A HIGH PRESSURE AND HIGH TEMPERATURE STUDY OF SERPENTINE AND ITS IMPLICATIONS TO EARTH'S LOWER MANTLE

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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BY

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Acknowledgment

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ABSTRACT

The decomposition of serpentine into different dense hydrous magnesium silicates (DHMS) is of much interest to the geochemistry of the mantle and in particular to the nature and extent of H₂O distribution in the mineral assemblages associated with the mantle. Motivated by the desire to build up an experimental base for the water budget in the mantle and its contribution to magmatic process, such as plate tectonics and other dynamic process associated with the Earth's interior, I have carried out high pressure and high temperature quench and in situ experiments. The results obtained on serpentine, superhydrous phase B and phase D are presented and their significances are discussed in this thesis.

High pressure, high temperature quench experiments were carried out on serpentine at pressures 13 to 53 GPa and temperatures between 800-1800 °C. Results show that the post-serpentine phase assemblages vary depending on the pressure and temperature. The sequence of phase transformation of DHMS phases is A, E, D + SB or D + brucite, then D + periclase with increasing pressure. The findings of phase E and superhydrous phase B as decomposition products of serpentine are supported by the recent report by Irifune et al. [1998]. Phase E is found to be unstable beyond 18.5 GPa. Superhydrous phase B is stable up to the P-T condition at the outer periphery of the lower mantle (about 700-800 km). Phase D decomposes at pressures equivalent to about 1250 km depth, which may define the lowest limit for a dense hydrous magnesium silicate. The decomposition reaction sequence outlined above could be one of the mechanisms for transporting H₂O within the mantle.

In-situ X-ray diffraction experiments on serpentine were carried out in this study at pressure from 22 GPa to 35 GPa and temperatures in the range of 1000-1300 °C.
Results show that phase D should be stable under the P-T conditions in the lower mantle. Besides phase D, there may be other unquenchable new phase(s), as observed under above high P-T conditions. However, these phases eventually break down into stishovite and brucite, as pressure is totally released. This indicates that the new phase may contain some H in the structure, thereby qualifying as a high P-T hydrous phase.

In-situ X-ray diffraction studies were carried out on single component phase, superhydrous phase B at about 43 GPa, 1340 °C and phase D at 42 GPa, 1300-1750 °C, respectively. Results show that they decompose at the given P-T conditions, where Superhydrous phase B transforms into phase D + stishovite + periclase; phase D decomposes into perovskite, stishovite and an unknown phase. These results on the single phase materials are in accord with the observations on serpentine, supporting the idea that superhydrous phase B and phase D will decompose under lower mantle conditions.
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Chapter 1

General introduction

Olivine, pyroxene and garnet are the most abundant minerals in the mantle and have been studied extensively in the past two decades. Based on the experimental results obtained under completely dry condition, the two well-known Earth models have been proposed: (1) pyrolite model – i.e. olivine 57%, orthopyroxene 17%, clinopyroxene 12% and pyrope garnet 14% (Fig. 1.1) [Ringwood, 1975], and (2) piclogite model – olivine 16%, orthopyroxene 3%, clinopyroxene 16% and pyrope garnet 36% at upper mantle [Bass and Anderson, 1984]. The above two models should be regarded as applicable to a dry mantle. However, there are many indications that water is a constituent of the mantle. Taking this possibility into consideration, I have carried out high-pressure high-temperature experiments on some serpentine materials. The results of these studies will be presented and discussed in this thesis.

It is well known that water plays an important role in the dynamics and composition of subducting material. The water released by dehydration of a subducting oceanic slab has long been considered as the cause of arc magmatism and the trigger for partial melting of the overlying mantle [Thompson, 1992; Davies and Stevenson, 1992; Pawley and Holloway, 1993; Nolet and Zielhuis, 1994; Revenaugh and Sipkin, 1994; Kirby, 1996; Peacock, 1996], and possibly also the cause of deep-focus earthquakes [Meade and Jeanloz, 1991]. Potentially, it could have an even broader role in global crustal and upper mantle processes, for its presence can change the physical and chemical properties of minerals and rocks. For instance, it could enhance the migration of magma [Thompson, 1992], modify seismic discontinuities at 410 km [Wood, 1995], and increase the electrical conductivity [Li and Jeanloz, 1991] in the mantle.
Fig. 1.1 Possible mineral assemblages and corresponding zero-pressure densities for a model mantle of pyrolite composition. Mineralogy to a depth of 700 km is based mainly upon direct static experiments. Mineralogy at greater depths is inferred on the basis of indirect methods and shock-wave methods.
(data from Ringwood, 1975)
The exact role of hydrogen in the transition zone and lower mantle, and how it is stored, as well as the total mantle H$_2$O budget remain unclear. Estimates of water in the mantle ranges from 0.1 wt% to 2.5 wt% depending on different assumptions made in the accretion model used [Rubey, 1951; Ringwood, 1979; Liu, 1987]. Based on the shock wave Hugoniot of serpentine to 150 GPa, Tyburczy et al. [1991] have suggested models containing 2 wt% H$_2$O in the lower mantle. If this is true, it simply means that the lower mantle would have a water reservoir of about 42 times the present ocean mass.

The H$_2$O in the deep mantle is either primordial water preserved and accumulated during the formation of the earth [Donahue, 1986; Ringwood, 1979; Liu, 1987], or recycled water transported back from the oceanic crust, via subducted lithosphere material [Meade and Jeanloz, 1991; Thompson, 1992]. From laboratory experiments, it has been argued that "water" in the Earth's mantle could be present as OH in many nominally anhydrous mantle minerals [Bell and Rossman, 1992; Bell et al., 1995], or as dense hydrous magnesium silicates (DHMS–A, B, Superhydrous phase B, D, E, F) as shown by synthesis from the MgO-SiO$_2$-H$_2$O system under high pressures and temperatures (e.g., Ringwood and Major, 1967; Yamamoto and Akimoto, 1974; Akaogi and Akimoto, 1980; Akimoto, and Akaogi, 1980; Liu, 1986, 1987; Ohtani et al., 1995; Luth, 1995). Because DHMS phases have a demonstrated stability under mantle conditions [Akaogi and Akimoto, 1977; Akimoto and Akaogi, 1984; Liu, 1986, 1987; Gasparik, 1993; Kanzaki, 1991; Ahrens, 1989, Luth, 1995; Pawley et al., 1996; Ohtani et al., 1995], they are at least thermodynamically plausible candidates to serve as H$_2$O reservoirs in the Earth's deep interior (Table 1.1 and 1.2, Fig. 1.2). Based on the results of high pressure-high temperature synthesis studies, phase A should be stable in the upper mantle conditions, phase B stable in the deeper part of the upper mantle and transition region, phase E only stable in the transition zone, and superhydrous phase B and phase D stable in the transition zone or even deeper; this uncertainty is due to the fact that the stability field of
Table 1.1 Dense hydrous magnesium silicates synthesized at different pressures and temperatures

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<th>Phase</th>
<th>Compositions</th>
<th>P (GPa)</th>
<th>T (°C)</th>
</tr>
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<tbody>
<tr>
<td>Phase A</td>
<td>Mg$_7$Si$_2$O$_8$ (OH)$_6$</td>
<td>6-10</td>
<td>700-1000 b</td>
</tr>
<tr>
<td>Phase E</td>
<td>Mg$<em>{2.3}$Si$</em>{1.3}$H$_{2.2}$O$_6$ c</td>
<td>13-17</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Mg$<em>{2.08}$Si$</em>{1.16}$H$_{3.2}$O$_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg$<em>{2.17}$Si$</em>{1.01}$H$_{3.62}$O$_6$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase B</td>
<td>Mg$_{2.4}$Si$<em>8$O$</em>{38}$ (OH)$_4$ d</td>
<td>11-16</td>
<td>1200-1300 b</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
<td>2300e</td>
</tr>
<tr>
<td>Anhydrous B</td>
<td>Mg$<em>{2.8}$Si$</em>{10}$O$_{48}$ d</td>
<td>16.5</td>
<td>2380f</td>
</tr>
<tr>
<td>Superhydrous B</td>
<td>Mg$_{10}$Si$<em>3$O$</em>{14}$(OH)$_4$ g</td>
<td>16</td>
<td>1200</td>
</tr>
<tr>
<td>Phase C</td>
<td>same as sB ?</td>
<td>13-16</td>
<td>800-1000 b</td>
</tr>
<tr>
<td>Phase D</td>
<td>Mg$<em>{1.11}$Si$</em>{1.89}$H$_{2.22}$O$_6$ h</td>
<td>17</td>
<td>1400</td>
</tr>
<tr>
<td>Phase G (=D) j</td>
<td>Mg$<em>{1.24}$Si$</em>{1.76}$H$_{2.48}$O$_6$ i</td>
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<td>1050</td>
</tr>
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</table>

a Akimoto and Akaogi, 1980  
 b Ringwood and Major, 1967  
 c Kanzaki, 1991  
 d Finger et al., 1991  
 e Kato and Kumazaw, 1985  
 f Herzberg and Gasparik, 1989  
 g Gasparik, 1990, 1993  
 h Yang et al., 1997  
 i Kudoh et al., 1993  
 j Frost and Fei, 1998
Table 1.2 The lattice parameters of dense hydrous magnesium silicates

<table>
<thead>
<tr>
<th>Phase</th>
<th>Compositions</th>
<th>Lattice parameter</th>
<th>ρ (g/cm³) Mg/Si</th>
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<tbody>
<tr>
<td>Phase A</td>
<td>Mg⁷IVSi₂O₈(OH)₆&lt;sup&gt;a&lt;/sup&gt;</td>
<td>a = 7.8603 (2) Å</td>
<td>2.959&lt;sup&gt;b&lt;/sup&gt; 3.5</td>
</tr>
<tr>
<td></td>
<td>P 6₃</td>
<td>b = 9.5730 (2) Å</td>
<td></td>
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<tr>
<td></td>
<td>Z = 2</td>
<td>V = 512.22 Å³</td>
<td></td>
</tr>
<tr>
<td>Phase B</td>
<td>Mg₂₄VI⁺Si₂IVSi₆O₃₈(OH)₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>a = 10.588 (2) Å</td>
<td>3.368&lt;sup&gt;b&lt;/sup&gt; 3.0</td>
</tr>
<tr>
<td></td>
<td>P 2₁/c</td>
<td>b = 14.097 (1) Å</td>
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<td></td>
<td>Z = 4</td>
<td>c = 10.073 (1) Å</td>
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<td></td>
<td></td>
<td>β = 104.10 (3)&lt;sup&gt;o&lt;/sup&gt;</td>
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<td></td>
<td></td>
<td>V = 1458.4 (3) Å³</td>
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<td>Anhydrous B</td>
<td>Mg₂₈VI⁺Si₂IVSi₈O₄&lt;sup&gt;b&lt;/sup&gt;</td>
<td>a = 5.868 (1) Å</td>
<td>3.435&lt;sup&gt;b&lt;/sup&gt; 2.8</td>
</tr>
<tr>
<td></td>
<td>P mcb</td>
<td>b = 14.178 (1) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z = 2</td>
<td>c = 10.048 (1) Å</td>
<td></td>
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<td></td>
<td></td>
<td>V = 835.9 Å³</td>
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<tr>
<td>Superhydrous B(sB)</td>
<td>Mg₁₀VI⁺Si₁IVSi₂O₁₄(OH)₄&lt;sup&gt;c&lt;/sup&gt;</td>
<td>a = 5.0894 (6) Å&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.327&lt;sup&gt;d&lt;/sup&gt; 3.3</td>
</tr>
<tr>
<td></td>
<td>P nm</td>
<td>b = 13.968 (7) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z = 2</td>
<td>c = 8.6956 (2) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V = 618.16 (10) Å³</td>
<td></td>
</tr>
<tr>
<td>Phase D</td>
<td>Mg₄.₁₁VI⁺Si₁.₈₉H₂₂₂O₆&lt;sup&gt;e&lt;/sup&gt;</td>
<td>a = 4.7453 (4) Å</td>
<td>3.50&lt;sup&gt;e&lt;/sup&gt; 0.6</td>
</tr>
<tr>
<td></td>
<td>P 3₃m</td>
<td>c = 4.3450 (5) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z = 1</td>
<td>V = 84.74 (2) Å³</td>
<td></td>
</tr>
<tr>
<td>Phase E</td>
<td>Mg₂₀.₀₈VI⁺⁺Si₁.₁₆H₃₂O₆&lt;sup&gt;f&lt;/sup&gt;</td>
<td>a = 2.9701 (1) Å</td>
<td>2.88&lt;sup&gt;f&lt;/sup&gt; 1.8</td>
</tr>
<tr>
<td></td>
<td>P 3₃m</td>
<td>c = 13.882 (1) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z = 1</td>
<td>V = 106.05 (4) Å³</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg₂₁.₀₇VI⁺⁺Si₁.₀₁H₃₁₆O₆&lt;sup&gt;f&lt;/sup&gt;</td>
<td>a = 2.9853 (6) Å</td>
<td>2.78&lt;sup&gt;f&lt;/sup&gt; 2.15</td>
</tr>
<tr>
<td></td>
<td>P 3₃m</td>
<td>c = 13.9482 (7) Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Z = 1</td>
<td>V = 107.65 (4) Å³</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Horiuchi et al., 1979
<sup>b</sup> Finger et al., 1991
<sup>c</sup> Gasparik, 1990, 1993
<sup>d</sup> Pacalo and Parise, 1992
<sup>e</sup> Yang et al., 1997
<sup>f</sup> Kudoh et al, 1993

Z: number of formula per unit cell
superhydrous phase B and phase D are not yet defined. Phase G have been confirmed to be the same as phase D [Frost and Fei, 1998] (Table 1.1). It appears that superhydrous phase B and phase D are the only two possible candidates that can be stable in the lower mantle. In general, most of the high pressure phases in the transition zone and lower mantle have a higher oxygen coordination and higher symmetry in the crystal structures [Finger and Hazen, 1991]. Under extreme conditions of pressure and temperature, like those prevailing in the Earth's deep interior, only certain structures can be stable. Generally, it is the case that some kind of phase transformation takes place forcing the system to a denser phase. The structure of the phases that can be stable under the lower mantle condition can be guessed based on high pressure crystal chemistry. Accordingly, the coordination number for all Si is 4 in phase A, 4 and 6 in superhydrous phase B, and 6 in phase D. Moreover, the cations, Mg and Si, in phase D all sit in octahedral sites, and in superhydrous phase B, while all Mg cations sit in octahedral sites, some of the Si cations occupy the tetrahedral sites (Table 1.2). A six fold coordination for Mg and Si is indicated for phases in the lower mantle. Hence, both superhydrous phase B and D are possible candidates stable at lower mantle conditions.

