). The activation energy corresponds to the height of the potential barrier between two oxygen atoms across an interlayer to be cleared by a proton diffusing perpendicular to the e axis. The potential barrier height was also theoretically estimated using the OH potential energy curve (OH-PEC) determined by optical absorption measurements. The potential barrier derived theoretically was 3.11 eV. There is the large difference of the potential barrier between the experimental and theoretical results. It suggests that the interaction between a diffusing proton and the vacancy of a proton site, and the shortening of interlayer oxygen distance by thermal vibration, which took no thought of the theoretical estimation, markedly reduce the potential barrier. Furthermore, the jumping frequency of the protons was determined from the frequency factor to be 1.7×10¹³ Hz. The value is in agreement with the frequency of the thermal vibration of the oxygen atoms. Consequently the thermal vibration of the oxygen atoms must be the dominant factor which controls on the proton migration.
# TABLE OF CONTENTS

Chapter 1: Introduction  
1.1 Proton in the crystal structure of portlandite .......................... 1  
1.2 Objective and Methodology ............................................. 2  
1.3 Measurement of H-D and $^{16}$O-$^{18}$O diffusion profiles  
using micro Raman spectroscopy ............................................. 5  
1.4 A theory of the OH-PEC .................................................. 8  

Chapter 2: Quantitative analysis using micro Raman spectroscopy  
2.1 Review of micro Raman spectroscopy ................................... 10  
2.2 Reference sample preparation ........................................... 11  
2.3 Micro Raman measurement .............................................. 13  
2.4 Rotating sample stage .................................................. 15  
2.5 Intensity calibration ..................................................... 15  
2.6 Raman spectra of four mixtures ....................................... 17  
2.7 Calibration curve: theory ............................................... 19  
2.8 Quantitative analysis of deuterium in portlandite .................. 25  

Chapter 3: Experimental methods  
3.1 H-D exchange diffusion experiment ................................... 27  
3.2 $^{16}$O-$^{18}$O exchange diffusion experiment ......................... 29  
3.3 Optical absorption measurements ..................................... 31  

Chapter 4: Results and discussions  
4.1 Determination of diffusion coefficient and activation energy ....... 34
4.2 Proton diffusion mechanism ................................................. 37
4.3 Estimation of potential barrier height .......................................... 39
4.4 The jumping frequency of a proton ............................................. 44

Summary ......................................................................................... 47
Acknowledgements ............................................................................ 48
References ......................................................................................... 49
CHAPTER 1: INTRODUCTION

Diffusion of hydrogen atoms in minerals often controls the macroscopic properties of minerals such as deformation, the kinetics of reactions and electrical conductivities. Previous experimental studies have reported the hydrogen diffusion coefficients of hydrous minerals using hydrogen-deuterium (H-D) exchange diffusion experiments for powdered samples (Ingrin and Blanchard 2006). No correlations have been reported between the hydrogen diffusion mechanism on an atomic scale and crystal structures because diffusion coefficients along a specific crystal axis cannot be determined using powdered samples. To determine the hydrogen diffusion mechanism at the atomic scale, namely, the fundamental process of hydrogen migration, the diffusion coefficient along a specific crystal axis must be determined using a single crystal. In this respect portlandite, Ca(OH)$_2$, is a good model system for studying the diffusion mechanism because its crystal structure is very simple, and paths of hydrogen migration can be easily identified in the crystal structure. In the present study, a H-D diffusion experiment has been conducted using a single crystal of portlandite in order to clarify the fundamental process of hydrogen migration.

1.1 Proton in the crystal structure of portlandite

Portlandite is isostructural with brucite, Mg(OH)$_2$ (space group: P$ar{3}$m1, Z = 1), which has a CdI$_2$ structure. In portlandite, distorted [CaO$_6$] octahedra are linked together by sharing edges to form a [CaO$_6$] octahedra layer (Fig. 1a). The [CaO$_6$] layers stack along the c axis and a hydrogen atom bonds to each apical oxygen atom in the [CaO$_6$] octahedra to form an OH dipole. The protons (H$^+$) form weak hydrogen bonds with the three nearest oxygen atoms of the adjacent [CaO$_6$] layer. Furthermore, there is a repulsive interaction between one proton and the three nearest-neighbor protons (Prewitt and Parise 2000; Parise 2006). This induces
disorder at the proton locations (Fig. 1b). The results of the neutron diffraction experiments on portlandite (Desgranges et al. 1993; Xu et al. 2007) suggest that a proton occupies three equivalent 6i Wyckoff sites, which are distant from the 2d site, with occupancies of 1/3. Hence, the disorder is generated by the OH dipole axis being tilted slightly relative to the c axis. The distance between the three 6i sites is small at low pressure (0.36 Å at 150 MPa), but it increases with increasing pressure (0.94 Å at 4.5 GPa; Xu et al. 2007). Furthermore, computer simulations based on first-principle calculations (Raugei et al. 1999; Mookherjee and Stixrude 2006) have demonstrated that a proton dynamically hops between the three equivalent sites at low pressure.

The protons between two [CaO₆] layers form a quasi-two-dimensional hydrogen-bonding network that has a honeycomb-like structure (Fig. 1b). Hydrogen self-diffusion through the honeycomb layer of portlandite is also of interest in the field of geosciences. The honeycomb layer of protons between [CaO₆] layers is similar to arrangements of protons on hydrated surfaces of olivine and the hydrated planer defect in olivine, which is main component in the upper mantle (Kitamura et al. 1987). The diffusing hydrogen through the planer defects may be controlled by the same mechanism of diffusion as that in the honeycomb layer of portlandite. Therefore, the hydrogen diffusion coefficient in the honeycomb layer provides useful information on the estimate of the hydrogen diffusion rate on the hydrated grain boundaries of the polycrystalline olivine in the mantle wedge.

1.2 Objective and Methodology

The aim of the current study is to make the hydrogen migration process in portlandite clear by experiments. I will consider the hydrogen migration process under the following heads: 1) the chemical form of the diffusing hydrogen, 2) the migration path of hydrogen in the crystal structure and 3) the potential energy along the migration path. Each head can be
Figure 1. Crystal structure of portlandite Ca(OH)$_2$.

a Side view of the portlandite crystal. A portion of two [CaO$_6$] layers and the proton layer between the [CaO$_6$] layers is shown. b A (001) view of a “honeycomb” proton layer. The bold solid lines and the thin solid lines show upper and lower [CaO$_6$] layers, respectively. The broken line indicates a unit cell.
experimentally approached as mentioned below.

In the case of hydroxide minerals such as portlandite, possibly its hydrogen does not diffuse independently but diffuse as a H$_2$O molecule or a H$_3$O$^+$ ion in its crystal structures, because O-H bonding is strong. Thus there are three possible chemical forms of the diffusing hydrogen, namely, a single proton, a H$_2$O molecule and a H$_3$O$^+$ ion. The chemical form of migrating hydrogen can be shown by a comparison between the diffusion coefficient of hydrogen and that of oxygen. If the hydrogen in portlandite diffuses as a H$_2$O molecule or a H$_3$O$^+$ ion, the diffusion coefficient of the hydrogen must be nearly equal to that of the oxygen, on the other hand, if the hydrogen does not cooperate with the oxygen atoms during diffusion, the hydrogen diffusion coefficient must be larger than the oxygen diffusion coefficient. I have carried out H-D and $^{16}$O-$^{18}$O exchange diffusion experiments in order to determine the hydrogen and oxygen diffusion coefficients.

The migration path of hydrogen can be inferred from crystal structure. In the case of the hydrogen diffusing through the honeycomb proton layer of portlandite, its migration path is restricted, because the hydrogen on a 6$i$ site migrates only one of the three neighboring 6$i$ sites (Fig. 1b). The macroscopic migration rate of hydrogen diffusing in a proton layer is reflected in the hydrogen diffusion coefficient perpendicular to the c axis.

As for the potential energy along the migration path of hydrogen, if the hydrogen in portlandite diffuses as a proton, the proton diffusing through a proton layer has to overcome a single potential energy barrier to migrate to the next 6$i$ site in the adjacent [CaO$_6$] layer. This activation energy of the proton diffusing perpendicular to the c axis includes energy corresponding to the height of the single potential barrier, because the activation energy of diffusion is generally energy required for a diffusing atom when it migrates to a neighboring site (Borg and Dienes 1988). An independent method for determining the height of the potential barrier to be cleared by the hydrogen involves deriving it theoretically from the
interatomic distance and the potential energy curve of an OH dipole (OH-PEC). Therefore, in order to determine the fundamental mechanism of hydrogen diffusion, the activation energy perpendicular to the e axis determined by H–D exchange diffusion experiments and a theoretical OH-PEC are required. The actual OH-PEC in portlandite can be estimated from optical measurements as described in the section 1.4.