If DHMS phases are indeed the mantle reservoir for hydrogen, total amounts of H$_2$O could be quite large because DHMS contain H$_2$O in weight percent levels [Akaogi and Akimoto, 1977; Kanzaki, 1991] which are orders of magnitude larger than the parts per million (ppm) amounts associated with anhydrous minerals [Bell and Rossman, 1992]. The H$_2$O budget in the mantle could be as much as the equivalent of several surface oceans [Thompson, 1993; Bell and Rossman, 1992]. Identification of the H$_2$O host mineral(s) in the mantle is thus essential for understanding the H$_2$O budget in the Earth's interior.
However, most of the DHMS phases synthesized from the system, MgO-SiO₂-H₂O may not be geologically relevant. Based on the above mentioned premises, the study of natural samples of serpentine (with a known amount of H₂O) under high pressures and temperatures would be a good starting point for evaluation of water-bearing phases in the Earth's lower mantle.

In this thesis, the decomposition of serpentine under high pressures and high temperatures, the stability of the superhydrous phase B and phase D, as well as the behavior of other DHMS phases under mantle conditions are presented. The consequence of the presence of H₂O-bearing phases for the mantle processes and their geological implications are briefly discussed.

In chapter 2, instrumentation and experimental set-ups used in this study are described, including different kinds of high pressure cells and laser heating system, conventional and synchrotron X-ray sources, and data acquisition and processing systems. Some resistive heating methods were developed to generate high temperature in the diamond anvil cell [Ming et al., 1987; Fei et al., 1992], but laser heating system was found to be a much easier way to heat samples in the range from 800 °C to 3000 °C. Therefore, the laser heating technique is presented and the advantage of using the new double-side laser heating technique is discussed in some detail. In this study both conventional and synchrotron radiation X-ray sources have been used for X-ray diffraction. Therefore, the conventional and synchrotron X-ray sources receive attention here. The data acquisition procedure and methods have made great advances in the past few years and are described in some detail.

In Chapter 3, the effect of high pressure and high temperature on serpentine is presented. The role of post-serpentine phases as possible water carrier(s) in the transition zone and the lower mantle is discussed. Results obtained from phase D are
compared with the results from previous studies. The implications of the results on DHMS for the mantle are discussed.

In Chapter 4, experimental results on serpentine under in-situ high pressure-temperature conditions are presented. Previous studies have shown that the superhydrinous phase B and phase D can be stable in the pressure range that prevail in transition zone and lower mantle. However, these studies are all from quenching experiments. The only in-situ experimental data on DHMS are from a study by Kuroda and Irifune [1998]. Only phases A and D can be identified from their data. Their results seem not consistent with the general observations in serpentine. It is, therefore, important to establish the thermodynamic stability limit of the hydrous phases to qualify them as important constituents for the transition zone and lower mantle. This motivated the present in-situ high pressure-high temperature studies. The results are presented in this chapter.

In Chapter 5, the results of in-situ high P-T experiments using a single phase superhydrinous phase B and phase D are presented. The decomposition phase assemblage of superhydrinous phase B is not clear and phase D has been claimed to persist to very high pressure by Frost and Fei [1998] but was observed to decompose in the study of decomposition of serpentine by Shieh et al. [1998]. Therefore using single phase component as the starting material will provide some information to evaluate and clarify the ambiguities. These experiments were designed to establish their respective high-pressure phase transformation(s) and to resolve the discrepancy in the stability field of phase D between the studies reported by Frost and Fei [1998] on the one hand and Shieh et al. [1998] on the other. In this chapter, the relationship between superhydrinous phase B and phase D is clarified, and the fate of most dense hydrous magnesium silicates investigated under high pressure and temperature is also discussed.
Chapter 2

Instrumentation

2.1 High pressure apparatus

Two different types of diamond-anvil cells (DAC) were used in this study. One is the modified Mao-Bell type cell which has a shorter piston and cylinder compared to the standard Mao-Bell cell. The advantage of this cell is that the two diamonds can be readily aligned by inserting 4 Allen wrenches without opening the cell. The other cell is the modified Merrill-Bassett cell which has a round shaped body instead of the triangular one. With the modified Merrill-Bassett type cell [Mao and Hemley, 1996] (Fig. 2.1) higher pressure can be reached compared to the earlier model (i.e. 50 GPa to 10 GPa). The symmetrical geometry is also good for double-side laser heating.

Two 1/3 or 1/4 carat gem-quality diamonds were mounted on disc seats using special epoxy glue (black color). The glue was a mixture of Stycast 2850FT epoxy resin (GRACE Specialty Polymers) and the Catalyst 24 LV-epoxy resin hardener (GRACE Specialty Polymers) in the ratio of $1 : 0.07$ by weight percent ratio. The mounted diamonds were then placed on a hot plate for curing overnight. In laser heated cell, the glued part required a covering which was a layer of high T resistant material-ZrO$_2$ or MgO powder mixed with some "940 adhesive". In this case, a further heat treatment in an oven ($\sim$150 °C) for 10 minutes was necessary.

2.2 Pressure measurement

The pressure generated in the diamond anvil cell is usually measured by the well known ruby fluorescence method, or using a standard marker such as NaCl, MgO, Au or Pt and using the X-ray diffraction method.
Fig. 2.1 The schematic diagram of modified Merrill-Bassett type diamond anvil cell (DAC). A is the side-view of DAC; B is the top-view of DAC. The four small circles along the biggest circumstance are the screw holes. The center (smallest circle) is the diamond window.
In the ruby fluorescence method, the shift of ruby R1 and R2 lines is measured and then is compared with its original wavelength, $\lambda_o = 6942.5 \text{ Å} (14402 \text{ cm}^{-1})$ for R1 and $\lambda_o = 6928 \text{ Å} (14432 \text{ cm}^{-1})$ for R2-line at ambient condition to obtain the pressure [Barnett et al., 1973; Piermarini et al., 1973]. In this study, most of the pressure calculation is based on the formula [Mao et al., 1986]

$$P = \frac{A}{B} \left\{ 1 + \left( \frac{\Delta \lambda}{\lambda_o} \right)^B \right\} - 1$$

where $P$ is the pressure in GPa, $\lambda$ is the wavelength of ruby R1 line, $A=1904$ GPa and $B=7.665$ for hydrostatic condition; $A=1904$ GPa, $B=5$ for non-hydrostatic condition.

The procedure for the pressure measurement at Geophysical laboratory is using OMA spectrography to detect the ruby fluorescence and then a CSMA program to analyze and process the data. For those experiments conducted at University of Hawaii, pressure was determined using a linear equation between the R1 shift and the pressure as described by Piermarini et al. [1975]:

$$P = 0.2740 (\Delta \lambda)$$

where $P$ is in GPa and $\Delta \lambda$ in angstrom (Å).

The other method uses X-ray diffraction and a suitable standard such as NaCl, MgO, Au, Pt. The prerequisites for using these pressure calibrants are (1) wide stability field, (2) simple in crystal chemistry, (3) chemically inert, and (4) well established equation of state (EOS), that is the pressure-volume relation at a given temperature. The pressure in the diamond anvil cell is determined by a combination of the lattice parameter measurement and the use of an equation of state such as the Murnaghan or Birch-Murnaghan equation of state. The Murnaghan equation of state is also called Murnaghan
integrated linear equation of state [Murnaghan, 1967] and is expressed in its original form as

\[
P = \frac{K_0}{\bar{V}_{K_0}} \left[ \left( \frac{V_0}{V} \right)^{\frac{K_0}{V_{K_0}}} - 1 \right]
\]

Where \( V_0 \) is the volume of starting material and the \( V \) is the volume of measured empirical data point. For example, the volume \( V \) at a certain pressure can first be obtained from the d-spacing measured by X-ray diffraction and then is plugged into the above formula—with known bulk modules and pressure derivative—to get the pressure.

2.3 Laser heating system and temperature measurement

The laser heating method is the most convenient way to heat the sample inside the diamond anvil cell to temperatures above 1000 °C. Therefore, the laser heating set-up plays an important role in the high pressure and high temperature experiment. In Geophysical Laboratory laser heating system a high power (100W) multimode continuous wave Nd:YAG laser was used as the source (Quantronic 118). The schematic of the system is shown in Fig. 2.2. This system was first developed at the Geophysical Laboratory. Detailed description has been given by Shen et al. [1996]. A brief summary is given here. The YAG laser beam is first expanded with a beam expander (the magnification is adjustable) and is then split into 2 beams by a sharp-edge dichroic mirror (or by a non-polarized cube 50/50 beamsplitter, BK7, grade A, fine annealed optical glass). The two laser beams are directed to the front and back side of the cell (see Fig. 2.2) and focused with adjustable lenses on the sample. The image of the sample can be monitored using another focusing lens (1000 mm focal distance) and viewed through a CCD camera. By monitoring the sample position, the two beams can be well aligned to hit the sample on the same spot from both sides. This minimizes the axial temperature
Fig. 2.2 The schematic diagram of laser heating system set-up. (After Shen et al., 1996)
gradient of the heating spot. The radial temperature gradient has been greatly reduced by applying the square-wave shaped multimode laser, instead of the Gaussian shaped TEM00 mode laser (Fig. 2.3 and 2.4). Sample temperature was measured by an imaging spectroradiographic system which consists of a thermoelectrically cooled CCD detector (Princeton Instruments, TE/CCD) and a 275 mm radius imaging spectrograph (Acton, SpectroPro-275). The CCD chip has 256 (rows) x 1024 (columns) pixels, each measuring 27 μm across. The black-body spectrum emitted from the sample was fitted to the Planck radiation curve (only fitting the thermal radiation between 600-800 nm). The entrance slit of the spectrograph is used to select a thin strip traversing the laser spot (Fig. 2.5). Through the spectrograph, this linear strip is imaged onto the 256 (rows) x 1024 (columns) 2-D CCD. Each row corresponds to a point on the strip with its thermal radiation wavelength spreading over each column. In this way the temperature profile across the hot spot is characterized at each measurement. Intensity measured by the CCD detector was calibrated with a tungsten ribbon lamp of known radiance, traceable to NIST standard. The sample was magnified by a lens-set (17X magnification in this setup) and projected on the CCD chip. Therefore, each row in Fig. 2.5 (B) recorded about 5 μm width of sample's temperature. In Fig. 2.6, a typical temperature profile across the sample is demonstrated. In the X-ray diffraction experiment using synchrotron X-ray radiation the beam size of X-ray was reduced to a very small spot, e.g., 20 X 20 μm. Therefore, the probed spot was within a very small temperature gradient region. In general, the temperature error is within 50-100 K range. If a larger size collimator was used, then the probed spot would have a larger temperature gradient.
Fig. 2.3 The schematic diagram of laser beam profile of different modes. (After Shen et al., 1996)
Fig. 2.4 The schematic diagram of double-side laser heating in the DAC. (After Shen et al., 1996)
Width defined by the entrance slit of spectrograph; height defined by pixel size and binning.

Fig 2.5 (A) The schematic image of laser heating spot in the CCD chip. (B) The schematic temperature profile obtained from binning area. There are 15 columns in total and 3 row's intensity data were binned together. (After Shen et al., 1996)
Fig. 2.6 The temperature profile across the sample.
2.4 Synchrotron radiation

Synchrotron radiation provides a very powerful source of X-ray and is commonly used in X-ray diffraction studies to determine the crystal structure of materials and identification of phases. It has proved to be particularly useful in high pressure and high temperature studies. The advantages of synchrotron radiation are (1) it is suitable for small samples, (2) fast, and (3) suitable for in-situ P-V-T experiments in the diamond cell.

Most of the experiments described here were carried out at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory; some were carried out at the Advanced Photon Source (APS), Argonne National Laboratory. In the former, the X-ray ring operates at 2.5 GeV to optimize radiation between 1 keV and 20 keV. At beamline X17C, there is a state-of-the-art superconducting wiggler insertion device. Operating at 2.58 GeV and current up to 300 mA, the device provides 100 to 1000 times higher photon flux than from a bending-magnet beamline, in the range of 20-60 keV. This is optimized for high pressure diamond cell experiment, because diamond anvil absorbs the photon energy below 10 keV. The X-ray radiation at beamline X17C is polychromatic and therefore the commonly used method is energy dispersive X-ray diffraction (EDXRD). In this method, the X-ray diffraction signals are first acquired by a liquid N2 cooled, Ge solid-state detector and then sorted out by a multi-channel analyzer (MCA) (Fig. 2.7). For the latter, all the experiments were carried at 13 BM-A with the X-ray ring operation at 2.8 GeV and 100 mA.

In the EDXRD method, the solid-state detector is set at a fixed angle (2θ= 120°) with respect to the direct beam. The detector angle is adjustable through a stepping motor which is controlled by a Vax computer installed on site. The entire X-ray diffraction energy can be stored in a MCA with either 4K memory (at NSLS) or 2K memory (at...
Fig. 2.7 The schematic EDXRD set-up at beamline X17C, Brookhaven National Laboratory
APS). The channel number of MCA was calibrated against photon energy (keV) using a variable X-ray radiation source. The diffraction lines appear at different energies, $E$. The interplanar, $d$, can be obtained from the relationship concerning photon energy and Bragg equation

$$E = h \nu = \frac{hc}{\lambda} \quad (1)$$

Where the $E$ is the photon energy (keV), $h$ is Plank’s constant, $6.62 \times 10^{-27}$ erg/sec, $\nu$ is frequency (1/sec), $\lambda$ is wavelength (cm), and $c$ is velocity of light.

$$2d \sin \theta = \lambda \quad (2)$$

From (1) and (2), it can be written as

$$2d \sin \theta = \frac{hc}{E}$$

rearranging this equation gives

$$Ed = \frac{hc}{2 \sin \theta} = \frac{6.1993 \text{ keV} \AA}{\sin \theta} \quad (3)$$

The photon energy is determined from the diffraction pattern and the detector angle was first set by the computer-controlled goniometer, and then calibrated by placing a standard material, e.g. Au. The interplanar, $d$, value can be obtained from equation (3).

### 2.5 Conventional X-ray diffraction method

The in-house X-ray machine is a conventional X-ray generator (Philips) operating at 45 keV and 15 mA. The source of the X-rays is from a Cu target tube with Ni-filter in the output window. The latter filters out K-beta and gives the Cu K-alpha wavelength.
The X-ray beam was collimated to 80 µm in diameter, using lead glass tube. The collimated beam struck the sample which was placed inside a modified Debye-Scherrer camera (28.648 mm in diameter) with film to record the diffracted X-rays. The sample-to-film distance was determined by placing a gold foil as calibrant. The total exposure time for one run is about 170 hours, using this set-up.