Summing up the contents of experiments, the diffusion coefficients perpendicular to the e axis for proton and oxygen were determined by H-D and $^{16}$O–$^{18}$O exchange diffusion experiments using single crystals of portlandite. The activation energy of the hydrogen diffusion was estimated from the temperature dependence of the hydrogen diffusion coefficient from 250 °C to 450 °C under 150 MPa. Furthermore, the OH-PEC was determined by optical absorption measurements. Based on the dual information for the hydrogen diffusion: the diffusion coefficients and the OH-PEC, I will discuss the migration mechanism of the hydrogen in the chapter 4.

1.3 Measurement of H-D and $^{16}$O–$^{18}$O diffusion profiles using micro Raman spectroscopy

Micro Raman spectroscopy was applied to measure diffusion profiles of D and $^{18}$O in samples. In the previous hydrogen diffusion experiments, micro IR spectroscopy was used for quantitative measurements of H-D diffusion profiles (Ingrin and Skogby 2000; Kurka et al. 2005). Micro Raman spectroscopy was first used to determine D and $^{18}$O profiles in this study. Micro Raman spectroscopy has two advantages over micro IR spectroscopy. First, since the spatial resolution of micro Raman spectroscopy (as small as 1 μm) is much higher than that of micro IR spectroscopy (≥10 μm), single crystals smaller than 100 μm can be used as starting material of diffusion experiments. Second advantage is simplicity in sample preparation. As micro Raman spectroscopy detects Raman scattering light from a focused point of a laser
excitation beam, there are no restriction on the sample thickness. On the other hand, analytical samples of the micro IR spectroscopy must be constant thickness because absorption spectra from the transmitted light of samples are required to analyze samples. In particular, when hydrous minerals such as portlandite are measured, their thicknesses must be below 50 μm to avoid saturation of signals due to the intense OH absorptions in IR absorption spectra. Such a thin section is difficult to prepare.

A calibration curve, which expresses the correlation between the concentration of a chemical species and the relative intensity of the Raman band due to the chemical species, must be constructed in order to obtain D and 18O diffusion profiles using micro Raman spectroscopy. In the Raman spectra of portlandite partially replaced with D and 18O, the relative Raman intensity of the OD stretching mode (A1g normal vibration; 2667 cm⁻¹) to OH stretching mode (3620 cm⁻¹, Fig. 2a), and that of the 18OH stretching mode (3608 cm⁻¹) to OH stretching mode is dependent on the concentrations of D and 18O, respectively. The substitution by 18O does not change O-H bond distance, and so the substitution does not yield the difference between 18OH and OH stretching modes in the vibrational Raman cross section, which depends on the polarizability (Kudoh 1996). Thus the relative Raman intensity of the 18OH stretching mode is proportional to the concentration of 18O. On the other hand, the substitution by D induces a very small change in the O-H bond distance and shortened the distance by approximately 0.01 Å (Jeffrey 1997). The change in the O-H bond distance due to the D substitution yields the small difference between OD and OH stretching modes in the vibrational Raman cross section. Consequently, the relative intensity of the OD stretching mode and the concentration of D do not have a linear relationship. It is necessary to determine the calibration curve between the relative intensity of the OD stretching mode and mole ratio of D to H by experiment. I have developed the practical method of the quantitative analysis for binary mineral mixtures using micro Raman spectroscopy, and the quantitative curve for
Figure 2. Normal modes related with OH stretching vibration.

a Raman active mode: \( \text{A}_{1g} \) mode, b Infrared active mode: \( \text{A}_{2u} \) mode. The arrows show the displacements of the atoms. The Raman and the IR active modes correspond to the in-phase stretching and the out-of-phase stretching of the two OH groups of the unit cell, respectively.
quantitative analysis of deuterium in portlandite was constructed by the method. The method will be introduced in the chapter 2.

1.4 A theory of the OH-PEC

The actual OH-PEC is asymmetrical to the equilibrium position. Deviation of the PEC from a simple parabolic function is called "anharmonicity" (Herzberg 1989). The anharmonicity cannot be neglected at any position apart from the equilibrium position. In the current work, the Morse function, \( U(r) \), is assumed to be an OH-PEC of portlandite (Morse 1929);

\[
U(r) = D_e (1 - \exp[-\alpha(r - r_0)])^2
\]

where \( D_e \) is dissociation energy, \( \alpha \) is a constant, \( r \) is the distance to the proton from the oxygen atom, and "\( r_0 \)" is the equilibrium O-H distance (= 0.95 Å; Xu et al. 2007). The eigenvalue \( G(n) \) of the Schrödinger equation representing the nuclei motion in OH;

\[
[-\frac{\hbar}{2m} \Delta + U(r)] \phi(r) = G(n) \phi(r),
\]

can be expressed as Eq. 2 when the Morse function is substituted for potential term in the equation (Herzberg 1989).

\[
G(n) = (n + \frac{1}{2}) \hbar \omega_e - (n + \frac{1}{2})^2 \hbar \omega_e \chi
\]

where \( n \) is the vibrational quantum number, \( \hbar \) is Plank's constant, \( \chi \) is an anharmonic coefficient, and \( \mu \) is the reduced mass of O-H, which is \( 1.563 \times 10^{-27} \) kg. \( D_e \) and \( \alpha \) in Eq. 1 are related with \( \omega_e \) and \( \chi \) as follows (Herzberg 1989),

\[
\omega_e = \frac{\alpha}{\pi} \sqrt{\frac{D_e}{2\mu}},
\]

\[
\chi = \frac{\hbar \omega_e}{4D_e} = \frac{\hbar \alpha}{4\pi \sqrt{2\mu D_e}}.
\]

The energy of the vibrational transition from the ground state to the \( n \)-th states is \( G(n) - G(0) \).
The OH-PEC of portlandite was estimated from the measured absorption bands due to the OH stretching vibration. Hence, assuming an absorption wavenumber of the $n$-th overtone mode of the OH stretching vibration is $\omega_n$, $G(n)-G(0)$ is expressed as;

$$G(n) - G(0) = h \omega_n = n h \omega_e \{1 - (1 + n) \chi\} \quad (5)$$

from Eq. 2. $\omega_e$ and $\chi$ can be obtained from Eq. 5, and the resultant $D_e$ and $\alpha$ also were derived from Eqs. 3 and 4. The absorption band due to the fundamental mode ($A_{2u}$ normal vibration; Fig. 2b) of the OH stretching vibration appears in the mid infrared (IR) region and absorption bands of overtone modes above the second mode appear from the near infrared (NIR) to the visible (VIS) regions. The OH absorption bands were measured using micro Fourier transform IR (FT-IR), NIR and VIS spectrometers in this study.
CHAPTER 2: QUANTITATIVE ANALYSIS
USING MICRO RAMAN SPECTROSCOPY

I have developed a method for the quantitative analysis of binary mixtures of minerals using a common micro Raman spectrometer having backscattering optical configuration (180° illumination) and a rotating sample stage. Using the averaged Raman spectra of mineral mixtures, the calibration curves of five mixtures of portlandite, calcium carbonate and silica minerals — portlandite (Ca(OH)$_2$) and deuterated portlandite (Ca(OD)$_2$), calcite and quartz, aragonite and calcite, quartz and cristobalite, and coesite and quartz — were constructed.

2.1 Review of micro Raman spectroscopy

Micro Raman spectroscopy is a powerful tool in mineralogical and petrological studies because Raman spectra can be measured quickly and with high spatial resolution (as small as 1 μm) without any destruction of the samples (McMillan et al. 1996). Moreover, polymorphs can be easily distinguished using micro Raman spectroscopy. Quantitative analyses of polymorphs using micro Raman spectroscopy make it possible to analyze and use natural mineral and rock samples in many unique ways. For example, the compositional analysis of very small solid inclusions including multiple phases, mapping analysis of calcium carbonate polymorphs on the surfaces of sedimentary carbonate rocks, etc., are potential applications of interest. However, quantitative analyses of mixed polymorphs using micro Raman spectroscopy have been rarely attempted in previous studies (Kontoyannis and Vagenas 2000; Fukuda et al. 2006); hence, the analysis methodology has not been established yet.