2.6 Film scanning method

The X-ray diffraction film was placed on a scanner (Sharp, JX-330) with a special fluorescence-free bottom plate and covered with a black color card board for reducing the background. The high resolution image was obtained in a 600 dpi quality scanning mode by using Adobe Photoshop program. Then, the image was converted to an intensity profile as a function of scattering angle 2θ, using a software program developed by Nguyen and Jeanloz [1993]. The spectrum thus derived could enhance the signal to noise ratio by 1-2 orders of magnitude over the traditional way, providing much more reliable results for complex X-ray diffraction patterns such as those from serpentine [O'Neill et al., 1993; Nguyen and Jeanloz, 1993]. Peak position vs. intensity can be obtained accurately using the well developed computer program.
Chapter 3

 Decomposition of serpentine under high pressure and high temperature and its implications for the Earth’s interior

3.1. Introduction

Serpentine (Mg_3Si_2O_7·2H_2O) is one of the major mineral constituents of the oceanic crust, and it is closely related to both olivine (Mg_2SiO_4) and pyroxene (MgSiO_3). Its H_2O content is well determined, namely ~13 wt%. Serpentine is known to decompose into different phase assemblages beginning at about 7 GPa, in the temperature range of 500-700 °C [Ulmer and Trommsdorff, 1995; Ulmer, 1996; Bose and Ganguly, 1995]. At higher pressures and temperatures, it breaks down to different assemblages consisting of phase A [Liu, 1986; Ulmer and Trommsdorff, 1995; Ulmer, 1996; Bose and Ganguly, 1995], phase B [Liu, 1986], phase E [Shieh and Ming, 1996], superhydrous phase B [Shieh and Ming, 1996; Shieh et al., 1997], brucite and phase D [Liu, 1986; Shieh and Ming, 1996; Shieh et al., 1997]. These experiments suggested that water could be carried into the transition zone and possibly down further to the lower mantle via different phase transformation products, at the pressure and temperature conditions prevailing in subduction zones [Meade and Jeanloz, 1991; Shieh and Ming, 1996; Irifune et al., 1996; Kuroda and Irifune, 1998].

Recently Tyburczy et al. [1991] have measured the equation of state of serpentine to 150 GPa using shock techniques and have found a high pressure phase (HPP) between 35 and 125 GPa (Fig. 3.1). Based on the Hugoniot data, they have suggested that the HPP of serpentine would be either an assemblage of H_2O + MgSiO_3 (perovskite) + MgO, or Mg(OH)_2 (brucite) + MgSiO_3 (perovskite) + SiO_2 (stishovite), along with some dense hydrous phases. It is motivated to carry out a systematic study on serpentine under...
Fig. 3.1 Serpentine P-T diagram in relation to serpentine on the serpentine Hugoniot and the mantle geotherm. Solid phase boundaries are from Yamamoto and Akimoto [1977]; dashed boundaries are from Liu [1986]. (data from Tyburczy et al., 1991)
lower mantle conditions, in the hope that the high-pressure phase breakdown products of serpentine could be identified and characterized. It is also worth noting in this connection that a number of much dense hydrous phases have been predicted theoretically, on the basis of chemical and structural considerations (Finger and Prewitt, 1989). In this chapter, experimental results obtained from decomposition of serpentine under mantle conditions are presented and followed by a discussion of the geological and geophysical implications relevant to the water storage in the lower mantle.

3.2 Experimental method

A natural lizardite sample with 12.7 weight percent H$_2$O was chosen as starting material (Table 3.1; also see Tyburczy et al., 1991). The Al$_2$O$_3$ and FeO are less than 1 weight percent, and therefore the sample could be regarded as a low iron-bearing serpentine. The high pressure and temperature experiments were performed with both Mao-Bell type and large-opening Merrill-Bassett type diamond anvil cells. A continuous-wave Nd YAG laser operating, either in the TEM$_{00}$ mode or multi-mode was used to heat the sample. The laser heating system set up at the University of Hawaii for the purpose was operated in the TEM$_{00}$ mode and this had a larger temperature uncertainty [Liu, 1986; Heinz et al., 1991]. The setup in the Geophysical Laboratory, Carnegie Institution of Washington operating in multil-mode had a higher precision temperature measurement capacity [Shen et al., 1996]. No pressure medium was used in the runs, but only graphite was admixed to improve absorption of the laser radiation, for heating the sample regions at high pressure. Pressure was determined by the ruby fluorescence technique as described by Ming and Manghnani [1978] for the system used at University of Hawaii, and by Mao et al. [1978] for the system used at Geophysical Laboratory. To avoid gasket contamination, the laser spot was kept away from the rim by at least 20 microns from the rim. The double-sided laser heating technique was used to reduce both axial and radial
Table 3.1 Chemical composition of serpentine, lizardite, Globe Arizona*

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>42.28</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.04</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.42</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>41.94</td>
</tr>
<tr>
<td>FeO</td>
<td>0.36</td>
</tr>
<tr>
<td>MnO</td>
<td>0.08</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>H₂O</td>
<td>12.70</td>
</tr>
</tbody>
</table>

Density, g/cm³  
97.88

2.50

Oxides in weight percent

*Data from Tyburczy et al., 1991
temperature gradients [Shen et al., 1996]. In some experiments, the samples were heated at a specific point, with spot size no less than 20 µm; thus the heated spot area was larger than the probing X-ray beam.

Serpentine was gradually pressurized in the range of 13–53 GPa, and then heated to temperatures in the range of 1000–1800 °C for ~5 minutes. The pressure after laser heating dropped by 8% to 21%. This difference arises from the combined effects of volume change during heating and stress relaxation after laser heating. Therefore, the sample pressure after laser heating should represent the minimum pressure at which the recovered assemblage was formed. The thermal pressure induced by the heating itself is not taken into consideration. Pressures reported here are therefore those measured after laser heating. The temperature uncertainty when using the TEM_{oo} mode laser was estimated to be about 200-300 °C [Liu, 1986; Heinz and Jeanloz, 1987, 1991] while the uncertainty when using the multi-mode laser was about 30-100 °C [Shen et al., 1996]. All of the run products were quenched to ambient conditions, removed from the diamond anvil cell, and examined by either in-house, or synchrotron X-ray sources, with angular and energy dispersive diffraction methods, respectively. The quenched samples were mounted in a Debye-Scherrer camera when using a conventional X-ray source, or placed in the energy dispersive X-ray diffraction (EDXRD) device when using the synchrotron radiation source. The former used an 80 µm collimator and the latter used 20x20 µm or 6x10 µm beam size to probe the quenched samples. To ensure that the X-ray beam probed the laser heated area only, the larger X-ray beam size was used only in the case of laser scanned samples over a larger area. The smaller X-ray beam was used for probing individual zones in the sample that had been laser heated with a fine spot, thus discriminating the heated region from the unheated sample. To ensure that the smaller X-ray beam hit right on the target, a 5 micron cross-head tungsten wire was used as standard
for centering and the system was aligned by adjusting the set of stepping motors and a microscope. The reproducibility of this system in centering position is within 5 µm.

3.3. Results

3.3.1 Angular dispersive X-ray diffraction analysis of quenched serpentine

Phase identification is one of the most important aspects in this kind of experiments. For pressures below 20 GPa, two runs were carried out at 15.2 and 19.6 GPa respectively. However, the pressure before and after laser heating was found to be different. In the former case, the pressure dropped from 15.2 GPa to 12.7 GPa and in the latter it dropped from 19.6 GPa to 13.7 GPa. The diffraction pattern of the sample subjected to 13.7 GPa and quenched is shown in Fig. 3.2 and the results are tabulated in Table 3.2. All the possible phases were considered and our analysis showed that the phase assemblage consists of phase E, brucite, stishovite, and clinoenstatite, as can be seen in Table 3.2. The observed d-spacings and the intensity of the peaks at 4.663 Å, 2.516 Å, 2.060 Å, and 1.431 Å are consistent with those found for phase E. The presence of phase E and absence of phase A are not consistent with Liu’s observation that serpentine breaks down into stishovite + phase A + brucite at 13 GPa and 1000 °C [1986]. These results are in accord with the fact that phase E has been synthesized at pressures between 13-17 GPa at temperature 800-1300 °C [Kanzaki, 1991; Kudoh et al., 1993; Ohtani et al., 1997]. Since no X-ray data were given in Liu’s paper [1986], it is not possible to compare the two results and to resolve the existing discrepancy.

In another experiment, the pressure was increased to 27.6 GPa, which after laser-heating dropped to 18.5 GPa. This pressure falls in the stability field of phase D, as reported by Liu [1986]. The X-ray diffraction results are tabulated in Table 3.3.
Serpentine recovered from 13.7 GPa and ~1100 °C

Fig 3.2 Serpentine recovered from 13.7 GPa and ~1100 °C (film data). Br: brucite, E: phase E, cEn: clinoenstatite, St: stishovite.
Table 3.2  X-ray diffraction data of laser-heated serpentine recovered from ~13.7 GPa and ~1100 °C.

<table>
<thead>
<tr>
<th>I/I₀</th>
<th>d, Å</th>
<th>Phase E&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Brucite&lt;sup&gt;b&lt;/sup&gt;</th>
<th>CEn&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Stishovite&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 b</td>
<td>4.663</td>
<td>4.64 (20)</td>
<td>4.41 (16)</td>
<td></td>
<td></td>
</tr>
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Note: I/I₀ represents the relative intensity.
a: Kanzaki, 1991
b: ASTM # 7-0239
c: ASTM # 19-769; clinoenstatite.
d: ASTM # 15-26
Table 3.3 X-ray diffraction data of laser-heated serpentine recovered from -18.5 GPa and -1100 °C.

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Note: number inside the parenthesis represents the relative intensity. b: broad; sh: shoulder.
a: Yang, et al., 1997
b: ASTM # 7-0239
c: ASTM # 15-26
d: Pacalo and Parise, 1992
Recently, Yang, et al. [1997] have reported the X-ray diffraction data of phase D from the study of a single crystal, which are more reliable than the results obtained by Liu [1986]. Therefore, their d-spacings are listed for comparison with our data and as our guide. As can be seen in Table 3.3, our data indicate clearly that phase D is the dominant phase in this run, followed by brucite and superhydrous phase B. The presence of stishovite is somewhat questionable, partly because that the most intense peak in stishovite does not match well with the observed data, and partly because that all the diffraction lines in stishovite overlap with those of superhydrous phase B. No periclase was observed in this run. In the same pressure range Liu [1986] reported phase assemblages which are different from this result. For instance, superhydrous phase B, that I have found does not mention in the above work of Liu. It is possible that different synthesis condition may have resulted in different phase assemblage. The final phase assignment is given in Fig. 3.3. The spectrum in the Fig. was converted from the X-ray film, using the software developed by Nguyen and Jeanloz [1993]. It shows clearly that the phase D, superhydrous phase B and brucite are the dominant phases in this run.

In the next experiment, pressure was increased to 30.1 GPa, but it dropped to 26.6 GPa after laser heating. The recovered sample was checked by X-ray diffraction and the results are tabulated in Table 3.4. Phase D is still the major constituent along with periclase, a new phase in this series of run. However, all the strong peaks in superhydrous phase B become very weak, namely 2.722 Å, 2.522 Å, 2.044 Å, and 1.434 Å indicating that superhydrous phase B is unstable in this P-T range. The d-spacings 4.788 Å, 2.357 Å, 1.787 Å, 1.568 Å and 1.362 Å belong to brucite but their intensities are reduced by a factor 2 compared to the run at 18.5 GPa. The presence of stishovite seems more positive as indicated by several non-overlapping lines at 2.225 Å, 1.976 Å, 1.872 Å, 1.524 Å,
Fig. 3.3 Serpentine recovered from 18.5 GPa and ~1100 °C (film data). SB: superhydrous phase B, D: phase D, Br: brucite, St: stishovite.
Table 3.4 X-ray diffraction data of laser-heated serpentine recovered from 26.6 GPa and ~1100 °C.

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Note: number inside the parenthesis represents the relative intensity; sh: shoulder
a: Yang, et al., 1997
b: ASTM # 4-0829
c: ASTM # 7-0239
d: ASTM #15-26
e: Pacalo and Parise, 1992
1.323 Å and 1.163Å. Based on the relative intensities of the peaks obtained in this run, it can be safely concluded that the superhydrous phase B is definitely unstable under the P-T condition in this experiment. The brucite peaks are somewhat weaker than in the previous run. In summary, it is concluded that phase D, periclase, brucite, and stishovite are the phase assemblage obtained in this P-T condition. The results are presented in Fig. 3.4.

In order to establish the stability field of phase D, some runs at much higher pressures were carried out. The results obtained at 53.3 GPa (after laser heating) are tabulated in Table 3.5. The results revealed that most of the major peaks of phase D have disappeared, and the peaks of the perovskite phase have appeared. The lattice parameter of the perovskite obtained by fitting the observed spacings to an orthorhombic cell are: $a=4.7868$ Å, $b=4.929$ Å and $c=6.8865$ Å. These values are comparable with the lattice parameters reported by Horiuchi et al. [1987]. However, extra $d$-spacings with 4.158 Å, 3.751 Å, and 3.575 Å were observed in this run. The 4.158 Å can be accounted on the basis of phase D as the (100) of this phase, but we cannot account for the weak peaks at 3.751 and 3.575 Å. The X-ray diffraction pattern on the products of this run is shown in Fig. 3.5. From Fig. 3.5 it is clear that perovskite and periclase are the dominant phases in the quenched sample. It is precisely these phases which would be stable under the P-T conditions in the lower mantle of the Earth.

Five selected spectra are shown in Fig. 3.6, summarizing the results described in this chapter. These spectra show clearly the sequence of the phase assemblages found as a function of pressure at 1100 (± 300) °C. The results are summarized below: The underlined phases are the dominant phases, while the rest are either minor phases, or residuals.
Fig. 3.4 Serpentine recovered from 26.6 GPa and ~1100 °C (film data). D: phas D, sB: superhydrous phase B, Br: brucite, St: stishovite, Pe: periclase.
Table 3.5 X-ray diffraction data of laser-heated serpentine recovered from \(-53.3\) GPa.

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Note: number inside the parenthesis represents the relative intensity; sh: shoulder
a: Based on orthorhombic cell with $a = 4.7868$ Å, $b = 4.929$ Å and $c = 6.8865$ Å
b: ASTM # 4-0829
c: ASTM # 15-26
d: Yang, et al., 1997
Fig. 3.5 Serpentine recovered from 53.3 GPa and ~1100 °C. D: phase D, Pv: perovskite, Pe: periclase, St: stishovite, *: unknown peak.
Fig. 3.6 Five selected spectra from film data of recovered pergolide at different PT conditions. The pressure footnotes denote those of before and after laser heating pressures. The phase abbreviations are same as previous figure.
**19.6/13.7 GPa** Clinoenstatite + phase E + brucite + stishovite

**27.6/18.5 GPa** Superhydrous phase B + brucite + phase D + stishovite

**30.1/26.6 GPa** Phase D + periclase + brucite + superhydrous phase B + stishovite

**43.5/37.6 GPa** Phase D + periclase + stishovite (?) + perovskite (?)

**46.8/42.1 GPa** Perovskite + periclase + phase D (?) + stishovite (?)

The above sequence is quite different from that reported by Liu [1986]. The discrepancy between the two studies may be partly due to the different starting materials used (i.e. Liu's chrysotile vs. lizardite in this study) and partly due to the fact that both phase E and superhydrous phase B have been successfully synthesized only after Liu's report.

Two points that deserve comments are (1) the perovskite phase appears to form at a much higher pressure from serpentine than from olivine and pyroxene. This must be due to the presence of the DHMS phases such as superhydrous phase B and phase D. (2) The appearance of brucite in the run 43.5/37.6 GPa may be attributed to lower temperature (<1000 °C) [Fei and Mao, 1993; Frost and Fei, 1998] in this run. It is to be noted that temperatures reported in this series of experiments were based on optical pyrometer and therefore there may be a large uncertainty in temperature evaluation. This could lead to some ambiguities in the reported phase assemblages, as a function of pressure.

### 3.3.2 Energy dispersive X-ray diffraction analysis of quenched serpentine

The results obtained by energy dispersive X-ray analysis on quenched samples of serpentine are regarded as more precise than angular dispersive X-ray analysis. The reasons for this are (1) the experiments were carried out with a better temperature...
measurement system (2) the X-ray diffraction studies were carried out with the synchrotron radiation source, which enables us to probe a small area of the sample, less than 20 µm, thus reducing complications arising out of a pressure gradient over the sample area.

More than 30 experiments were done, but only those runs in which pressure was measured after laser heating are reported. This is because thermal pressure and stress relaxation effects that occur during the laser heating process affect the final pressure results. The phase assemblage varied with increasing pressure. Four select spectra (Fig. 3.7) demonstrate the changes in the phase assemblage. In Fig. 3.7 (a), phase D, superhydrous phase B (SB) and brucite (Br) are the dominant phases (Table 3.6). In Fig 3.7 (b), the superhydrous phase B disappears and a new phase, periclase, is evident. The disappearance of superhydrous phase B is consistent with previous results obtained through angular dispersive XRD for phase identification. The periclase can easily be recognized from the peak positions at 24.5 and 39.9 keV and also Table 3.7. While the brucite disappears at higher pressure, stishovite is present as a minor phase (as shown in Fig. 3.7 (c) and Table 3.8). Phase D is the only hydrous phase persisting up to this P-T range. When pressure is increased to 46 GPa and temperatures above 1320 °C, phase D disappears (Fig. 3.7 (d)) and perovskite appears as the dominant phase, along with periclase (Table 3.9). There may be some small amount of stishovite present in this run as indicated by a shoulder peak at 2.957 Å.

All of the EDXRD data obtained in this study are plotted in the pressure – temperature diagram (Fig. 3.8). The open symbols represent data obtained from energy dispersive method, the solid symbols are data derived from two sets of multi-anvil studies, of Kuroda and Irifune [1998] and Frost and Fei [1998]. Our results are consistent with those obtained from multi-anvil experiments [Gasparik, 1993; Irifune et al., 1996;
Fig. 3.7 Comparison of 4 selected spectra from EDXRD data. Spectra a was recovered from 21.8 GPa, 1030°C; b was from 27.5 GPa, 1530°C; c was from 37 GPa, 1560°C; d was from 46 GPa, 1320°C.
Table 3.6 X-ray diffraction data of laser-heated serpentine recovered from 21.8 GPa and 1030 °C.

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<th>Phase D&lt;sup&gt;c&lt;/sup&gt; d, Å hkl I/I₀</th>
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Note: sh denotes shoulder; b denotes broad, the intensity of observed value represents the relative intensity

a: ASTM 7-239.
Table 3.7 X-ray diffraction data of laser-heated serpentine recovered from 27.5 GPa and 1530 °C.

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Note: the intensity of observed value represents the relative intensity.
a: Yang et al., 1997
b: ASTM # 4-829
c: ASTM # 7-239
Table 3.8 X-ray diffraction data of laser-heated serpentine recovered from 37 GPa and 1560 °C.

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Note: the intensity of observed value represents the relative intensity.

a: Yang et al., 1997
b: ASTM # 4-829
c: ASTM #15-26
Table 3.9 X-ray diffraction data of laser-heated serpentine recovered from ~46 GPa and 1320 °C.

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Note: sh denotes shoulder; b denotes broad, the intensity of observed value represents the relative intensity.

a: Horiuchi et al., 1987
b: ASTM # 4-829
c: ASTM # 15-26
Fig. 3.8 The recovered sample from serpentine at the indicated P-T conditions. The dashed lines are the phase boundaries; the hatched lines are the uncertainties.
Kuroda and Irifune, 1998; Frost and Fei, 1998]. The boundaries shown between region I and II, and II and III are probably dehydration boundaries, because the superhydrous phase B and phase D completely disappear in the region of II and III, respectively. The negative slope of the boundaries I–II and II–III are also consistent with the general characteristic of a dehydration curve under high pressure conditions [e.g., Ulmer and Trommdorff, 1995; Fei and Mao, 1993; Holland et al., 1996]. It is evident that brucite has a wide stability field (1 bar to 37 GPa) at lower temperatures, in agreement with the study of brucite by Simakov [1974] and Fei and Mao [1993]. However, there are two data points from this study, which show brucite existing around 1600 °C (see Fig. 3.8) as well as at 1000 °C. Frost and Fei [1998] found that the brucite is confined to the lower temperature region, compared with the stability field of superhydrous phase B. Only near the phase boundary brucite and superhydrous phase B can be observed together. The higher temperature data points for brucite are not consistent with the P-T diagram of serpentinite given by Irifune et al. [1998]. According to their study brucite should not exist above 800 °C. Therefore, it is believed that it may be a quenched product. Our study establishes that phase D becomes unstable at pressures above 46 GPa and temperatures near 1320 °C. This result is in accord with the observations based on the shock wave Hugoniot experiments by Tyburczy et al. [1991], but it is inconsistent with those reported by Li and Jeanloz [1991]. Shock wave data has indicated that there might be a high pressure phase assemblage different from lower pressure phase assemblage at pressures above 30-40 GPa (Fig. 3.1). Our results suggest that the phase transformation above 40 GPa is to the denser perovskite + periclase + another phase, which supports the shock wave results. However, the discrepancy of the decomposition pressure of phase D between this study and that of Li and Jeanloz could be explained by (1) difference in the starting material; their starting material is MgSiO3 + water which is different from lizardite in this study, (2) differences in pressure calibration; in Li and Jeanloz [1991]
study pressure was calculated from the load applied by the spring washer of the diamond cell before laser heating, and (3) the size of X-ray beam used to probe the sample (i.e. ~100 µm in Li and Jeanloz [1991] vs. 20 µm in this study). In the present work, the ruby fluorescence method was used and stress relaxation after laser heating was taken into account. Thus the weak lines of phase D they observed at an equivalent pressure may be due to an overestimate of pressure and/or temperature difference in their work.

From multi-anvil data [Frost and Fei, 1998], it was concluded that the Mg/Si ratio of phase D varies with P-T conditions; the Mg/Si ratio as well as the H2O content decreases with increasing temperature. In addition, the H2O content in the phase D varies from 10 to 18 wt%. The results plotted for the system of MgO-SiO2-H2O shows that phase D is spread out over a certain range (Fig. 3.9), and is not a fixed component. The MgO content appears to be within a narrow range, but SiO2 and H2O vary over a wider range. Single crystal analysis on the phase D indicated that there are about 6% of Si4+ sites being substituted by Mg2+ [Yang et al., 1997]. Substitution of Mg2+ + 2 H+ for Si4+ would, therefore, be possible [Frost and Fei, 1998]. The appearance of stishovite from the recovered assemblage can be attributed directly to the Si−deficiency in phase D, which is in accord with Frost and Fei’s suggestion.

3.3.3 Comparison of X-ray data of phase D from different studies

The d-spacing values of phase D obtained in the present study are comparable with those reported by Liu [1986], Kuroda and Irifune [1997] and Yang et al.[1997] (Table 3.10). Two observations are worth noting: (1) there is good agreement between the present data and those of Liu [1986], except that three peaks at 9.5 Å, 3.37 Å, and 2.53 Å given by Liu [1987] are not observed in this study (also see Table 4 of Frost and Fei, 1998). (2) the d-spacings of phase D obtained in the present study are generally larger than those obtained from multi-anvil experiments, such as (100), (201), (112), and (300). The lattice
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</table>

* mixed with periclase phase
parameter derived from the diffraction data in this study has a longer a-axis and higher volume, but smaller c-axis compared to those obtained from multi-anvil studies (Table 3.11). Notably, both the results from diamond cell and multi-anvil apparatus show that phase D synthesized at high pressure has a larger volume (Fig. 3.10). However, the relationship between volume of phase D and Mg/Si and as well H₂O content is unclear. The ideal formula of phase D (MgSi₂H₂O₆) has the Mg/Si ratio equal to 0.5 and 10 wt% H₂O. But almost all the phase D obtained from multianvil studies have the Mg/Si ratio higher than 0.5 and higher than 10 wt% H₂O (see Table 3.11). Frost and Fei [1998] reported experiments at high temperature result in lower Mg/Si and H₂O content, but at high pressure result in higher Mg/Si and H₂O content. It seems indicating that an ideal phase D favors at a relatively lower pressure but high temperature conditions. However, this speculation need further investigation.

3.3.4 Raman spectroscopy data

The nearly linear function of OH bond distance versus OH frequency shift is a useful guide to the various types of hydrogen bonding in hydrogen systems (Fig. 3.11) [Nakamoto et al., 1955; Novak, 1973]. On this basis, we examined the quenched phase D by Raman spectroscopy. The O-H stretching frequency of phase D appeared near 2696 cm⁻¹. This value is smaller than the frequency reported by Frost and Fei [1998], namely 2847 cm⁻¹. The lower vibration frequency could be due to a change in the O-H bond distance. If this is true, then the corresponding bond distance for O-H in phase D would be similar. Based on Fig. 3.12, the frequency at 2696 cm⁻¹ gives a value of O-H distance at 2.63 Å which is very close to the value of 2.676 Å reported by Yang, et al. [1997] for phase D. The O-H stretching frequency of phase D obtained from different synthesized P-T condition still exhibited some minor difference. This seems
Table 3.11 The lattice parameters, volumes and H₂O wt% of different studies on phase D

<table>
<thead>
<tr>
<th>Composition</th>
<th>P</th>
<th>T</th>
<th>a</th>
<th>c</th>
<th>V</th>
<th>H₂O</th>
<th>Mg/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(GPa)</td>
<td>(°C)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg₁₀.₁₀Si₁₆.₆₀H₃₄.₀₆O₆</td>
<td>20</td>
<td>1200</td>
<td>4.7453</td>
<td>4.345</td>
<td>84.74</td>
<td>18</td>
<td>0.69</td>
</tr>
<tr>
<td>Mg₁₁.₁₁Si₁₈.₉₂H₂₂.₂₂O₆</td>
<td>16</td>
<td>800</td>
<td>4.770</td>
<td>4.341</td>
<td>85.46</td>
<td>12.3</td>
<td>0.59</td>
</tr>
<tr>
<td>Mg₁₄.₁₄Si₁₇.₃₂H₂₈.₈₁O₆</td>
<td>22</td>
<td>1050</td>
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<td>4.344</td>
<td>86.3</td>
<td>14.5±2</td>
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<td>18</td>
<td>1000</td>
<td>4.768</td>
<td>4.345</td>
<td>85.5</td>
<td></td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>26</td>
<td>1200</td>
<td>4.789</td>
<td>4.343</td>
<td>86.25</td>
<td>12.34</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>22</td>
<td>1000</td>
<td>4.814</td>
<td>4.313</td>
<td>86.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>30</td>
<td>1220</td>
<td>4.833</td>
<td>4.326</td>
<td>87.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>–</td>
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<td>1530</td>
<td>4.818</td>
<td>4.325</td>
<td>86.95</td>
<td></td>
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<tr>
<td></td>
<td>–</td>
<td>24</td>
<td>1530</td>
<td>4.796</td>
<td>4.337</td>
<td>86.39</td>
<td></td>
</tr>
</tbody>
</table>

a: Phase D, Frost and Fei, 1998
b: Phase G (=D), Ohtani et al., 1997
c: Phase D, Kuroda and Irfune, 1998
d: Phase D, Liu, 1986
e: Phase D, this study

*(Mg+Fe)/Si; MgO = 26.65 wt%, FeO = 0.74 wt%, SiO₂ = 58.81 wt%.
Fig. 3.10 The nearly linear relationship of volume and pressure of phase D obtained from numerous studies.
Fig. 3.11 The representative Raman spectrum of phase D. The peak of OH stretching vibration appear at 2696 cm$^{-1}$. 
Fig. 3.12 The O-H bond distance as a function of frequency. The vertical hatched bar represents the data obtained in this study. The horizontal hatched bar is the relative OH bond distance.
suggested that the O-H bond distance in the phase D may depend on P-T conditions of synthesis.

3.4 Discussion

3.4.1 Decomposition of serpentine

The above results on serpentine show that the hydrous phases, phase E, superhydrous phase B and the denser hydrous silicate phase D, decompose in different pressure ranges. Phase E is unstable at pressures above 18.5 GPa, which is in accord with the report by Kanzaki [1991]. The decomposition of SB is confirmed by the present study, but there is no direct evidence for SB transforming to phase D. Most notably, the stability range of phase D has been clarified in the present study. Our data at P= 42 GPa and T= -1550 °C, and at P=46 GPa and T= -1320 °C, help to define the phase boundary between II and III (see Fig. 3.8) with a negative slope. Both the SB and phase D have a negative P/T slopes at the limits of their stabilities.