Micro Raman spectrometers can have many optical configurations. In geosciences, the backscattering (180° illumination) configuration is typically used; here, a typical method is to
perform coaxial illumination and light collection using the same objective (Fig. 3; Turrell and Corset 1996; McMillan et al. 1996). The backscattering micro-spectrometer is easy to operate and has a good spatial resolution. However, quantitative analyses of solid mixtures are difficult using this optical configuration because it is difficult to obtain reference powder samples for the construction of quantitative curves. The reference powder sample must be mixed homogenously within a limited area that is as small as the spatial resolution of the micro Raman spectrometer. For accurate quantitative analyses of mixed polymorphs, the calibration curves compiled from the Raman spectra of weighted mixtures of reference materials are required.

In this chapter, I will explain a practical technique for the quantitative analyses of binary mixtures of minerals using a backscattering micro Raman spectrometer, and calibration curves for, in addition to portlandite and deuterated portlandite, silica (quartz, cristobalite, and coesite) minerals and calcium carbonate (calcite, aragonite) minerals have been determined. Furthermore, a method for sensitivity calibration of spectrometer, which is essential to carry out accurate quantitative analysis, is also discussed.

2.2 Reference sample preparation

Ca(OD)$_2$ was synthesized by reacting lime (CaO, Wako Co.) powder with deuterated water (D$_2$O). The hydration reaction of lime is a highly exothermic reaction. The heat of the reaction prevents the synthesis of the pure Ca(OD)$_2$ under open air, because the heat of the reaction promotes exchange of D$_2$O in the reactor with H$_2$O vapor in air. A Y-type glass ampoule was used as the reactor in order to avoid contamination by the isotopic exchange. The lime powders were placed in one end of the Y ampoule and heavy water was injected into the other end. The two reagents were mixed after sealing the Y-type glass ampoule and it was heated at 180 °C for 48 hours. The recovered product was confirmed to be Ca(OD)$_2$ by
Figure 3. Schematic diagram of the typical backscattering micro Raman spectrometer.
powder X-ray diffraction and infrared absorption spectra. The Ca(OD)₂ powder and Ca(OH)₂ powder of the reagent were mixed well after determining the mixed ratio by careful weighing. The mixed powder was stuffed in the sample base of a tablet die and shaped into pellets by applying a pressure of 8000 kgf/m² for 10 minutes.

Reagent-grade calcite and quartz were obtained from Wako Pure Chemical Industries, Inc. Furthermore, a clear single crystal of aragonite from Molina de Aragon (Guadalajara, Spain) was used as the reference material. The cristobalite was synthesized by heating powdered quartz in an electrical furnace at 1500 °C for 24 h and then cooled to 268 °C. On cooling, cristobalites undergo a displacive phase transition from β phase to α phase (Heaney 1994). This synthetic cristobalite was confirmed to be in the α phase by powder X-ray diffraction (XRD) at room temperature. The coesite used in this study was synthesized by using a belt-type high-pressure apparatus at the National Institute for Research in Inorganic Materials. The starting material of powdered quartz was enclosed in a Pt capsule with water, and then maintained at 6.75 GPa and 1900 °C for 30 min; subsequently, its temperature was decreased to 1000 °C at a rate of 3 °C/min. By using powder XRD, we confirmed that the synthetic coesite is free of impurities.

The synthetic and natural minerals were powdered using an agate mortar. The mean grain size of the powders was approximately 1 μm. The two types of powdered samples—synthetic and natural—were mechanically mixed using an auto-mixer after their mixture ratios were determined by careful weighing. The mixed powder was placed in a tablet die and shaped into tablets.

2.3 Micro Raman measurement

Raman measurements were performed using a micro Raman spectrometer at the Osaka City University (OCU). This spectrometer is a single monochromator (250IS, Chromex
Inc.) equipped with a cooled 128 × 1024 charge-coupled device (CCD) detector. The instrument has an asymmetric geometry similar to Czerny-Turner spectrometers, where the diffractive grating has 2400 grooves per mm. The Raman shift axis of the CCD data was calibrated using a cubic polynomial fit to the positions of the emission lines of neon. The 488 nm line of an Ar⁺ laser (5500ASL, Ion laser Technology Inc.) was used for exciting the Raman scattering. The laser beam was introduced into the micro Raman spectrometer via an optical fiber, and it was focused on the surface of a sample through an objective (M Plan Apo SL 20×, N.A.0.28, Mitutoyo Inc.); its theoretical beam spot size is 5 μm in diameter. The optical fiber scrambles the initial polarization of the laser beam, and hence, a depolarized laser beam was focused on the samples. Moreover, the polarization effect of Raman spectra may affect the quantitative analyses of the aggregates of small grains, and this effect can be drastically decreased by using a depolarized laser beam. The intensities of the Raman band of the crystalline material depend on the geometric relations between the polarized direction of the laser light and the crystallographic orientation of the sample (cf. Kudoh 1996). The backscattered light was collected using the same lens. The measurement time was varied from 60 s to 100 s to provide adequate signal-to-noise ratios in the spectra.

Since the sensitivity of a Raman spectrometer differs significantly with wavelength, the intensity axis of the raw Raman spectra must be corrected so that the intrinsic spectra before passing through the optics can be obtained. The sensitivity of the instrument depends on the sensitivity of the CCD detector and the diffractive efficiency of the diffraction grating etc. (Mark et al. 1993). Therefore, for obtaining accurate values of the intensity of a Raman band, it is important to correct the intensity axis of the raw spectra. We calibrated the sensitivity of the micro Raman spectrometer using a radiometric calibration standard, the LS-1-CAL (Ocean Optic Inc.), as the standard light source. Assuming that \( R_{\text{ref}}(\nu) \) is the reference intensity of the light radiating from the standard lump, \( I_{\text{ref}}(\nu) \) is the intensity of the
standard lump after passing through the micro Raman spectrometer, and $I_{\text{raw-R}}(v)$ is the raw Raman spectrum. Then, the intensity-corrected Raman spectrum $I_{\text{corr-R}}(v)$ is given by

$$I_{\text{corr-R}}(v) = \frac{I_{\text{raw-R}}(v) R_{\text{ref}}(v)}{I_{\text{ref}}(v)}.$$

(6)

The correction of the intensity axis of the Raman spectra is very important for obtaining the relative intensities of the Raman bands, as will be discussed later.

To determine the intensities of Raman bands accurately, curve-fitting analysis was carried out using GRAMS/Al software (Thermo Galactic Inc.). The corrected Raman bands were then fitted by a Lorentzian function with background correction using a linear baseline.

2.4 Rotating sample stage

The size of a focused laser beam spot is almost equal to the size of a grain of the powdered sample. Accordingly, normal measurements lead to a large deviation from the average spectra, even if the two reference powders are homogeneously mixed in the tablet. To obtain the averaged spectra, I constructed a rotating sample cell (Fig. 4), which rotates the sample horizontally during the Raman measurement at approximately 40 rpm. The spectra of the averaged compositions of the binary mineral mixtures can be obtained by measuring a larger area using the rotating sample stage. Each sample was measured five times with different rotational tracks which were illuminated by a laser beam.

2.5 Intensity calibration

In the Raman spectra of a material, the Raman bands are unique characteristics of the material, just like finger prints are unique to a human; hence, the intensity ratios of the Raman bands have to be universally constant when the crystallographic settings or conditions are identical. However, the intensity ratios of the Raman bands of one of the materials vary with
Figure 4. a Cross-section, and b view from the top of a rotating sample stage. The rotating sample stage is made of stainless steel. The sample surface is adjusted to be perpendicular to the laser beam by a radial alignment of a hemispherical sample stage. The radial alignment is achieved by tightening the three screws that hold the hemispherical sample stage. c Geometry of the rotating sample stage placed under the objective.
different spectrometers. This represents a contradiction, and this variation has to be a result of the differences in the sensitivity of the detectors and optical elements. To discuss the quantitative relationship between the intensity ratio and quantitative ratio, the intensity axis of the Raman spectra must be corrected by using a standard light. We checked the Raman spectra of a pellet of powdered calcite using two micro Raman spectrometers: spectrometer-A at Osaka City University and spectrometer-B at the Institute for Study of the Earth’s Interior at Okayama University. The optical configuration of spectrometer-B has been described in detail by Tsujimura et al. (2004). Figures 5a and 5b show the raw Raman spectra of the powdered calcite measured using spectrometer-A and -B, respectively. Figures 5e and 5d show the corrected Raman spectra of Figures 5a and 5b, respectively. The three peaks at 281 cm⁻¹, 713 cm⁻¹, and 1085 cm⁻¹ in each spectrum are intrinsic Raman bands of calcite. The intensity of the 1085 cm⁻¹ mode was normalized to 100. The relative intensities of the Raman bands at 281 cm⁻¹ and 713 cm⁻¹ in the raw spectrum obtained using spectrometer-A were 10 and 9, respectively (Fig. 5a), and the relative intensities in the raw spectrum obtained using spectrometer-B were 20 and 13, respectively (Fig. 5b). The discrepancy in the ratio of the intensities \( (I_{281}/I_{713}) \) in the two spectra indicates different sensitivities of the spectrometers. Figure 6 shows the sensitivities of both spectrometers under the same experimental setting. After correcting the spectra by using Eq. 6, the relative intensities of the Raman bands at 281 cm⁻¹ and 713 cm⁻¹ are 31 and 10 in the spectrum of spectrometer-A (Fig. 5e), respectively, and 31 and 11 in the spectrum of spectrometer-B (Fig. 5d), respectively. This indicates that the correction of the intensity axis is an essential procedure for obtaining a universal calibration curve with different instruments.