Our starting material, serpentine, has a well-constrained water content to start with. Despite this, no hydrous phase is observed at pressures higher than 46 GPa; the only phases observed are perovskite, periclase and occasionally stishovite. We therefore must address the question of the missing water needed for mass balance. We suggest some possibilities: (1) formation of an unrecovered aqueous phase, like water, (2) unquenchable high P-T phase that transforms to an end member oxide components, like SiO₂ plus water, (3) transformation to a new hydrous phase, which is undetectable by the present X-ray diffraction technique. The hypothesis of a new DHMS phase should be testable, unless the total amount is beyond x-ray detection range, i.e. less than 5 volume percent. We tentatively exclude this possibility. The options (1) is in accord with the phase relations
predicted from shock wave Hugoniot data, particularly in the 40-60 GPa range [Tyburczy et al., 1991].

3.4.2 Geological implication for the subducting slab

The decomposition of SB and phase D at lower mantle P-T conditions could have important geophysical implications. Serpentine is a good candidate for the initial transport of water into the deep mantle with a subducting slab [Meade and Jeanloz, 1991; Ulmer and Trommsdorff, 1995; Ulmer, 1996]. Its subsequent high pressure phases may also serve as water reservoirs, once formed in the mantle [Ulmer and V. Trommsdorff, 1995; Ulmer, 1996; Bose and Ganguly, 1995; Irifune et al., 1996, 1998; Kuroda and Irifune, 1998]. Serpentine is stable up to ~7.0 GPa and ~540 °C and then its dehydration will produce phase A + enstatite + water along a cold-slab geotherms [Ulmer and Trommsdorff, 1995; Bose and Ganguly, 1995; Ulmer, 1996; Irifune et al., 1998]. The temperature in a subducting plate is not well defined and may vary with the slab conditions, e.g. at ~210 km, it could be 600 ± 200 °C in a cold-slab [Thompson, 1992]. Serpentine preserved in cold and mature (>50 Myr) subducted slabs could penetrate to ~210 km [Thompson, 1992; Ulmer and Trommsdorff, 1995; Ulmer, 1996; Bose and Ganguly, 1995] where it would then decompose. The P/T stability limits (as reported by several different investigators) for phase A, phase E and superhydrous phase B are shown in Table 3.12. These results show that phase A, phase E and SB could be resident in subducting slabs. The sequential phase transformation of DHMS phases (A, E, SB and D) from serpentine could then occur, as the critical depths are reached. Therefore each DHMS phase, in turn, (A, E, SB and D) would assume the role of a "water carrier" within different pressure and temperature ranges [e.g. Li and Jeanloz, 1991; Ahrens, 1989; Luth, 1995; Pawley and Wood, 1996; Ulmer and Trommsdorff, 1995; Ulmer, 1996; Bose and Ganguly, 1995; Irifune et al., 1996, 1998; Kuroda and Irifune, 1997; Tyburczy et al., 1991].
Table 3.12 The upper P-T stability limits for phase A, E and superhydrous phase B from various experiments

<table>
<thead>
<tr>
<th>Phase</th>
<th>Pressure (GPa), Temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase A</td>
<td>12.0, 1000</td>
<td>Luth, 1995</td>
</tr>
<tr>
<td></td>
<td>16.0, 1172</td>
<td>Burnley and Navrosky, 1996</td>
</tr>
<tr>
<td>Phase E</td>
<td>18.0, 1100</td>
<td>Irifune et al., 1998</td>
</tr>
<tr>
<td></td>
<td>17.0, 1000</td>
<td>Kanzaki, 1991</td>
</tr>
<tr>
<td></td>
<td>17.4, 950</td>
<td>Ohtani et al, 1995</td>
</tr>
<tr>
<td></td>
<td>20.0, 1290</td>
<td>Ohtani et al, 1997</td>
</tr>
<tr>
<td></td>
<td>21.0, 1240</td>
<td>Ohtani et al, 1997</td>
</tr>
<tr>
<td>Superhydrous phase B</td>
<td>22.3, 1850</td>
<td>Gasparik, 1993</td>
</tr>
<tr>
<td></td>
<td>22.5, 1000</td>
<td>Ohtani et al., 1995</td>
</tr>
<tr>
<td></td>
<td>20.0, 1400</td>
<td>Pacalo and Parise, 1992</td>
</tr>
<tr>
<td></td>
<td>22.0, 1360</td>
<td>Ohtani et al, 1997</td>
</tr>
<tr>
<td></td>
<td>26.0, 1200</td>
<td>Irifune et al., 1998</td>
</tr>
</tbody>
</table>
For a better understanding of the relationship between these DHMS and the mantle, the results obtained in this study together with the available data on the decomposition boundaries of serpentine [Ulmer and Trommsdroff, 1995; Ulmer, 1996], appearance of SB [Gasparik, 1993], appearance of D [Frost and Fei, 1998] are all plotted in Fig. 3.13. The data of cold and hot slabs are from Thompson [1992] and geotherms are from Anderson [1982], Williams and Jeanloz [1990], and Ita (pers. comm.). It will be seen from the Fig. 3.13 that phase A is stable at pressures in the range 6-16 GPa and temperature in the range 800-1200 °C, which is suitable for slabs in the upper mantle region, but may become unstable in the transition zone [Ulmer and Trommsdroff, 1995; Ulmer, 1996; Bose and Ganguly, 1995; Irifune et al., 1998]. Phase E is observed at 13.7 GPa, but disappears at 18.5 GPa (this is not shown in Fig. 3.13 in order to simplify the P-T diagram), in agreement with previous reports that phase E is stable in the P-T ranges 13–18 GPa and 600-1100 °C. This indicates that phase E would be present in slabs at the transition zone [Kanzaki, 1991; Ohtani et al., 1995; Irifune et al., 1998]. Superhydrous phase B appears to be stable at pressures above 18 GPa and temperatures above 800 °C, which would make it a good candidate in hotter slabs [Ohtani et al., 1995, 1997]. Finally it decomposes at P-T conditions existing around 700-800 km, which would correspond to the outer part of the lower mantle. Phase D can exist up to 45 GPa and T ~ 1250 °C that is at pressures and temperatures prevailing at a depth of about 1250 km within the Earth.

The extent of dehydration in slabs may vary. In hotter slabs, the breakdown of the hydrous phases, e.g. serpentine and superhydrous phase B, will allow certain amount of water to be released from the dehydration, and move the water into the overlying mantle wedge, causing arc-type volcanism [Thompson, 1992; Ulmer and Trommsdroff, 1995; Ulmer, 1996] or even possibly deep-focus earthquakes [Meade and Jeanloz, 1991]. Nolet and Zielhuis [1994] observed a strong low S velocity anomaly at 300–500 km depth,
Fig. 3.13 The serpentine P-T phase diagram related to geotherms and cold and hot slabs.
which they interpret as an injection of water. DHMS phases are most likely agents for transport of this water to the transition zone [Nolet and Zielhuis, 1994]. In cold and mature slabs phase D could persist down to ~1250 km and then break down into perovskite, periclase and an unknown hydrous phase or free "water". The appearance of perovskite and periclase are consistent with the expected mantle compositions. The negative pressure–temperature slope of the phase D decomposition boundary implies that if the slab temperature is relatively lower than that of surrounding mantle, the transformation of phase D to perovskite and periclase will occur at a much deeper depth, and the density contrast would prevent the cold slab from going down further. But on the other hand, the temperature difference will cause a thermal density anomaly which may further cause the slab to move downward [Wysession, 1996]. Then the penetration depth would depend upon the slab area and the rate of heat transfer from the surrounding mantle rock to the slab, and the density contrast between phase D and its high pressure assemblage. This transformation may be limited to a certain P-T range; a higher temperature is certainly possible causing phase D to decompose at an earlier stage. The absence of seismicity below a particular depth does not necessarily mark the demise of the slab [Meade and Jeanloz, 1991].

The behavior of subducted slabs in the lower mantle is still unclear [Wysession, 1996], and hence the role of water in these processes cannot be described with certainty. Nevertheless, the results obtained in this study may have implications for a mid-mantle discontinuity beneath the Indonesian arc, that is characterized by large depth (900-1080 km) and a large velocity contrast variation (up to 1.6 %) in different subduction zone [Niu and Kawakastu, 1997]. Furthermore, release of water into the lower mantle due to the decomposition of phase D could influence what we assume to be a global mantle process such as partial melting, which could trigger plume genesis and enhance mantle convection. Finally, the decomposition of phase D indicates that there are no denser
hydrous magnesium silicates stable at higher pressure and that the reaction limits the
highest pressure for lower iron-bearing dense hydrous magnesium silicate phases in the
Earth's mantle.
Chapter 4.

In-situ high pressure and high temperature experiment on serpentine

4.1 Introduction

In the previous chapter it was shown that the decomposition of serpentine at different pressures and temperatures can result in a host of DHMS phases, viz, A, E, SB and D. All of the above DHMS phases were obtained from quenching experiments, using either the diamond anvil cell [Liu, 1986; Shieh and Ming, 1996; Shieh et al., 1997, 1998], or the multianvil press [e.g. Ringwood and Major, 1967; Gasparik, 1993; Kanzaki, 1991; Frost and Fei, 1998]. Recently Irifune et al. [1998] have reported a phase diagram for serpentine to 26 GPa and for the temperature range 500-1400 °C. Their results are comparable to those described in chapter 3. Notably, there was no H$_2$O released below 800 °C from the transformation of serpentine to phase D + brucite, but above 800 °C there will have 4.3 wt% of H$_2$O went into liquid phase in the same pressure range, which gave phase D + superhydrous phase B [Irifune et al., 1998]. Kuroda and Irifune [1998] demonstrated from in-situ high pressure and temperature data on serpentine at pressure up to 28 GPa and temperature to 1500 °C, that phase D was the only hydrous phase observed for pressures up to about 21 GPa and temperatures from 350 to 800 °C; P=17.6 GPa, T=500 °C and P=18.5 GPa, T=800 °C. But phase A was observed at P=9.7 GPa and T=470 °C. When this information is compared with the serpentine phase diagram of Irifune et al. [1998], it is evident that either the phase E and superhydrous phase B were the quenched phases, or the X-ray diffraction resolution of their study was not high enough to identify these phases. The multi-anvil apparatus are limited to 26 GPa maximum pressure. It would be significant to determine the thermodynamically stable hydrous phases that would preserve the H under the mantle condition. The truly stable
high pressure hydrous phase would help us in understanding the water budget in the lower mantle and provide important geophysical implication to the Earth's interior. These questions motivated us to carry out in-situ high pressure and temperature experiments using the diamond anvil cell, to explore the hydrous phases that would be relevant for the mantle conditions.

### 4.2 Experiment

In this experiment, two kinds of serpentine samples were used as starting materials: lizardite and antigorite. Lizardite was pressurized to over 60 GPa. Antigorite was pressurized to about 37 GPa. All of these experiments used a modified Merrill-Bassett type cell and the double-side laser heating method. To ensure that the sample won't be overheated and transformed into anhydrous phases, the experiments on lizardite sample were carried out at about 1300 °C and on antigorite sample at about 1000 °C. The other object of using lower temperature was to prevent the melting of the sample, and to identify in-situ phases, phase D and superhydrous phase B. Using the same power, the laser beam was focused on two spots in lizardite; center and edge respectively. In the case of antigorite, sample was heated at a number of spots to ensure that there was no unreacted material. Due to the constraint on the laser heating system, it was not possible to get temperature below 1000 °C, for temperature measurement could not be carried out reliably in the range below 1000 °C. The heated samples were probed by energy dispersive X-ray diffraction using the synchrotron beam line X17C at the Brookhaven National Laboratory (the detail experimental procedure was described in Chapter 2).
4.3 Results

4.3.1 Photo image

Lizardite was compressed in a gasketed diamond cell directly to about 66 GPa as measured in the center area. However, there was a pressure gradient and the pressure near the edge was found to be 42 GPa. The sample was laser heated to about 1310 °C. Fig. 4.1. shows the laser heated lizardite and antigorite inside the diamond cell. The upper picture shows the lizardite sample and the lower one the antigorite. In lizardite the center spot is yellow brown color and the edge spot is transparent. This may be due to two different phase assemblage in this sample, possibly due to pressure gradient in the cell. Antigorite was pressurized to about 36 GPa as measured at the center, and 25 GPa at the edge. This was heated at several points across the whole sample to about 1000 °C. The heated antigorite sample in this run was clear across the whole sample area.

After laser heating, the pressure at the yellow brown spot was measured as 35 GPa, a pressure drop of 47 % from the original pressure of 66 GPa. The pressure near the edge dropped to 36 GPa from 42 GPa after heating. In the case of antigorite, the center pressure dropped to about 34 GPa, a ~5 % pressure decrease, while at the edge, the pressure dropped to 22 GPa representing a 12 % pressure drop. It is believed that laser heating relaxes the stress and strain, leveling out the pressure gradient. The large drop may be due to other factors, such as heating of the loading washer in the diamond cell.

To resolve the abnormal ruby pressure observed in lizardite after laser heating, sample pressure of lizardite at the edge spot was calculated based on the in-situ volume of periclase and the established equation of state [Jamieson et al., 1982]. The periclase yielded a pressure equal to 27.5 GPa. Pressure measurement by the ruby indicates a higher pressure and it is possible that ruby was in a different place. The pressure
Fig. 4.1 Photographic picture of serpentine sample after laser heating. A (upper) is lizardite heated in the center (brownish) and edge (clear) area; B (bottom) is antigorite heated by whole sample.
measured using phase D yields a different value. However, the pressure obtained from periclase should be regarded as more reliable, since its bulk modulus is better constrained by using various techniques including ultrasonic interferometry [e.g. Jackson and Niesle, 1982], Brillouin scattering [Zha, unpublished data] and hydrostatic powder X-ray diffraction data [e.g. Mao et al., 1979]. In the phase D, there is only a single measurement available [Frost and Fei, 1998]. Pressures reported here are therefore those measured from periclase.

4.3.2 In-situ X-ray diffraction results on lizardite

The lizardite sample was probed by the energy dispersive X-ray diffraction method, for phase identification. The XRD spectrum is presented in Fig. 4.2. In Table 4.2 the calculated spacings for phase D, periclase and perovskite are given. Most of the observed peaks sort out under the above three phases. However some weak peaks do not fit to any of them; for example, the 1.479 Å is too strong to be the peak of Pv (130), the 1.228 Å does not fit phase D, periclase, or perovskite phase. When diffraction data were checked with a different 2Θ angle for checking the orientation effect, it did not result in any better agreement. After this checking out procedure, the peaks were labelled in Fig. 4.2 according to the best fit, which shows that the assemblage consists of perovskite + phase D + periclase.