2.6 Raman spectra of four mixtures

Figure 7 shows the Raman spectra of the four mixtures: (a) calcite/quartz, (b)
Figure 5. Raman spectra of the powdered calcite. a and b are raw Raman spectra obtained from spectrometer-A and spectrometer-B, respectively. c and d are Raman spectra corrected for the intensity of a and b, respectively. Each spectrum is normalized for the intensity so that the intensity of the Raman band of the 1085 cm$^{-1}$ mode is 100.

Figure 6. The detection efficiencies of the spectrometers; $l_{ref}(v)/R_{ref}(v)$.  

18
aragonite/calcite, (e) quartz/cristobalite, and (d) coesite/quartz. The $W$ values are weight ratios of the subscript minerals; for example, $W_{\text{Cal}}$ is the weight ratio of the calcite in the calcite/quartz mixture. All the spectra for the four mixtures shown in Fig. 6 were measured using the rotating stage. For calcite, the most intense peak is at 1085 cm$^{-1}$, and a second peak occurs at 281 cm$^{-1}$. In the case of aragonite, the most intense peak occurs at 1084 cm$^{-1}$, which is not shown in Fig. 7, and the second peak is at 208 cm$^{-1}$. The first peaks of calcite and aragonite overlap, while the second peaks are well separated. Although the most intense peaks are usually adopted for the quantitative analysis, the first peaks of calcite and aragonite are too close to be decomposed. Therefore their second peaks have been adopted to calculate the weight fraction of calcite and aragonite in the next section. The intensities of the two second peaks of calcite (281 cm$^{-1}$) and aragonite (208 cm$^{-1}$) are represented by $I_{\text{Cal}}$ and $I_{\text{Arg}}$, respectively. The most intense Raman bands of cristobalite, quartz, and coesite are 420 cm$^{-1}$ ($I_{\text{Cr}}$), 465 cm$^{-1}$ ($I_{\text{Qz}}$), and 512 cm$^{-1}$ ($I_{\text{Coe}}$), respectively. Since these three bands are not superimposed on each other, their three first peaks have been adopted for calculating the weight fraction.

2.7 Calibration curve: theory

All the minerals treated in this study are transparent with less absorption in the visible light. In the Raman spectra of binary mixtures consisting of the transparent minerals, the intensity ratio among the Raman bands, which results from one component, does not depend on the concentration of another component, because the “matrix effect” due to the absorption of laser beams and Raman scattered light (Shriver and Dunn 1974) can be neglected. Thus the calibration curve that represents the relationship between the relative intensities of Raman bands and the weight fractions has the form of a simple function, as will be subsequently explained.
Figure 7. Raman spectra of calcite/quartz (a), aragonite/calcite (b), quartz/cristobalite (c), and coesite/quartz mixtures (d). The weight fraction ratio of one component in each mixture is shown in each spectrum.
The measured intensity of the Raman scattering species $i$ can be represented ideally as follows (Strommen and Nakamoto 1984):

$$I(v) = I_0 K(v_i) C_i.$$  \hspace{1cm} (7)

Here $I_0$ is the incident intensity of the laser beam; $v$, the Raman frequency; and $C_i$; the number of moles of $i$ per unit volume. $K(v_i)$ is an original factor that includes the frequency-dependent term, spectrometer response, self-absorption of the medium, and vibrational Raman scattering cross section. The absolute value of $K(v_i)$ cannot be determined experimentally because it is difficult to evaluate the spectrometer response.

If we replace the concentration $C_i$ in Eq. 7 with $\rho_i$, which is the weight of $i$ per unit volume of the sample, $\rho_i = m_i C_i$ ($m_i$; the molecular weight of $i$), we obtain

$$I(v_i) = I_0 K(v_i) \rho_i,$$  \hspace{1cm} (8)

where $K(v_i)$ is given by $K_i(v_i)/m_i$. Next, we consider the mixture of the transparent minerals “a” and “b” having Raman bands with Raman frequencies $v_a$ and $v_b$, respectively. Since the matrix effect due to self-absorption in the mixture is negligible, the measured intensities of the Raman bands of “a” and “b”—$I_a(v_a)$ and $I_b(v_b)$—obey Eq. 8. The relative intensity of the Raman band of “a” to the Raman band of “b” can be expressed as follows:

$$\frac{I_a(v_a)}{I_a(v_a) + I_b(v_b)} = \frac{W_a}{W_a + f(v_a, v_b)(1 - W_a)}.$$  \hspace{1cm} (9)

\[ f(v_a, v_b) = \frac{K_b'(v_b)}{K_a'(v_a)}, \]

where $W_a$ is the weight fraction of “a” in the mixture; $W_a$ is given by $W_a = \rho_a/(\rho_a + \rho_b)$. The constant $f(v_a, v_b)$ defined in the above expression determines the form of the calibration curve, and therefore, constructing the calibration curve will involve determining the constant $f(v_a, v_b)$ from experimental data.

Figure 8a shows the relationship between $W_{Cal}$ of the calcite/quartz mixture and the
relative intensities of the Raman bands of calcite for the first band of quartz at 465 cm$^{-1}$. The filled squares, filled circles, and filled triangles are the relative intensities of calcite Raman bands at 1085 cm$^{-1}$, 281 cm$^{-1}$, and 731 cm$^{-1}$, respectively. The dashed curves are least squares fitting curves assuming Eq. 9. The resultant $f(v_a, v_b)$ values are listed in Table. 1. In Fig. 8a, the relative intensities of the calcite Raman band at 1085 cm$^{-1}$ measured without the rotating stage have been superimposed as open circles. It can be seen that the results measured without rotation have a large standard deviation and are not reliable for obtaining $f$ values. The large standard deviation is probably a result of the very high spatial resolution of micro Raman spectroscopy. On the other hand, the data obtained from the spectra measured with the rotating sample show small standard deviation and a reduction to a few percent. Therefore the measurements with the rotating sample have clearly proven to be more effective in obtaining the spectra of the average compositions of mixtures. Figures 8b, 8c, and 8d show the correlations between $W_{A}$ and $I_{A}/(I_{A} + I_{C})$ for aragonite/calcite, $W_{Q}$ and $I_{Q}/(I_{Q} + I_{C})$ for quartz/cristobalite mixtures, and $W_{C}$ and $I_{C}/(I_{C} + I_{Q})$ for coesite/quartz mixtures, respectively. The $f$ values of the four mixtures are listed in Table 1. When the calibration curves are applied to the Raman spectra of the natural samples, the equation derived from the transformation of Eq. 9,

$$W_a = \frac{I_a}{I_a + f(v_a, v_b)^{-1} I_b}$$

is useful for converting the relative Raman intensity into a weight fraction. The quantitative limits determined from the standard deviation of the $f$ values are 2 wt% for the calcite/quartz mixture, 4 wt% for the aragonite/calcite mixture, 7 wt% for the quartz/cristobalite mixture, and 3 wt% for the coesite/quartz mixture.
Figure 8. Correlations between the relative Raman intensity and the weight fraction for calcite/quartz (a), aragonite/calcite (b) quartz/cristobalite (c), and coesite/quartz mixtures (d). Error bars in each graph represent the standard deviation calculated from five measurements. Dashed curve is the curve obtained by fitting the plots to Eq. 10.
Table 1. Constant $f(v_a, v_b)$