To connect the results of in-situ and quenched phases, the sample was gradually released to ambient pressure at room temperature. The X-ray diffraction spectra obtained during decompression at several different pressures are presented in Fig. 4.3. Although the general features in the spectra are similar, there are some significant changes: (1) the 1.479 Å (40 keV) and 1.289 Å (46 keV) peaks disappear as pressure is released, (2) the perovskite peak at 2.346 Å (25.2 keV) becomes broader as pressure is released from 35 GPa to 30 GPa; additionally, a weak peak is seen near 17.5 keV in the 30 GPa spectrum.
Fig. 4.2 The spectrum of lizardite at ~35 GPa and 1310 °C. D: phase D, Pv: perovskite, Pe: periclase, e: escape peak.
Table 4.1 X-ray diffraction data of laser-heated lizardite at ~35 GPa and 1310 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase D&lt;sup&gt;a&lt;/sup&gt;</th>
<th>MgO&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Perovskite&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d, Å</td>
<td>hkl</td>
<td>I/I₀</td>
</tr>
<tr>
<td>5</td>
<td>3.857</td>
<td>3.951</td>
<td>100 16</td>
</tr>
<tr>
<td>17</td>
<td>2.854</td>
<td>2.854</td>
<td>101 100</td>
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<td>1.996</td>
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</tr>
<tr>
<td>80</td>
<td>1.530</td>
<td>1.530</td>
<td>112 76 2T2</td>
</tr>
<tr>
<td>10</td>
<td>1.479</td>
<td>1.427</td>
<td>202 2</td>
</tr>
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<tr>
<td>10</td>
<td>1.173</td>
<td>1.178</td>
<td>113 12</td>
</tr>
</tbody>
</table>

Note: the intensity of observed value represents the relative intensity.

a: Calculated values based on a hexagonal unit cell: a=4.562 Å, c=4.126 Å, V=74.38 Å³.
b: Calculated values based on a cubic unit cell: a=4.029 Å, V=65.41 Å³.
c: Calculated values based on a orthorhombic unit cell: a=4.580 Å, b= 4.695 Å, c=6.680 Å, V=143.64 Å³.
Fig. 4.3 The decompression spectra of lizardite at center spot. Pv: perovskite, D: phase D, Pe: perovskite, e: escape peak, *: unknown or doubt peak.
(3) the peak near 30 keV splits into a clean doublet in the spectrum recorded at 0.5 GPa,
(4) the perovskite triplet near 24 keV is as clear as seen at ambient pressure, and finally
(5) two new peaks near 17.0 and 38.5 keV appear in the 0.1 MPa spectrum.

The quenched lizardite spectrum recorded at the center spot is presented in Fig. 4.4. The calculated d-spacings from this spectrum is tabulated in Table 4.2, and compared with the d-spacings of phase D, periclase, perovskite and stishovite. The stishovite phase has been added, since the new peak at 1.532 Å cannot fit the Pv (222). The (211) of stishovite can explain this peak well. Then the question is why stishovite peak is not seen in the in situ experiment. It is likely that the extra Si in the form of SiO₂ might have dissolved in the liquid phase at high P-T conditions and came out as stishovite, when quenched to ambient condition.

The 1.261 Å peak (see Table 4.2) does not fit the Pe (311) (d=1.270 Å) and the intensity also does not agree. Therefore, assignment to periclase was excluded. However, the 1.284Å peak is very close to the spacing of the 311 of Pe and hence it is reasonable to assign it to periclase. The 1.261 Å peak does not seem to fit any of the structure that we have in Table 4.2 and at the present time we cannot account for it. The in-situ X-ray diffraction spectrum of the clear spot (edge spot) is shown in Fig. 4.5. To determine the phase assemblage in this case, the periclase and phase D were considered and the results are given in Table 4.3. The calculated values of both periclase and phase D fit the observed peaks very well, except in the case of D (300) which is somewhat lower than the observed value. This may be due to error in measurement because of the low intensity (I/I₀) of the peak. However, there are still 5 peaks which remaining unexplained. Both stishovite [Tsuchida and Yagi, 1989] and brucite [Fei and Mao, 1993] phases were considered, but the peaks do not fit them. It is believed that these 5 peaks may be coming from a previously unrecognized phase.
Fig. 4.4 The spectrum of lizardite recovered from ~35 GPa and 1310 °C. Pv: perovskite, D: phase D, Pe: periclase, St: stishovite, e: escape peak, *: unknown peak.
Table 4.2 X-ray diffraction data of laser-heated serpentine recovered from ~35 GPa and 1310 °C.

<table>
<thead>
<tr>
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Note: the intensity of observed value represents the relative intensity; sh: shoulder.

a: Yang et al., 1997
b: ASTM # 4-829
c: Horiuchi et al., 1987
d: ASTM # 15-26
Fig. 4.5 The spectrum of lizardite at ~27.5 GPa and 1310 °C. D: phase D, Pe: periclase, e: escape peak, *: unknown peak.
Table 4.3 X-ray diffraction data of laser-heated lizardite at ~27.5 GPa and 1310 °C.

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Note: the intensity of observed value represents the relative intensity.

<sup>a</sup>: Calculated values based on a hexagonal unit cell: a=4.632 Å, c=4.129 Å, V=76.71 Å³.
<sup>b</sup>: Calculated values based on a cubic unit cell: a=4.032 Å, V=65.55 Å³.
The pressure was finally reduced to ambient condition and the EDXRD spectrum of the quenched material is presented in Fig. 4.6. The peaks with the asterisk marks are unknown peaks mentioned earlier. These are lost in the quenched sample. On a more careful examination, we find only those of peaks at about 24.4 and 48 keV actually disappear, while those around 23, 27.5 and 31.5 keV are still present in the spectrum at ambient condition. The brucite peaks emerge when pressure is completely released (Fig. 4.6). The \( d \) values obtained from the X-ray diffraction pattern of the quenched material are compared with the \( d \)-spacings of possible phases (Table 4.4) and the results show that the phase assemblage consists of phase D + periclase + brucite (Fig. 4.7). From the decompression sequence it is clear that the brucite phase is a quench phase. This is in accord with the report of Frost and Fei [1998]. The minor peaks with asterisks are the residual from unknown phases.

For further clarifying the phase assemblage and its dependence on the pressure relationship in this run, the center and edge spot spectra (in-situ) are presented together (Fig. 4.8). It can be seen that the positions of the most intense peaks are close, but the relative intensities of phase D appears to be somewhat different in the two spectrum. The position of phase D in the A-spectrum is shifted toward to the right compared to the B-spectrum. This suggests that the pressure at the center spot, A, is higher than the edge spot, B; a result supports the pressure measurements from periclase, but again denies the measurements from ruby chips (35 GPa to A and 36 GPa to B). Fig. 4.9 shows the results on the two samples quenched from the two spots. The coexistence of perovskite and phase D in the A spot can be rationalized as follow: The temperature was not high enough to decompose phase D although the pressure was beyond the stability field of phase D before laser heating, but the pressure drop on heating put the latter phase within its stability field after laser heating. This could explain the coexistence of the two phases.
Fig. 4.6 The decompression spectra of lizardite at edge spot, B. D: phase D, Pe: periclase, Br: brucite, e: escape peak
*: unknown peak.
Table 4.4  X-ray diffraction data of laser-heated lizardite recovered from about 27.5 GPa and 1310 °C.

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Note: the intensity of observed value represents the relative intensity.
a: Yang et el., 1997  
b: ASTM # 4-829  
c: ASTM # 7-239
Fig. 4.7 Lizardite recovered from about 27.5 GPa and 1310 °C. D: phase D, Pe: periclase, Br: brucite, e: escape peak, *: unknown peak.
Fig. 4.8 Comparison of in-situ lizardite spectra at center, A and edge position, B. D: phase D, Pv: perovskite, Pe: periclase, e: escape peak, *: unknown peak.
Fig. 4.9 Comparison of recovered lizardite spectra at center, A and edge spot, B. D: phase D, Pv: perovskite, Pe: periclase, St: stishovite, Bu: brucite, e: escape peak, *: unknown peak.
4.3.3 In-situ X-ray diffraction results of antigorite

The center part of this sample was first probed by synchrotron X-ray diffraction and the result is presented in Fig. 4.10. The d-spacings obtained are listed in Table 4.5. Phase D and periclase were taken into account for the in-situ phases. The calculated unit cell for phase D was $a=4.613 \, \text{Å}$, $c=4.153 \, \text{Å}$ and $V=76.52 \, \text{Å}^3$; for periclase, $a=4.048 \, \text{Å}$, $V=66.33 \, \text{Å}^3$. The peaks at 1.948 Å, 1.499 Å and for 1.224Å are assignable to stishovite. However, there are 4 unassigned peaks; 3.789 Å, 2.176 Å, 2.146 Å and 1.861 Å that is believed to be from an unknown phase. Hence, it is concluded the phase assemblage at 24.6 GPa and ~1000 °C to be phase D + periclase + stishovite + unknown.

The sample near the edge spot was X-rayed to find out if there is any difference in the results from the center and the edge of the sample. The spectrum is presented in Fig. 4.11. The d-spacings obtained for the edge spot are tabulated in Table 4.6. The observed features are very similar to the center spot spectrum, from which it is concluded that phase D, periclase and stishovite are the phases in this sample region. The calculated spacings compare well with those observed, except for 4 peaks; at 2.193 Å, 2.164 Å, 1.893 Å, and 1.631 Å. The unassigned peaks are believed to be from an unknown phase which is different in some respects from that found with the center spot: (1) the two peaks at about 27-28 keV are more intense and closer in the lower pressure spectrum (B, edge position) (2) the peak of the higher pressure spectrum (A, center position) is weaker at 31-32 keV (3) the peak at about 36.5 keV is not seen in the higher pressure spectrum (A-center position). These facts suggest that the unknown phase is different and probably represents a lower pressure phase.

To find out more about the behavior of the unknown peaks and to establish the phase relationship between in-situ and quench material, the sample was gradually unloaded to ambient condition and the decompression spectrum at the center and edge spots were
Fig. 4.10 The spectrum of antigorite at about 24.6 GPa and 1000°C. D: phase D, Pe: periclase, St: stishovite, e: escape peak, *: unknown peak.
Table 4.5 X-ray diffraction data of laser-heated antigorite at $\sim$24.6 GPa and $\sim$1000 °C.

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Note: the intensity of observed value represents the relative intensity; sh: shoulder.
a: Calculated values based on a hexagonal based on a=4.613 Å, c=4.153 Å, V=76.52 Å³.
b: Calculated values based on a cubic based on a=4.048 Å, V=66.33 Å³.
c: Calculated values based on a tetragonal based on a=4.080 Å, c=2.630 Å, V=43.78 Å³.
Fig. 4.11 The comparison of in-situ antigorite spectra at center (A, 24.6 GPa) and edge spot (B, 22 GPa). D: phase D, Pe: periclase, St: stishovite, e: escape peak, *: unknown peak.
Table 4.6 X-ray diffraction data of laser-heated antigorite at 22 GPa and ~1000 °C.

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Note: the intensity of observed value represents the relative intensity.

a: Calculated values based on a hexagonal unit cell: a=4.627 Å, c=4.166 Å, V=77.24 Å³.
b: Calculated values based on a cubic unit cell: a=4.066 Å, V=67.22 Å³.
c: Calculated values based on a tetragonal unit cell: a=4.071 Å, c=2.628 Å, V=43.55 Å³.
recorded. This is shown in Fig. 4.12 and 4.13, respectively. Fig. 4.12 shows the unknown peaks near 27-28 keV which persist to 1.5 GPa and then abruptly disappear. Instead, two new peaks emerge at 26 and 27.3 keV. The sample spectrum recovered in this run was checked immediately and the results are listed in the Table 4.7 and 4.8. All the possible phases were taken into account. The results show that phase D + periclase + brucite + stishovite are present. Phase D and periclase are the dominant phases, as in the in-situ high pressure and temperature experiment. The minor phases are brucite and stishovite which show up only in the quenched sample. The two peaks at 2.357Å and 2.251 Å are the Br (101) and Si (101) peaks respectively. The unknown peaks gradually fade out from the 31-32 keV position. Besides these two unknown peaks, the features of the quenched and in-situ phases are almost the same. Comparison indicates that although stishovite was observed in the in-situ high P-T spectrum, actually more of the stishovite must have come out along with brucite, as quenched phases.

4.4 Discussion

Zerr and Boehler [1993] reported that enstatite single crystal changed color from clear to dark (brown) after laser heating under high pressure, and attributed the change to the formation of the perovskite phase. When lizardite transforms to the perovskite phase, the sample turns yellow brown in color. If this transformation did not occur, the sample appears clear or translucent, when laser heated.

To compare the phase relationships in the two kinds of serpentine studied, the in-situ high pressure and temperature spectra are presented together (in Fig. 4.14). It is evident that the phase D is the only known hydrous phase existing for spectrum under the given P-T conditions. Examining the features in the spectra carefully, it is clear that the peak positions in both periclase and phase D shift toward left-hand side in going from top to
Fig. 4.12 Decompression of antigorite from 24.6 GPa and ~1000°C. D: phase D, Pe: periclase, St: stishovite, Br: brucite, e: escape peak, *: unknown peak.
Fig. 4.13 Decompression of antigorite from about 22 GPa and 1000°C to ambient condition. D: phase D, Pe: periclase, St: stishovite, e: escape peak, *: unknown peak.
Table 4.7 X-ray diffraction data of laser-heated antigorite recovered from ~24.6 GPa and ~1000 °C.

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Note: the intensity of observed value represents the relative intensity.

a: Yang et al., 1997
b: ASTM # 4-829
c: ASTM # 7-239
d: ASTM # 15-26
Table 4.8 X-ray diffraction data of laser-heated antigorite recovered from ~22 GPa and ~1000 °C.

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2T1

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- 20  1.879  1.858 201 26  1.870 210 14  
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- 35  1.611  1.602 112 76  

2T2

- 5   1.578  1.573 110 35  
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- 32  1.496  1.493 202 2  1.489 220 52  1.494 111 18  1.478 220 18  
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- 6   1.223  1.216 222 12  
- <5  1.059  1.059 213 4  1.053 400 5  

Note: the intensity of observed value represents the relative intensity.

a: Yang et al., 1997
b: ASTM # 4-829
c: ASTM # 7-239
d: ASTM # 15-26
Fig. 4.14 Comparison of the in-situ lizardite and antigorite spectra at high pressure and room temperature. D: phase D, Pv: perovskite, Pe: periclase, St: stishovite, e: escape peak, *: unknown peak.
bottom in the Fig. This indicates that the top spectrum represents the highest pressure and bottom one the lowest pressure. This is consistent with the pressure measurements obtained using periclase as the pressure scale. It is believed that using an internal standard in in-situ experiment is the best way to calibrate pressure, rather than relying on ruby since the ruby chip may be in a different place from the area probed by the X-ray beam, in non-hydrostatic situation.

The unknown peaks seen in Fig. 4.14 are considered further. As pressure increases, the unknown peaks between 26-28 keV split and one of them disappears. In the top spectra both have disappeared. The other unknown peak between 31-32 keV becomes stronger as pressure increases and eventually disappear at the highest pressure. The one at 36.5 keV is seen only in the bottom spectrum. From this, it is concluded that whatever phases those peaks represent exist only over a certain lower pressure range. Further, it appears from the behavior that there may be two unknown phases, one showing up in the lower pressure range, i.e. around 22 GPa and another at higher pressures, i.e. near 27.5 GPa. Once the perovskite phase comes out all the unknown peaks disappear. The peak at about 48 keV though assigned to the perovskite phase PvP (133), does not fit as far as the relative intensity goes. One possible explanation is that there is preferred orientation in this sample. To check out the assignment, the spectra of all the quenched phases are put together for comparison in Fig. 4.15. Recalling the statement in the previous paragraph regarding the quenched phase spectrum of lizardite from 35 GPa, there was a peak in question at about 47 keV, d=1.261 Å. This could not be assigned to any phase. From Fig. 4.15, it is clear that in the other 3 spectra, the peak of periclase is located at about 46.5 keV. The peak at d = 1.261 Å has shifted slightly to the right compared to the other periclase peaks and could not belong to periclase. The peak positions of phase D are all in good accord. Checking the other unknown peaks (labelled with asterisk) in the
Fig. 4.15 Comparative analysis of recovered lizardite and antigorite spectra at ambient conditions. The synthesis condition is denoted with each spectrum. D: phase D, P: perovskite, Pe: perovskite, St: stishovite, Br: brucite, e: escape peak, *: unknown peak.
case of lizardite (27.5 GPa) with the other 3 spectrum, it can be seen that no known phases match these peaks; even stishovite is excluded.

The spectra presented in Fig. 4.15 indicates that brucite is not present under in-situ conditions and it can be quenched from 27.5 GPa. This result provide us with an explanation for the appearance of brucite in the quenched experiments on serpentine at same pressure range but high temperatures (see Chapter 3, Fig. 3.7). Therefore, it is concluded that brucite is a quenched phase from 25-36 GPa and temperature above 1000°C. However, a different situation may occur for stishovite, e.g., lizardite 35 GPa and 1310 °C run. The appearance of stishovite may be the result of the nonstoichiometry associated with phase D. It is well known that the chemical composition of phase D varies with P-T conditions [Frost and Fei, 1998]. Variable proportion of substitution of Si^{4+} by Mg^{2+} + 2H^{+} could take place and this may be the main reason for the presence of the stishovite phase in this study.

According to the serpentine P-T phase diagram (Fig. 3.8), the run on antigorite (edge spot) at P=22 GPa and T~ 1000 °C, should have in-situ superhydrous phase B, but this superhydrous phase B was not seen in this run. If however the temperature was below 1000 °C, brucite phase should be seen, instead of superhydrous phase B. The absence of superhydrous phase B from the phase assemblage suggests that the temperature at which the experiment was carried out below 1000 °C. However, it is surprising that no brucite phase was observed either at this P-T condition. Instead, a new phase was observed. In the case of the quenched sample (Fig. 4.13) the peak (near 29 keV) with d=2.022 Å is close to the most intense peak of superhydrous phase B, i.e. sB 143. The P-T conditions for this run were within the stability field of superhydrous phase B and hence the presence of superhydrous phase B is expected. But the question remains why this peak is only observed in the quench spectrum, and not in the in-situ spectrum. Comparing the in-
situ spectrum of Kuroda and Irifune's at 21 GPa and 800 °C with the results of the present study at similar P-T condition, namely P=22 GPa and T~1000 °C, it is evident that many more peaks belonging to periclase are observed in this study, along with an unknown phase. Whether the superhydrous phase B is a quenched phase needs further studies.

The results on both lizardite (edge position) and antigorite (whole sample) indicate that there is a new phase which is unquenchable. The available d-spacing data cannot be fitted to any known structures. A ternary phase diagram is presented in Fig. 4.16 to throw some light on the relationship between starting material and the run product. From Fig. 4.16 it is seen that the composition of phase D might play a critical role in determining the new phase. If the phase D has a high Si content, then the new phase will have a magnesium-rich hydrous phase residing on the D-Br joint or D-H2O joint. In this connection, the brucite phase was considered but was ruled out, since the unknown peaks do not fit the lattice parameters of brucite. It could be that the new phase is an unknown Mg silicate. On the other hand, if phase D of the run product has a low Si component, then the new phase would be a silicon-rich phase lying either residing on the D-Pv joint or D-SiO2 joint. From Fig. 4.6 and 4.12 it seems that when brucite is a quench phase, the stishovite peaks are weak. The appearance of stishovite in in-situ high pressure and temperature conditions may be indicative of nonstoichiometry of phase D. The increasing intensity of stishovite peaks in the quench spectrum, near 26.2, 30 and 38.7 keV of antigorite B, edge spot (Fig. 4.13) suggests that a part of stishovite comes out as quench product. From these it could be inferred that higher Mg content leads to unquenchable phase. Frost and Fei [1998] found that the Mg/Si ratio of phase D is low along with the H2O content, if the temperature is high. This indicates that the Si would remain in phase D at high temperature, but will prefer the liquid phase at lower temperature. Thus, the appearance of stishovite may be driven by the competition for Si from phase D and liquid phase depending on the temperature
Fig. 4.16 The schematic plot of the possible new phase derived from the serpentine under high P-T conditions. (a) represents the phase D with high Si content and (b) represents phase D with low Si content. Serp: serpentine, D: phase D, Br: brucite, Ol: olivine, Pv: perovskite. The new phase may be located on the dashed lines.
4.4.1 The implication of this new phase

The appearance of the unquenchable phase falls in the pressure range of 22-27.5 GPa. This pressure range corresponds to the lower part of the transition zone and the uppermost region of the lower mantle. However, the synthesis temperature was low, T=1000-1300 °C, and therefore, it is more relevant to a thick and cold subducting slab. If this is really the case, then this indicates that the thick and cold slab could have two hydrous phases existing at pressure between 22-27.5 GPa; the new phases that we discussed and phase D. The dehydration of this new hydrous phase may have some implications to the mantle dynamics. For example, a decrease of the melting temperature of rocks could result, or it may trigger partial melting in the overlying mantle wedge.

4.5 Conclusion

From in-situ high P-T experiments, it has clearly shown that phase D is a thermodynamically stable phase in the lower mantle condition. Evidence for the existence of a new unquenchable phase at high pressure and temperature has also been presented. Brucite and stishovite appear as the result of the disappearance of this new phase at ambient condition. This indicates the new phase may contain some proportion of H in the structure. It needs more data to characterize this unknown hydrous phase and then it is possible to say something with certainty. It is also shown that a proper pressure scale is important. In in situ high P-T experiments, used of ruby as pressure calibrant is not suitable, for the ruby fluorescence signal decreases strikingly after laser heating and can lead to a large uncertainty in pressure. This study has shown that periclase (MgO) is a more reliable internal standard in non-hydrostatic laser heating experiments, if the diffraction peaks of periclase are not overlaps by peaks from other phase present.
4.6 Future direction

Phase E and superhydrous phase B were not observed in this experiment. Therefore the stability fields of both phase E and superhydrous B should be checked in the in-situ experiments. This will further clarify whether these hydrous phase are relevant to the mantle. In situ high P-T experiment demonstrates that there is a new hydrous phase that was not recognized by quench experiments. This indicates the in situ experiment is important and is the only way to provide the correct answer. The nature of the new phase is of interest to us, whether it has relevant to superhydrous phase B or phase E. In order to characterize this phase, some experiments are designed to be carried out in next step.

1. The brucite phase at higher pressure and lower temperature; Although Fei and Mao [1993] had demonstrated that brucite can persist to about 30 GPa and 300 K and 78 GPa at 600 K, there is no data in the higher P-T range, except shock wave data. It would be useful to investigate the higher temperature stability of brucite to T > 600 K. This study has shown that the brucite phase can be quenched from the high P-T conditions.

2. Serpentine with water as pressure medium: The new phase may have a higher OH content. Hence, the use of water as pressure medium may increase the relative proportion of the new phase and at the same time retard phase D and periclase to come out under the same P-T conditions

3. Enstatite with saturated water: This experiment is similar to serpentine with water, but with a simpler component and to check if the new phase can be synthesized with a simple component.
Chapter 5

Decomposition of superhydrous phase B and phase D at high pressure and temperature

5.1. Introduction

Superhydrous phase B and D are two of the possible dense hydrous magnesium silicate candidates which may be stable in the transition zone and lower mantle [Frost and Fei, 1997; Irifune et al., 1997]. Superhydrous phase B was first reported by Gasparik [1990] at pressures 17.8-18.8 GPa and temperatures of 1350-1450 °C. Recently, superhydrous phase B was found to coexist with phase D at about 17 GPa and 1100 °C to 26 GPa, 1200 °C and/or 18 GPa, 800 °C to 27 GPa and 1100 °C, depending on the starting materials [Frost and Fei, 1997; Irifune et al., 1997]. Shieh et al. [1998] suggested that the phase boundary for the decomposition of superhydrous phase B may be around 28 GPa, from their study on serpentine. The stability field of superhydrous phase B should be above 15 GPa, which is equivalent to the pressure in the transition zone. The structure of superhydrous phase B, \( \mathrm{Mg}^{\text{VI}}_{10}\mathrm{Si}^{\text{IV}}\mathrm{Si}^{\text{IV}}\mathrm{O}_{14}(\mathrm{OH})_{4} \), has shown that all the Mg occupy octahedral sites, while part of Si occupy octahedral sites and part the tetrahedral sites. This indicates that the superhydrous phase B should be stable thermodynamically in the transition zone. At pressure higher than 28 GPa it may undergo structural changes. To check this hypothesis, experiments on superhydrous phase B at pressure above 28 GPa were undertaken.

Phase D is the most dense of the DHMS (\( \rho = 3.5 \text{ g/cm}^3 \)) and the only DHMS with all the Si in octahedral sites, an Si coordination commonly found in the lower mantle phases [Yang, et al., 1997]. Thus crystal chemistry of phase D would be a phase that is relevant for the interior of the Earth. Phase D has been found to be stable from 15 GPa and 800
°C to about 50 GPa and 930 °C, according to multianvil data using Mg$_2$SiO$_4$ + 20.3 wt% H$_2$O as starting materials, and from experiments using externally heated diamond anvil cell [Frost and Fei, 1997]. This extensive stability field of phase D indicated that it will be stable in the Earth's lower mantle. However, from the study of the decomposition of serpentine, phase D was found to disappear at about 42 GPa and 1300 °C [Shieh et al., 1998]. To resolve the conflicting results and to determine whether the discrepancy is not due to different starting materials, the experiment on the phase D was carried out and described below.

5.2 Experiment

The starting materials, superhydrous phase B and phase D, were synthesized in a multianvil apparatus. The chemical composition of superhydrous phase B was checked by electron microprobe and the phase identified using the lattice parameters reported by Gasparik [1992]. Phase D was selected from the same source sample used by Frost and Fei [1998] in their experiments, using externally heated diamond anvil cell. No pressure medium was used and the material was mixed with graphite to improve the absorption of the laser radiation. Pressure was determined by the ruby fluorescence method [Mao et al., 1978]. The double-side laser heating technique [Shen et al, 1996] was employed. The gasket material used for superhydrous phase B was T301 stainless steel. In the case of phase D T301 stainless steel was used in run B and Rhenium in run C.

5.3. Result

5.3.1 Decomposition of superhydrous phase B

Superhydrous phase B was pressurized to 36 GPa and was found to be still crystalline in-situ at this pressure (Fig 5.1). After laser heating, the diffraction pattern had changed, indicating a phase transition (Fig 5.1). This is in agreement with the suggestion from the
FIG. 5.1 Three selected diffraction spectra, before and after heating and quenching, of supercritical phase B (sb).

Intensity (arb.) ~ 0

Photon Energy (KeV)

25°C
36 GPa
1340°C
434°C
25°C
0.1 MPA

D222+Pe400

10x10^3

Intensity (arb.)
decomposition study of serpentine that superhydrous phase B may decompose at pressure above 28 GPa. The d-spacings obtained from the new spectrum are listed in Table 5.1 and are compared with the d-values calculated for three unit cells. From Table 5.1 it shows that the in-situ phase assemblage consists of phase D, periclase (Pe), and stishovite (St). There are four weak peaks at 2.718 Å (21.8 keV), 2.488 Å (23.8 keV), 1.660 Å (35.7 keV), and 1.364 Å (43.5 keV), which do not fit to any of the above phases. When pressure was completely released to the ambient condition, the diffraction pattern became more complex (see Fig. 5.1). The results for the recovered sample is tabulated in Table 5.2. The four characteristic peaks at 4.336 Å (13.7 keV), 4.174 Å (14.2 keV), 2.994 Å (19.8 keV), and 1.609 Å (36.8 keV) show that phase D is one of the phases. The other intense peaks, like 2.963 Å (20.0 keV), 2.249 Å (26.4 keV), 1.980 Å (29.9 keV), 1.872 Å (31.7 keV), 1.530 Å (38.7 keV), 1.332 Å (44.5 keV), and 1.235 Å (48.0 keV) fit stishovite. The 2.105 Å can be accounted for periclase (Pe 200), but for Pe (111), Pe (220), Pe (222) are just acceptable. The spacing 2.454 Å (24.2 keV) can be assigned to perovskite (020) and (112); 1.746 Å (34.0 keV) to Pv 004/220. By comparing the relative positions of the two spectra, middle and upper in Fig. 5.1, the 1.660 Å (35.7 keV) of 43 GPa and 1340 °C is assignable to Pv 004 + Pv 220 ,and 1.364 Å (43.5 keV) to Pv 132 + Pv 024 + Pv 204 + Pv 312. However, there are still two extra peaks at 1.030 Å (57.5 keV) and 1.008 Å (58.8 keV) which are not accounted. From the fact that these two unknown peaks (with asterisk) are present in the pressure released spectrum. It is concluded that the phase may be quenched from the in-situ phase. This needs further investigation. According to the dominant phases present, it is certain that the decomposition of superhydrous phase B results in a phase assemblage consisting of phase D, stishovite and periclase. These results are in accordance with the results on serpentine discussed in Chapter 3.
Table 5.1 X-ray diffraction data of laser-heated superhydrous phase B at ~43 GPa and 1340 °C.