<table>
<thead>
<tr>
<th>Mixture species</th>
<th>$v_a$ (cm$^{-1}$)</th>
<th>$v_b$ (cm$^{-1}$)</th>
<th>$I_a/(I_a+I_b)$</th>
<th>$W_a$</th>
<th>$f(v_a, v_b)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite and quartz</td>
<td>281 cm$^{-1}$</td>
<td>465 cm$^{-1}$</td>
<td>(Cal)</td>
<td>Calcite</td>
<td>0.63 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>713 cm$^{-1}$</td>
<td>465 cm$^{-1}$</td>
<td>(Cal)</td>
<td>Calcite</td>
<td>2.02 ± 0.42</td>
</tr>
<tr>
<td></td>
<td>1085 cm$^{-1}$</td>
<td>465 cm$^{-1}$</td>
<td>(Cal)</td>
<td>Calcite</td>
<td>0.24 ± 0.03</td>
</tr>
<tr>
<td>Quartz and cristobalite</td>
<td>465 cm$^{-1}$</td>
<td>420 cm$^{-1}$</td>
<td>(Qtz)</td>
<td>Quartz</td>
<td>0.53 ± 0.16</td>
</tr>
<tr>
<td>Coesite and quartz</td>
<td>521 cm$^{-1}$</td>
<td>465 cm$^{-1}$</td>
<td>(Coe)</td>
<td>Coesite</td>
<td>0.85 ± 0.10</td>
</tr>
<tr>
<td>Aragonite and calcite</td>
<td>208 cm$^{-1}$</td>
<td>281 cm$^{-1}$</td>
<td>(Arg)</td>
<td>Aragonite</td>
<td>2.29 ± 0.39</td>
</tr>
</tbody>
</table>
2.8 Quantitative analysis of deuterium in portlandite

The relative intensity of the OD stretching mode (2667 cm\(^{-1}\)) to OH stretching mode (3620 cm\(^{-1}\)), \(I_{OD}/(I_{OD}+I_{OH})\), in which the \(I_{OD}\) and \(I_{OH}\) are intensities of the OD and OH stretching modes, respectively, and mole fraction of deuterium to hydrogen, \(c_{OD}\), was determined by the method mentioned above.

The rotating sample stage was used in order to obtain averaged spectra of the Ca(OH)\(_2\)/Ca(OD)\(_2\) pellets. Each pellet was measured five times with different rotational tracks in order to reduce error for data due to uniformity of the pellets (Fig. 9a). The deviation of the \(I_{OD}/(I_{OD}+I_{OH})\) values of five spectra was very small; the relative standard deviations for each pellet were below 2%. Figure 9b shows the relationship between \(c_{OD}\) of the pellets and the relative intensities of the OD bands, \(I_{OD}/(I_{OD}+I_{OH})\). By fitting five data with the modified Eq. 10 which is derived by changing the unit of the left side of Eq. 10 to the mole fraction unit, the concentration \(c_{OD}\) can be calculated from

\[
c_{OD} = \frac{I_{OD}}{I_{OD} + 0.76I_{OH}}.
\]
Figure 9. a Raman spectra of Ca(OD)$_2$/ Ca(OH)$_2$ mixtures. The mole fraction of deuterium to hydrogen ($c_{OD}$) of Ca(OD)$_2$/Ca(OH)$_2$ in each mixture is shown in each spectrum. b Correlation between $c_{OD}$ and $I_{OD}/(I_{OD}+I_{OH})$ for Ca(OD)$_2$/ Ca(OH)$_2$ mixtures. Solid line shows the calibration curve to convert $I_{OD}$ and $I_{OH}$ into $c_{OD}$ (Eq. 11).
CHAPTER 3: EXPERIMENTAL METHODS

3.1 H-D exchange diffusion experiment

Single crystals of portlandite were synthesized from a saturated solution of Ca(OH)$_2$ as follows. Reagent Ca(OH)$_2$ powder (Wako Co. Ltd.), which is a little soluble in water at low temperature, was dissolved in the water cooled with ice. The solution was maintained under a N$_2$ atmospheric evaporator at 70 – 80 °C for one week, leaving single crystals of portlandite. Optically clean and hexagonally column shaped portlandite single crystals (50 – 300 µm; length) and 50 – 400 µm in diameter were synthesized. Two or three single crystals were placed into a gold capsule with a quantity of 10 µL of D$_2$O (Cambridge Isotope Laboratories, Inc.) and the gold capsule was sealed by welding. To promote H-D exchange in portlandite, the gold capsules were placed in a cold-seal test tube type pressure vessel and annealed at 250 – 450 °C under 150 MPa for 5 – 150 hours (Table 2). In an effort to avoid convection of water (the pressure medium) in the test tube and to maintain the temperature of the gold capsules in the vessel constant, a stainless steel rod was inserted inside the vessel (Boettcher and Kerrick 1971). IR absorption spectra of every fluid recovered from the gold capsule after annealing experiments were measured in order to determine the D$_2$O/H$_2$O ratio ($c_0$ in Table 2) using molar absorption coefficients of D$_2$O and H$_2$O (Veniaminov and Prendergast 1997). The D$_2$O/H$_2$O ratio is very important in order to properly calculate the diffusion coefficients. The initial D$_2$O in the gold capsule was contaminated by H$_2$O in the air, when the gold capsule was welded. The portlandite was analyzed after the diffusion experiments using a micro Raman spectrometer (Seki Technotron Co.). A single-monochromator (250IS; CHOROMEX Co.) equipped with a cooled 128 × 1024 CCD detector and a diffractive grating consisting of 1200 grooves/mm was used in the analyses. The diffractive grating enabled us to obtain Raman
Table 2 Experimental conditions and diffusion coefficients

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$T$ (°C)</th>
<th>$P$ (MPa)</th>
<th>$t$ (h)</th>
<th>$c_0^a$</th>
<th>Direction</th>
<th>$D$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td><strong>H-D exchange diffusion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>616</td>
<td>250</td>
<td>150</td>
<td>145</td>
<td>0.70</td>
<td>[210]</td>
<td>$(7.3 \pm 0.9) \times 10^{17}$</td>
</tr>
<tr>
<td>124</td>
<td>250</td>
<td>150</td>
<td>91</td>
<td>0.90</td>
<td>[100]</td>
<td>$(1.4 \pm 0.1) \times 10^{16}$</td>
</tr>
<tr>
<td>124</td>
<td>250</td>
<td>150</td>
<td>91</td>
<td>0.90</td>
<td>[210]</td>
<td>$(1.8 \pm 0.1) \times 10^{16}$</td>
</tr>
<tr>
<td>723</td>
<td>300</td>
<td>150</td>
<td>90</td>
<td>0.95</td>
<td>[210]</td>
<td>$(7.3 \pm 1.1) \times 10^{16}$</td>
</tr>
<tr>
<td>130</td>
<td>300</td>
<td>150</td>
<td>120</td>
<td>0.87</td>
<td>[210]</td>
<td>$(3.1 \pm 1.2) \times 10^{16}$</td>
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<tr>
<td>821</td>
<td>300</td>
<td>150</td>
<td>149</td>
<td>0.77</td>
<td>[210]</td>
<td>$(5.1 \pm 0.9) \times 10^{16}$</td>
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<tr>
<td>919</td>
<td>350</td>
<td>150</td>
<td>18</td>
<td>0.59</td>
<td>[100]</td>
<td>$(3.2 \pm 0.5) \times 10^{15}$</td>
</tr>
<tr>
<td>114</td>
<td>350</td>
<td>150</td>
<td>18</td>
<td>0.59</td>
<td>[210]</td>
<td>$(3.8 \pm 1.3) \times 10^{15}$</td>
</tr>
<tr>
<td>114</td>
<td>350</td>
<td>150</td>
<td>18</td>
<td>0.59</td>
<td>[210]</td>
<td>$(1.4 \pm 0.6) \times 10^{15}$</td>
</tr>
<tr>
<td>713</td>
<td>350</td>
<td>150</td>
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<td>0.55</td>
<td>[100]</td>
<td>$(1.3 \pm 0.6) \times 10^{15}$</td>
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<tr>
<td>718</td>
<td>350</td>
<td>150</td>
<td>48</td>
<td>0.94</td>
<td>[210]</td>
<td>$(1.4 \pm 0.2) \times 10^{15}$</td>
</tr>
<tr>
<td>907</td>
<td>450</td>
<td>150</td>
<td>5</td>
<td>0.32</td>
<td>[210]</td>
<td>$(4.0 \pm 2.4) \times 10^{15}$</td>
</tr>
<tr>
<td>716</td>
<td>450</td>
<td>150</td>
<td>22</td>
<td>1.00</td>
<td>[100]</td>
<td>$(5.5 \pm 1.6) \times 10^{15}$</td>
</tr>
<tr>
<td>716</td>
<td>450</td>
<td>150</td>
<td>22</td>
<td>1.00</td>
<td>[210]</td>
<td>$(4.9 \pm 0.9) \times 10^{15}$</td>
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<tr>
<td>813</td>
<td>450</td>
<td>150</td>
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<td>0.89</td>
<td>[100]</td>
<td>$(5.4 \pm 1.2) \times 10^{15}$</td>
</tr>
<tr>
<td>118</td>
<td>450</td>
<td>150</td>
<td>22</td>
<td>0.95</td>
<td>[100]</td>
<td>$(7.0 \pm 0.5) \times 10^{15}$</td>
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<tr>
<td><strong>¹⁶O-¹⁸O exchange diffusion</strong></td>
<td></td>
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</tr>
<tr>
<td>1801</td>
<td>450</td>
<td>150</td>
<td>400</td>
<td>(1.00)</td>
<td>[210]</td>
<td>$(8.0 \pm 1.6) \times 10^{17}$</td>
</tr>
<tr>
<td>1801</td>
<td>450</td>
<td>150</td>
<td>400</td>
<td>(1.00)</td>
<td>[100]</td>
<td>$(7.4 \pm 1.3) \times 10^{17}$</td>
</tr>
</tbody>
</table>