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Note: the intensity of observed value represents the relative intensity.

a: Calculated values based on a hexagonal unit cell: $a=4.609$ Å, $c=4.070$ Å, $V=74.90$ Å³.
b: Calculated values based on a cubic unit cell: $a=3.998$ Å, $V=63.90$ Å³.
c: Calculated values based on a tetragonal unit cell: $a=4.059$ Å, $c=2.593$ Å, $V=42.72$ Å³.
Table 5.2 X-ray diffraction data of laser-heated superhydrous phase B recovered from about 43 GPa and 1340 °C.

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Note: the intensity of observed value represents the relative intensity. sh: shoulder.

a: Yang et al., 1997
b: ASTM # 4-829
c: ASTM # 4-829
d: Horiuchi et al., 1987
5.3.2 Decomposition of phase D

Phase D was compressed to a pressure above 42 GPa and heated to temperature about 1300 °C. Under these conditions, phase D transformed and this is shown in Fig. 5.2. It decomposed into perovskite + stishovite and when pressure was released to the ambient, these two phases were retained, proving that the two high P-T phases were quenchable (see Fig. 3.2). Besides perovskite and stishovite, peaks of phase D were still distinct. This may be due to the lower temperature and/or the reaction time was insufficient, ~10 minutes heating time. The X-ray data on the quenched phases are tabulated in Table 5.3. Although the triplet of perovskite was not strong, the d-spacings fit to perovskite phase very well. This can be observed from the three d-spacings: 2.464 Å (Pv 020), 2.433 Å (Pv 112) and 2.390 Å (Pv 200), and other nonoverlapping peaks at 3.436 Å (Pv 110), 1.719 Å (Pv 004 + Pv 220), and 1.668 Å (Pv 023 + Pv 221). Additionally, ten X-ray diffraction peaks in the recovered sample match very well with those of stishovite. Thus, the decomposition of phase D into perovskite and stishovite at 42 GPa and 1300 °C is confirmed.

In another run, phase D was compressed to about 57 GPa and heated to about 1750 °C which caused the pressure dropped to about 42 GPa. The phase identification was carried out by X-ray diffraction method (Fig. 5.3). To check the quenchability of the in-situ phases, the pressure was gradually released and the powder pattern of the sample was taken. The three peaks at 34.0 keV (1.740 Å), 57.5 keV (1.03 Å), and 59.1 keV (1.003 Å) emerge when pressure was totally released and cell opened (Table 5.4). If the intense peak at 2.391 Å is due to preferred orientation of D 110, then the similar situation should also be true for D 220. However, this is not observed. The intensity of the 2.391 Å may be due to the perovskite (Pv 020 + Pv 112 + Pv 200). The 1.740 Å peak is 9% larger than Pv 004 and 14% larger than Pv 220. In addition, the intensity of 1.740 Å is
Fig. 5.2 The comparison of phase D before and after heated at about 42 GPa. The upper spectrum demonstrates the quenched result. Pv: perovskite, D: phase D, St: stishovite, e: escape peak, F: fluorescence peak.
Table 5.3 X-ray diffraction data of laser-heated phase D recovered from \(~42\text{GPa}\) and 1300 °C.

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Note: the intensity of observed value represents the relative intensity
a: Horiuchi et al., 1987
b: Yang et al., 1997
c: ASTM # 15-26
Fig. 5.3 The decompression spectra of phase D after laser heating (run C). D: phase D, St: stishovite, e: escape peak, F: fluorescence peak, Pv: perovskite, *: unknown peak.
Table 5.4 X-ray diffraction data of laser-heated phase D recovered from ~42GPa and 1750 °C.

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<td>1.870 210 14</td>
</tr>
<tr>
<td>8</td>
<td>1.873</td>
<td>1.611 112/2T2 76</td>
<td></td>
<td>1.602 112/2T2 76</td>
</tr>
<tr>
<td>5</td>
<td>1.532</td>
<td>1.536 222 9</td>
<td></td>
<td>1.530 211 50</td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.481</td>
<td>1.479 311 3</td>
<td>1.463 211/3T1 25</td>
<td>1.478 220 18</td>
</tr>
<tr>
<td>14</td>
<td>1.382</td>
<td>1.398 204 16</td>
<td>1.370 300 34</td>
<td></td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.322</td>
<td>1.387 312 41</td>
<td></td>
<td>1.370 300 34</td>
</tr>
<tr>
<td>6</td>
<td>1.231</td>
<td>1.232 040 4</td>
<td>1.236 113 12</td>
<td>1.333 002 10</td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.196</td>
<td>1.194 400 4</td>
<td>1.186 220 3</td>
<td>1.235 301 25</td>
</tr>
<tr>
<td>5</td>
<td>1.157</td>
<td>1.193 140 3</td>
<td>1.184 203 6</td>
<td>1.159 320 8</td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.053</td>
<td>1.154 134 4</td>
<td>1.059 213/3T3 6</td>
<td></td>
</tr>
<tr>
<td>&lt;5</td>
<td>1.030</td>
<td>1.031 135 4</td>
<td>1.041 222/432 12</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>1.003</td>
<td>1.003 044 4</td>
<td>1.003 044 4</td>
<td></td>
</tr>
</tbody>
</table>

Note: the intensity of observed value represents the relative intensity; sh: shoulder.

a: Horiuchi et al., 1987
b: Yang et al., 1997
c: ASTM # 15-26
less than what is expected for Pv 004 and Pv 220. This could be attributed to the coarsening of the perovskite grains during heating. Further, the 1.003 Å remains still unexplained. With some uncertainty, the phase assemblage of this run is tentatively assigned to perovskite and stishovite. Notably, the intensity of the peaks of phase D is weaker than run B, which is a definite indication that phase D is unstable at higher temperature.

5.4 Discussion

The proposal for decomposition of superhydrous phase B at pressures above 28 GPa [Shieh et al., 1998] is confirmed in this study. The superhydrous phase B completely disappeared above 36 GPa resulting in a phase assemblage consisting of phase D, periclase, stishovite, and perovskite. In a ternary system, a single component decomposes at any given P-T conditions, it shall result in at most three phases. However, the appearance of four phases suggests that the P-T condition was right on the phase boundary. To verify this, the data points of superhydrous phase B after transformation has been plotted in the Fig. 5.4. The data point of decomposition of superhydrous phase B (solid circle) is just sitting on the phase boundary of D + Pe + St and Pv + Pe, which supports above contention. Considering the results obtained from the decomposition of superhydrous phase B and serpentine, the relationship of starting material and run product are listed below.

\[ \text{Mg}_{10}\text{Si}_{3}\text{O}_{14}(\text{OH})_{4} \text{(sB)} \rightarrow \text{MgSi}_{2}\text{H}_{2}\text{O}_{6} \text{(D)} + 9 \text{MgO} + X (\text{SiO}_{2}\cdot\text{H}_{2}\text{O}) \]  \(5.1\ a\)

\[ \text{Mg}_{3}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4} \text{(Serp)} \rightarrow \text{MgSi}_{2}\text{H}_{2}\text{O}_{6} \text{(D)} + 2 \text{MgO} + X (\text{H}_{2}\text{O}) \]  \(5.1\ b\)

The run products of these two starting materials is similar, except the proportion of MgO and unknown composition. Notably, as mentioned before, the appearance of
Fig. 5.4 The P-T phase diagram of serpentine related to the single phase D and sB. D: phase D, Pe: periclase, St: stishovite.
stishovite in the in-situ high P-T conditions is due to the Si-deficiency in phase D. The appearance of stishovite in the quenched product of decomposition of superhydrous phase B but not in serpentine is due to the quench effect out of the unknown phase.

Phase D only partially decomposed at 42 GPa and 1300 °C because the peaks of phase D are distinct in the diffraction pattern, compared with those of perovskite and stishovite. This is further evidence that the pressure of 42 GPa is close to the phase boundary. The data points of the two runs, B and C (solid square) are also plotted in Fig. 5.4. The dashed line represents the phase boundary obtained with the single component system which is quite close to the phase boundary determined from the study of serpentine. The run C was carried out at a higher temperature and showed less of phase D (see Fig. 5.2 and 5.3). This is in accord with the previous studies of Frost and Fei [1998] and Irifune et al. [1998].

The unknown peak at 1.003 Å and 1.008 Å obtained from the decomposition of the superhydrous phase B and 1.003 Å from phase D may be from a new phase. Mass balance requires that H₂O from the decomposition of phase D,

\[ \text{MgSi}_2\text{O}_6\text{H}_2 \text{(D)} \rightarrow \text{MgSiO}_3 \text{(Pv)} + \text{SiO}_2 \text{(St)} + \text{H}_2\text{O} \quad (5.1 \text{c}) \]

Notably, the result of decomposition of phase D obtained from the study of serpentine can be expressed as

\[ \text{Mg}_3\text{Si}_2\text{O}_5\text{(OH)}_4 \text{(Serp)} \rightarrow 2 \text{MgSiO}_3 \text{(Pv)} + \text{MgO} + 2 \text{H}_2\text{O} \quad (5.1 \text{d}) \]

The ideal phase D has been assumed in this formula. Both perovskite + stishovite and perovskite + periclase + stishovite were observed in the diffraction patterns, except the H₂O phase. The small amount of stishovite observed in the decomposition of
serpentine due to Si deficient of phase D is expected from the comparison of formula (5.1 c).

5.5 Conclusion

The decomposition of superhydrous phase B into phase D, periclase, and stishovite is confirmed in this study. This result is in accord with the study on serpentine in Chapter 3. The most dense hydrous magnesium silicate, phase D is also decomposed and transformed into perovskite and stishovite. The decomposition of superhydrous phase B and phase D support the study of decomposition of serpentine. The post superhydrous phase B phase assemblage is clarified in this study.

Summary

The high pressure and high temperature study on serpentine shows that serpentine will transform into various DI-IMS phases at elevated pressures and temperatures. The sequence of pressure-temperature induced phase transformation in serpentine from the quenched experiments is as followings:

13.7 GPa/1100 (±300) °C Clinoenstatite + phase E + brucite + stishovite
18.5-28 GPa/1000-1800 °C Superhydrous phase B + phase D ± stishovite
28-42 GPa/1200-1600 °C Phase D + periclase ± stishovite
>42 GPa/1300-1600 °C Perovskite + periclase + ?

Phase A will be the first DHMS comes from the decomposition of serpentine [Ulmer, 1996]. If temperature is lower than ~600 °C, phase A would be stable at higher pressure, but at higher temperature it will change to phase E [Kanzaki, 1991; Irifune et al., 1998]. As pressure increases further (~17 GPa), the phase A and/or phase E will be replaced by either phase D + superhydrous phase B under high temperature conditions or phase D + brucite under lower temperature conditions. When pressure exceeds 28 GPa, the superhydrous phase B will disappear, and phase D would be the only DHMS persisting
to temperatures above 1200 °C. Finally, all the DHMS disappear, yielding perovskite and periclase, at pressure above 45 GPa.

In the in-situ experiment, lizardite and antigorite under high P-T conditions the phase assemblages are given below.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>~1000</td>
<td>Phase D + periclase + unknown phase + stishovite</td>
</tr>
<tr>
<td>24.6</td>
<td>~1000</td>
<td>Phase D + periclase + unknown phase + stishovite</td>
</tr>
<tr>
<td>27.5</td>
<td>1310</td>
<td>Phase D + periclase + unknown phase</td>
</tr>
<tr>
<td>~35</td>
<td>1310</td>
<td>Phase D + perovskite + periclase</td>
</tr>
</tbody>
</table>

The appearance of phase D confirms that it is thermodynamically stable under P-T conditions prevailing in the lower mantle. The appearance of stishovite is believed to be due to the Si-deficient phase D. The unknown phase could be a new H-bearing phase at lower temperature and at pressures lower than 35 GPa.

The results obtained on the decomposition of single component of superhydrous phase B and phase D are as follows,

For superhydrous phase B

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>43</td>
<td>1340</td>
<td>Phase D + periclase + stishovite + perovskite</td>
</tr>
</tbody>
</table>

For phase D

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Phase Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>1300-1750</td>
<td>Perovskite + stishovite + ?</td>
</tr>
</tbody>
</table>

The appearance of phase D as a result of the decomposition of superhydrous phase B shows that it will be the H2O-bearing phase after superhydrous phase B. Notably, the appearance of stishovite following the decomposition of phase D, as opposed to periclase in the case of the decomposition of serpentine, which is due to high Si-bearing starting material. Phase D is confirmed to be a stable phase under the mantle P-T conditions, but ultimately it breaks down into perovskite and stishovite at above 42 GPa and temperature
higher than 1300 °C. The transformation to the perovskite is the ultimate fate of low Fe-bearing DHMS under high P-T conditions.

As discussed above, it is difficult to ascertain the nature of liquid phase from diamond cell work. But from a combination of the results of in-situ experiments on lizardite and antigorite and the results obtained in multi-anvil experiments [Frost and Fei, 1998, Irifune et al., 1998], it is concluded that the appearance of stishovite is due to the Si-deficient phase D, whereas the appearance of brucite at high temperature is coming out of solution from aqueous phase under in-situ condition. Under low temperature conditions, brucite may coexist with phase D and no liquid phase will be observed in the run product [Frost and Fei, 1998, Irifune et al., 1998]. Notably, if superhydrous phase B is indeed thermodynamically stable in the transition zone, then it will transform into phase D + periclase + stishovite above 28 GPa and 1200 °C. However, based on this in-situ studies on serpentine, the stability of phase E and superhydrous phase B need further investigations under in-situ high P-T conditions.
Appendix

Publication List:

A. Referred Journal & Symposium Volume


B. Abstract


Shieh, S. R., L. C. Ming, and J. Xu, Back transition of spinel-olivine in (Fe,Mg)$_2$SiO$_4$-spinel at temperatures using synchrotron radiation, AGU Spring Meeting, 1994.
References


Finger, L. W., R. M. Hazen and C. T. Prewitt, Crystal structure of Mg$_{12}$Si$_4$O$_{19}$(OH)$_2$ (phase B) and Mg$_{14}$Si$_5$O$_{24}$ (phase AnhB), *Am. Mineral.*, 76, 1-7, 1991.


Inoue, T., Effect of water on melting phase relations and melt composition in the system Mg_2SiO_4-MgSiO_3-H_2O up to 15 GPa, *Phys. Earth Planet. Inter.*, 85, 237-263, 1994.


Revenaugh, J and S. A. Sipkin, Seismic evidence for silicate melt atop the 410-km mantle discontinuity, Nature, 369, 474-476, 1994