* $c_0$ is the mole fraction of the tracer (D or $¹⁸O$) contained in the fluid (see text)
spectrum from 1800 cm\(^{-1}\) to 3900 cm\(^{-1}\) in a single measurement. The wavenumber of the Raman spectra was calibrated using neon emission lines. The intensity of Raman spectra was calibrated using a standard halogen light source, the LS-1-CAL (Ocean Optic Inc.). The 488 nm line of an Ar\(^{+}\) laser was used to excite Raman scattering. The laser beam was focused on a sample surface through an objective (M Plan Apo SL 50 magnification, N.A.0.42; Mitutoyo Inc.) and the theoretical beam spot size was \(\sim 2 \, \mu m\). The backscattered light was collected using the same lens. The measurement time varied from 30-60 seconds in order to gain adequate signal-to-noise ratios in the spectra.

Portlandite has perfect cleavage parallel to the (001) plane. Thin (001) sections of about 20 \(\sim\) 30 \(\mu m\) were made from the core of the crystal by cleaving portlandite along the cleavage (Fig. 10a). Thin sections parallel to the c axis were also made in order to obtain a diffusion profile along the c axis. Line profiles for the Raman spectra were measured from the edge of the thin sections to the other edge along [100], [210] and [001] directions at intervals of 4 \(\mu m\) (Fig. 10b). To determine accurate intensities of the OH stretching mode \((I_{OH})\) to OD stretching mode \((I_{OD})\), curve-fitting analysis was conducted using GRAMS/AI software (Thermo Galactic Inc.). The Raman bands in each spectrum were fitted using a Lorentzian function with linear background correction. The \(c_{OD}\) profiles were determined from \(I_{OH}\) and \(I_{OH}\) profiles using Eq. 11.

### 3.2 \(^{16}\)O-\(^{18}\)O exchange diffusion experiment

The \(^{16}\)O-\(^{18}\)O exchange diffusion experiments were conducted by the almost same method as the H-D exchange diffusion experiment. The gold capsule sealed the three single crystals of portlandite and \(H_2^{18}\)O of 5 \(\mu L\) (Taiyo Nippon Sanso Co. Ltd.) was annealed at 450 \(^\circ C\) under 150 MPa for 400 hours in the pressure vessel. The thin section parallel to the (001) of portlandite after annealing was analyzed by the micro Raman spectrometer with a
Figure 10. Photograph of a thin section of portlandite parallel to the (001) plane and the profile of Raman spectra obtained by line analysis of the thin section.

a The (001) thin section cut from the crystal after hydrothermal treatment at 300 °C and 150 MPa for 90 hours (Run. 723; Table 2). The arrow in the photo, which is parallel to the [210] direction, indicates the track of Raman line. Scale bar is 100 μm. b Sequential spectra measured at intervals of 4 μm along the arrow in a using micro Raman spectroscopy. Peaks at 2667 cm⁻¹ and 3620 cm⁻¹ were assigned to be OD and OH stretching vibration, respectively.
diffractive grating consisting of 2400 grooves/mm. Line profiles for the Raman spectra were measured along [100] and [210] directions at intervals of 4 μm (Fig. 11a). The Raman band due to $^{18}$OH stretching mode (3608 cm$^{-1}$) overlaps with that due to OH stretching mode (3620 cm$^{-1}$). They were separated by the curve-fitting analysis using a Lorentzian function, and their intensities were determined. The relative Raman intensity of the $^{18}$OH stretching mode to OH stretching mode converted to mole fraction of $^{18}$O to $^{16}$O, $c_{18O}$. The $c_{18O}$ profile is shown in Fig. 11b.

3.3 Optical absorption measurements

Optical absorption measurements of portlandite were carried out using micro VIS, NIR and FT-IR spectrometers under ambient conditions. Mid IR absorption spectra (800-4000 cm$^{-1}$) were recorded on an micro FT-IR spectrometer (FTIR 4200 IMS-1; Shimadzu Co.) equipped with a MCT detector. The resolution of the spectrum was 4 cm$^{-1}$. The NIR (4000-11000 cm$^{-1}$) and VIS (11000-30000 cm$^{-1}$) spectra were measured using a lock-in amplifier type micro NIR-VIS spectrometer. The spectrometer was a single-monochrometer (M-10; JASCO Co.) equipped with PbS detector and photomultiplier. Resolution in the NIR region and VIS region were about 9 cm$^{-1}$ and 5 cm$^{-1}$, respectively. The wavenumber of the measured spectra was calibrated using a cubic polynomial fit to positions of absorption bands of polystyrene. Pellets of powdered portlandite were used as an analytical sample. The absorption of the overtone modes was significantly weaker than that of the fundamental mode, and several pellets were stacked when high order overtone modes were measured. Figures 12a - d show the fundamental, the 2nd, 3rd and 4th overtone modes of portlandite, respectively.
Figure 11. a Raman spectra obtained by line analysis of the thin section of portlandite after the $^{16}$O-$^{18}$O exchange experiment (Run. 18O1, Table 2). The sequential Raman spectra were measured along the [210] direction at intervals of 4 μm. The distance from the edge of the thin section to the measurement point is shown in the figure. The Raman bands at 3608 cm$^{-1}$ and 3620 cm$^{-1}$ were assigned to be $^{18}$OH and $^{18}$OH stretching vibration, respectively. b The $c_{18O}$ profile was converted from the Raman profile shown in a. Solid line indicates least-squares fit of Eq. 13 to the data.
Figure 12. MIR (a) and NIR (b, c), VIS (d) absorption spectra of portlandite under ambient conditions. Absorption bands due to the fundamental mode (a) and 2nd (b), 3rd (c) and 4th (d) overtone modes of OH stretching vibration.
CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Determination of diffusion coefficient and activation energy

If the migration of deuterium/hydrogen, or $^{18}\text{O}/^{16}\text{O}$ is driven by the concentration gradients, the deuterium/hydrogen, or $^{18}\text{O}/^{16}\text{O}$ flux in the portlandite will obey Fick’s first law. Thus, the $c_{OD}$ (or $c_{18O}$) can be described by a one-dimensional diffusion equation:

$$\frac{\partial c_{OD}(x,t)}{\partial t} = D \frac{\partial^2 c_{OD}(x,t)}{\partial x^2},$$

(12)

where $D$ is the diffusion coefficient, $t$ is the time, and $x$ is the distance. In the case of diffusion in a plane sheet bound by two parallel planes at $x = 0$ and $x = L$, the solution for the diffusion equation can be written as:

$$c_{OD}(x,t) = c_0 + \frac{2}{\pi} \sum_{n=1}^{\infty} c_0 \cos n\pi - c_0 \sin \frac{n\pi x}{L} \exp\left(-\frac{D n^2 \pi^2 t}{L^2}\right),$$

(13)

where $c_0$ is the mole fraction of the tracer, $D$ or $^{18}\text{O}$ (Table 2), at the boundaries ($x = 0$ and $L$) (Crank 1956). The $c_{OD}$ profiles obtained by Raman line analyses are shown in Figs. 13a - d as examples of the analyses. The $c_{OD}$ profile of Fig. 13a was obtained from the Raman profile of Fig. 10b, and the $c_{OD}$ profiles of Fig. 13b, c, d were obtained from the samples after hydrothermal treatment at 250 $^\circ\text{C}$, 450 $^\circ\text{C}$, 300 $^\circ\text{C}$ for 145 hours, 22 hours, 120 hours, respectively. The diffusion coefficients of each run were determined by least-squares fitting the $c_{OD}$ and $c_{18O}$ profiles with Eq. 13 (Table 2). The values of $c_0$ determined using IR measurements for the recovered D$_2$O/H$_2$O fluid in the gold capsule are consistent with the value of $c_{OD}$ at the edges of the thin sections. In addition, some of diffusion coefficients were determined not only by Eq. 13 but by applying the two-dimensional diffusion equation for a cylindrical sample to the diffusion profiles. The two-dimensional diffusion equation and its solution can be expressed as a function of the cylinder radius, $r$, as follows:
Figure 13. $c_{OD}$ profiles perpendicular to the $c$ axis under various experimental conditions (a, b, c) and the $c_{OD}$ profile along the $c$ axis (d).

a The $c_{OD}$ profile was converted from the Raman profile shown in Fig. 9b using Eq.11. Solid line indicates least-squares fit of Eq. 13 to the data. b, c The $c_{OD}$ profiles of the samples after hydrothermal treatments at 250 °C for 145 hours (Run. 616; Table 2) and at 450 °C for 22 hours (Run. 813). d The $c_{OD}$ profile along the $c$ axis was determined by Raman analysis for the thin section parallel to the $c$ axis constructed from the sample after hydrothermal treatments at 300 °C for 120 hours (Run. 130). The base surface was 0 μm. The central position is 80 μm from the base surface. The thin sections cut from the central position were used to measure the diffusion profile perpendicular to the $c$ axis.
\[
\frac{\partial c_{OD}(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( rD \frac{\partial c_{OD}(r,t)}{\partial r} \right), 
\]  
(14)

\[
c_{OD}(r,t) = c_0 \left\{ 1 - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{a_n} J_0(r/a_n) \exp(-D a_n^2 t) \right\}, 
\]  
(15)

where \( a \) is the radius of the cylindrical sample (= \( L/2 \)), \( J_n \) is a Bessel function of order \( n \), and \( a_n \) is the root of \( J_n(r/a_n) = 0 \) (Crank 1956). In this study, all diffusion profiles were obtained in the early stages of diffusion, for which the run times for each experiment satisfied \( 4Dt/L^2 \) (or \( D/t/a^2 \)) \(< 0.06 \). At such an early stage of diffusion, the diffusion profiles based on one-dimensional and two-dimensional diffusion equations are almost the same as each other. For example, the \( D \) values along the [210] direction for Run.723 (Table 2) derived from the one and two-dimensional analyses are \( 7.3 \times 10^{-16} \) m\(^2\)/s (Fig. 13a) and \( 6.6 \times 10^{-16} \) m\(^2\)/s, respectively. In this study, we adopted diffusion coefficients from the one-dimensional analyses because of the simplicity of the calculation by the least-squares fitting (Table 2). As for anisotropy of the \( D \), no significant difference was noted between the \( D \) values determined along the [100] and [210] directions (Table 2). Furthermore, the \( c_{OD} \) profile along the \( c \) axis was determined by Raman analysis through the center of the thin section parallel to the (100) plane. The diffusion profile from the base surface of the crystal to the core is shown in Fig. 13d. It indicates that there is no deuterium at the core of the crystal, namely, the deuterium diffused from the base surface along the \( c \) axis had not reached the core. The thin sections parallel to the (001) plane cut from core of the crystal, therefore, the \( D \) values perpendicular to the \( c \) axis determined from experimental data were not affected by deuterium atoms that diffused along the \( c \) axis.

Compared with the \( D \) values for hydrogen and oxygen at 450 °C (Table. 2), the \( D \) values for hydrogen is two orders of magnitude higher than those for oxygen. This indicates that hydrogen in portlandite diffuses much faster than oxygen, and that hydrogen migrates not
as a H$_2$O molecule or a H$_3$O$^+$ ion but a single proton.

Arrhenius parameters for the proton diffusion, activation energy \( E \), and frequency factor (pre-exponential factor, \( D_0 \)) perpendicular to the \( c \) axis are determined from the slope and intercept of Arrhenius plot for the \( D_s \) of proton (Fig. 14), respectively. The Arrhenius equation is

\[
D = 1.0 \times 10^{10} \exp\left[\frac{-0.61 \pm 0.03 \text{ eV}}{kT}\right] \text{ (m$^2$/s)},
\]

where \( k \) is the Boltzmann constant. The diffusion perpendicular to the \( c \) axis of portlandite is fast compared to hydrogen diffusion in other hydrous minerals. Hydrogen diffusion in a crystal must be strongly related to the crystal structure. In this case, there are no atoms that disturb protons jumping between the proton sites. The faster proton diffusion in portlandite must be to the shorter distances between the proton sites compared with other hydrous minerals.

4.2 Proton diffusion mechanism

Microscopic mechanisms of self-diffusion of atoms in crystals can typically be categorized into two types: the vacancy mechanism and the interstitial mechanism (Borg and Dienes 1988). In the vacancy mechanism, the diffusion jump occurs by a proton exchanging positions with a neighboring vacancy. By contrast, in the interstitial mechanism, a diffusing atom migrates via sites located between rational lattice sites. The vacancy mechanism is thought to be the dominant mechanism of proton diffusion perpendicular to the \( c \) axis of portlandite, because there are no possible interstitial sites in the proton layer. The space between two neighboring protons in the proton layer is unstable as the interstitial site of proton because of the proton-proton repulsive interaction. The interstitial mechanism, however, plays an important role in proton diffusion parallel to the \( c \) axis. Protons diffuse via
Figure 14. Arrhenius plots of D and $^{18}$O diffusion coefficients perpendicular to the c axis of portlandite and D diffusion coefficients of various hydrous minerals. The filled and open circles show D and $^{18}$O diffusion coefficients of portlandite, respectively. The solid line is the least-squares fit to the data for D of portlandite. Data for lowsonite, kaersutite, muscovite and chlorite are from Marion et al. (2001), Ingrin and Blanchard (2000) and Graham et al. (1987), respectively, and those for epidote and zoisite are from Graham (1981).
interstitial sites in the [CaO₆] layer, which are quasi-stable and are not detectable by X-ray and neutron diffraction techniques.

For one of the three protons neighboring a vacant site to jump to the vacant site, the proton must overcome the potential energy barrier between the two oxygen atoms. In general, a vacancy can be formed by either intrinsic or extrinsic mechanisms (Borg and Dienes 1988). In the intrinsic mechanism, vacancies are thermally generated at relatively high temperatures. When vacancies generated by the intrinsic mechanism control the proton diffusion, the diffusion activation energy is equal to the sum of the formation energy of thermally generated vacancies and the proton migration energy. On the other hand, in the extrinsic mechanism, vacancies are introduced to compensate the charge balance due to impurities in the structure. The activation energy of the extrinsic mechanism is simply the activation energy of proton migration. The extrinsic vacancy mechanism must control the proton diffusion observed in this investigation, because the experimental temperature is too low to generate thermal vacancies. Differential thermal analysis by Bai et al. (1994) indicated that proton vacancies were not formed in portlandite by dehydration up to 450 °C. Furthermore, Matsunaga and Kuwabara (2007) suggested that an energy as high as about 1.5 eV is required to introduce a proton vacancy into a covalent OH bond. The self-diffusion activation energy (E) of portlandite was 0.61 eV, which is too low to be explained by the intrinsic mechanism. Therefore this value is attributed to the activation energy when a proton migrates to a neighboring vacant site.

4.3 Estimation of potential barrier height

When a proton migrates to a neighboring vacant site, we assume that the proton does not jump directly from a 6i site to the vacant site, but undergoes the following processes. We estimate the potential barrier height based on the migration model. A proton generally hops
between the three \(6i\) sites because of the almost flat potential barriers between the three \(6i\) sites (Fig. 15). In addition to this hopping motion, the OH dipole can easily tilt away from the \(6i\) site due to the very low tilting energy and this causes the proton to move to the \(H_1\)' site (see Fig. 15). According to Matsushita (2001), the tilting motion requires only 0.01 eV. When the proton moves to the \(H_1\)' site and the equivalent \(H_2\)' site is vacant, the jumping path is minimized allowing the proton to jump to the neighboring site with the lowest expenditure of energy. In such a proton migration process, the activation energy for a proton to migrate from a \(6i\) site to its neighboring site is mainly the energy to overcome the potential barrier between \(H_1\)' and \(H_2\)'.

The potential barrier between \(H_1\)' and \(H_2\)' can be estimated by overlapping \(OH_1\)'-PEC and \(OH_2\)'-PEC at an interval of the interlayer oxygen distance \((d_{O-O}\), in Fig. 15). The intersection of the \(OH_1\)'-PEC and the \(OH_2\)'-PEC is a saddle point in the potential energy curve between the two oxygen atoms, and the energy of the saddle point corresponds to the potential barrier (Eyring 1941). In the following, we assume that an OH-PEC determined by the optical absorption measurements corresponds to \(OH_1\)'-PEC and \(OH_2\)'-PEC and we estimate the potential barrier by overlapping the two OH-PECs.

An OH-PEC can be determined from the wavenumbers of the OH absorption bands. By substituting the four wavenumbers from the fundamental mode \(\omega_1\) to the fourth overtone mode \(\omega_4\) in Table 3 into Eq. 5, the most probable \(\omega_e\) and \(\chi\) were respectively determined to be \(3781 \pm 29\) cm\(^{-1}\) and \(0.0216 \pm 0.0057\) by the method of least squares. The \(D_e\) and \(\alpha\) in the Morse potential equation (Eq. 1) were derived from Eqs. 3 and 4. The estimated OH-PEC is:

\[
U(r) = (5.54 \pm 1.43)(1 - \exp[-(2.11 \pm 0.63)(r - r_0)])^2 \quad \text{(eV)}.
\]

The OH-PEC described by Eq. 17 is shown in Fig. 16a. To estimate the potential energy barrier, the two OH-PECs are overlapped at the interval of the equilibrium \(d_{O-O}\), which is 3.32 Å at room temperature and 0.5 GPa (Nagai et al. 2000). Figure 16b shows the two
Figure 15. The (110) section of the unit cell including a proton vacancy. 2d and 6i are Wyckoff sites. $H_1'$ and $H_2'$ are positions occupied by a proton on tilting of the OH dipole so that $H_1'$ and $H_2'$ and two oxygen atoms become aligned. The jump path is minimized when a proton moves to the $H_1'$ position, and the proton jumps to the vacant $H_2'$ position via the $H_1'$ position. $d_{O-O}$ indicates the interlayer oxygen distance.
Figure 16. a The potential energy curve of OH (OH-PEC) of portlandite determined from spectroscopic measurements. b A potential barrier between two oxygen atoms across the proton layer of portlandite. The solid line and broken line indicate OH$_1$'-PEC and OH$_2$'-PEC which are given by Eq. 17, respectively. The H$_1$' position is occupied by the proton and the H$_2$' position is vacant (see Fig. 15). They are overlapped at an interval of 3.32 Å.
Table 3. List of frequencies of fundamental and overtone modes for OH stretching vibration and their pressure dependency

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\omega_n - \omega_0$ (cm$^{-1}$)</th>
<th>$G(n) - G(0)$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0*</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>3645</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>7067</td>
<td>0.88</td>
</tr>
<tr>
<td>3</td>
<td>10341</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>13501</td>
<td>1.67</td>
</tr>
</tbody>
</table>

*$\omega_0$ is 1870 cm$^{-1}$, which was estimated from $G(0)$.\)
overlapping OH-PECs and it indicates that the energy at the intersection point of the two OH-PECs is 3.35 eV. Subtracting the zero-point energy of the proton (G(0) = 0.24 eV) from this value gives the energy of the potential barrier (3.11 eV) that a proton needs to overcome to jump to neighboring proton sites. The $E$ determined by the diffusion experiments is 0.61 eV. Therefore, the potential barrier for the equilibrium distance of 3.32 Å is too high to be the activation energy of proton diffusion.

This high potential energy barrier must be due to the following two factors, which have not been considered in the above estimation. The first factor is that the oxygen at the vacancy site has an excess electron due to a dangling bond. The oxygen atom becomes negatively charged by the excess electron, which increases the electrostatic force between the oxygen and the proton. The energies of the OH$_1'$-PEC and OH$_2'$-PEC are lowered by the electrostatic interaction as shown in Fig. 17a, and the potential barrier is reduced. The second factor is the thermal vibrations of oxygen atoms. The interlayer oxygen distance, $d_{O\cdotO}$ deviates from the equilibrium distance as a result of such vibrations. When $d_{O\cdotO}$ is shorter than the equilibrium distance, the potential barrier is lowered by shortening of the jumping path (Fig. 17b). These two factors are thought to be responsible for reducing the potential barrier to 0.61 eV.

4.4 The jumping frequency of a proton

Analyzing the frequency factor ($D_0$) is valuable for understanding the microscopic mechanism of diffusion, because it is related to the jumping rate for diffusing atoms. When an atom bonded in a crystal migrates to the nearest neighboring site by jumping, Fick's first law for the atom flux, $J$, can be expressed as:

$$J = -J^2 \frac{\partial \psi}{\partial x},$$

(18)
Figure 17. a Schematic image of a reason for lowering the potential barrier by the electrostatic interaction between the negatively charged oxygen and the proton. The broken line is the potential energy barrier determined by overlapping two OH-PECs determined from spectroscopic measurements (Fig. 16b). b Schematic image of the potential barrier at the instant when the potential barrier height reduced to 0.61 eV by the shrinking $d_{oo}$. The "0.85 eV" in the figure is the sum of the zero point energy of proton, $G(0) = 0.24$ eV and the potential barrier height, 0.61 eV.
where \( l \) is the jump distance, which is equivalent to the distance to the neighboring site, and \( v \) is the jump frequency (Borg and Dienes 1988). In the case of the vacancy mechanism, \( D_0 \) can be related to \( l \) and \( v \) in Fick’s first law as follows:

\[
D_0 = \frac{1}{2d} f l^2 X_v v. \tag{19}
\]

In the above equation, \( d \) is the dimension of the diffusible medium. In the case of diffusion in the proton layer of portlandite \( d = 2 \). \( f \) is the tracer correlation factor, which relates to the crystal structure. \( f \) is determined to be 1/2 by considering the geometry of the crystal structure (honeycomb lattice) (Borg and Dienes 1988). For diffusion perpendicular to the \( c \) axis, \( l \) is the distance between two proton sites across a proton layer. Here the splitting of proton sites by disorder is neglected and the distance between two \( 2d \) sites (2.18 Å, Xu et al. 2007) is substituted for \( l \) in Eq. 19. \( X_v \) is the fraction of vacant sites and for the extrinsic vacancy mechanism it corresponds to the impurity concentration in the crystal, as mentioned above. Based on the purity of the reagent Ca(OH)\(_2\) (99.9%), \( X_v \) must be of the order of \( 1.0\times10^{-3} \).

Substituting the above values into Eq. 19, gives a jump frequency, \( v \), of \( 1.7\times10^{13} \) Hz. This jump frequency is the same order as the frequencies of the lattice vibration modes of \([\text{CaO}_6]\) (~\(10^{13} \) Hz). This indicates that the reduction in \( D_0 \) induced by thermal vibrations may control proton jumping.

For proton diffusion at a pressure as high as 150 MPa, the effects of splitting of proton sites and dynamic disorder were not remarkable (Raugei et al. 1999; Mookherjee and Stixrude 2006). However, they must affect the proton diffusion mechanism at high pressure and high temperature. The large splitting between the three disorder sites and dynamic hopping between their sites must control proton diffusion. Such a novel diffusion mechanism, which does not depend on the thermal vibrations of oxygen atoms, may be induced by pressure. It is important to investigate this experimentally and by computer simulations.
SUMMARY

- Large differences between diffusion coefficients of D and those of $^{18}$O showed the hydrogen diffuses as a single proton in the crystal structure of portlandite.

- The activation energy of proton diffusion perpendicular to the c axis and the frequency factor were experimentally determined to be $0.61 \pm 0.03$ eV ($58.5 \pm 2.7$ kJ/mol) and $1.0 \times 10^{-10}$ m$^2$/s, respectively.

- Based on optical absorption measurements, the OH-PEC was determined to be $U(r) = (5.54 \pm 1.43)(1 - \exp[-(2.11 \pm 0.63)(r - r_0)])^2$ (eV).

- The height of the potential barrier between two oxygen atoms across an interlayer to be cleared by a proton diffusing through a proton layer was derived to be $3.11$ eV from the OH-PEC. The theoretical potential barrier is too high to be the activation energy of the proton diffusion. It implies that the interaction between a diffusing proton and the vacancy of a proton site, and the shortening of interlayer oxygen distance by thermal vibration reduce the potential barrier. Furthermore, the jumping frequency of the protons which determined from the frequency factor was in agreement with the frequency of the thermal vibration of the oxygen atoms. Consequently the thermal vibration of the oxygen atoms must be the dominant factor which controls on the proton migration.
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50


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