Polymerization of methane molecules and phase transition of san carlos olivine under the Earth's mantle conditions

To cite this article: A Shinozaki et al 2010 J. Phys.: Conf. Ser. 215 012104

View the article online for updates and enhancements.

You may also like
- The structural phase transition and phase stability of TiO$_2$ (P42/nmc) under high pressure from first-principles calculations
  Hai-Kuan Dong, Ming-Biao Li, Guo-Quan Qi et al.
- Superconducting behavior of a new metal iodate compound, SrIr$_2$ under pressure
  Xiaofan Yang, Huan Li, Tong He et al.
- Strain induced electronic transition in 1T MoTe$_2$: high pressure Raman, x-ray diffraction, resistivity measurements and first principles theoretical studies
  Bishnupada Ghosh, Pinku Saha, Bidisha Mukherjee et al.
Polymerization of methane molecules and phase transition of San Carlos olivine under the Earth’s mantle conditions.

A Shinozaki\textsuperscript{1}, H Hirai\textsuperscript{1}, H Kagi\textsuperscript{2}, T Kondo\textsuperscript{3}, T Yagi\textsuperscript{4}

\textsuperscript{1}Geodynamics Research Center, Ehime University, 2-5 Bunkyocho, Matsuyama, Ehime 790-9577, Japan

\textsuperscript{2}Geochemical Laboratory, Graduate School of Science, The University of Tokyo, Hongo, Tokyo 113-0033, Japan

\textsuperscript{3}Graduate school of science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

\textsuperscript{4}Institute for Solid State Physics, The University of Tokyo, Kashiwanoha 5-1-5, Kashiwa, Chiba 277-8581, Japan

Email: shinozaki@sci.ehime-u.ac.jp

Abstract. High-pressure and high-temperature experiments of the olivine-methane-water system were performed using a laser-heated diamond anvil cell at pressure range from 5.8 GPa to 29.4 GPa and temperatures up to 2000K. The samples were examined by X-ray diffractometry and Raman spectroscopy under high pressures and room temperature. The heated areas of the samples changed to black color. Raman spectroscopy revealed the existence of ethane, heavier hydrocarbons, graphite and glassy carbon besides methane molecules. X-ray diffractometry showed that olivine was remained in the sample heated at 5.8 GPa, 2000K. Wadsleyite and ringwoodite were observed in the samples heated at 14.5 GPa and 19.5 GPa, respectively. At 29.4 GPa, the diffraction line of Mg-perovskite and magnesiowustite were observed. The observed phase changes were similar to those observed in anhydrous and hydrous conditions. The present results suggest that polymerization of methane molecules occurred and that phase transition of olivine occurred even under the existence of methane-water fluid in the deeper part of the mantle.

1. Introduction

C-O-H fluids composed of carbon dioxide, water, methane and hydrogen influence considerably melting temperatures and properties of the mantle minerals [1, 2]. Thus, the existence, compositions and states of C-O-H fluids in the Earth’s mantle are important issues to understand its properties and dynamics.

The speciation of C-O-H fluids are thought to be controlled by the oxidation states. The oxidation states of the mantle were estimated by using a lot of methods such as analysis of the mantle xenoliths [3, 5], thermodynamical calculations [5, 6] and high-pressure and high-temperature experiments [7, 8]. These studies suggest that the oxidation states of the mantle become to be reduced with depth, and the compositions of C-O-H fluids in the mantle are estimated [3, 6, 9]. According to the estimation, the
crust and the upper part of the mantle are relatively oxidized, thus CO$_2$-H$_2$O fluids are dominant unlike rare CH$_4$ fluids. The rates of CO$_2$ fluids decrease with depth, while the rates of CH$_4$ fluids increase with depth. CH$_4$-H$_2$O fluids are dominant in the deeper part of the upper mantle, the mantle transition zone and the lower mantle [10].

Olivine is the most abundant mineral in the upper mantle. It is important subject to examine influence of methane-water fluids to phase transition of olivine. As for the effect of water on the phase transitions of olivine, many studies were performed. In hydrous condition, high pressure phase of olivine, to wadsleyite, ringwoodite, Mg-perovskite and magnesiowustite were also reported. While reaction of methane and mantle minerals were extremely limited. In this study, high-pressure and high-temperature experiments using laser-heated diamond anvil cell (LHDAC) were performed to investigate phase transition of olivine under the existence methane-water fluids and changes of methane.

2. Experiments

As the starting materials, San Carlos olivine, methane and water were used. The composition of the San Carlos olivine was measured to be (Mg$_{0.90}$Fe$_{0.10}$)$_2$SiO$_4$ using electron probe micro-analysis (EPMA). A lever-and-spring type diamond anvil cell (DAC) was used. High-pressure and temperature conditions were generated by laser heated diamond anvil cell (LHDAC). Pressure measurements were made by a ruby fluorescence method. The samples of olivine were filled into the gasket hole as powder. Methane were filled into the gasket hole by a gas-loading vessel in which methane gas (99.99%) was compressed to supercritical fluid at approximately 0.15 GPa at room temperature. The samples were pressured at room temperature. Heating operations were carried out using a focused multimode continuous-wave Nd: YAG laser with the double side heating method. Temperature was measured by a spectroradiometric method from one side. The uncertainly of the sample temperature was estimated to be ±200K from the temperature distribution and temperature fluctuations in the sample. Four heating experiments were conducted in the pressure range of from 5.8 to 29.4 GPa and in the temperature range up to approximately 2000K. During heating, the samples were observed by a CCD camera monitor. XRD, Raman spectroscopy and optical microscopy were performed for the samples before and after the heating at room temperature. XRD was performed using synchrotron radiation on a BL18-C at the Photon Factory, High Energy Accelerator Research Organization (KEK).

3. Results

Figure 1 shows the optical microscopic photographs of a sample before and after heating. After heating, the heated areas of the samples change to black color.

![Figure 1. Optical micrographs of a sample. Before heating (left) and after heating (right) at 29.4 GPa.](image)

In addition to methane, ethane, heavier hydrocarbons, graphite and glassy carbon were observed by the Raman spectroscopy Figure 2 shows XRD patterns of the samples after heating. Diffraction lines of olivine were observed after heating at 5.8 GPa. Diffraction lines of solid methane and other hydrocarbons were also observed. In addition to olivine and solid methane phase B, the diffraction lines of wadsleyite and ringwoodite were observed at 14.5 GPa and 19.5 GPa, respectively. Diffraction lines of olivine might come from the surrounding parts of the heated area. At 29.4 GPa, Mg-perovskite and magnesiowustite were observed. Some diffraction lines were observed at 29.4 GPa.
that could not assign as olivine and solid methane phase B and as other known dense hydrous minerals such as phase D and phase B.

![Figure 2. Representative X-ray diffraction patterns of after heating. $\lambda=0.619\text{Å}$. $\alpha$: olivine, $\beta$: wadsleyite, $\gamma$: ringwoodite, $\text{Pv}$: Mg-perovskite, $\text{Mw}$: magnesiowustite. $\text{R}$: ruby](image)

4. Discussion

The Raman measurements suggest that some amount of methane was polymerized. A detail description for polymerization will be published elsewhere. Olivine was observed in the sample of after heating at 5.8 GPa. A theoretical calculation study has predicted that methane could be equilibrium with olivine in upper mantle conditions [11]. The present study confined experimentally that olivine might exist with methane fluid at the upper mantle conditions. Wadsleyite, ringwoodite, were observed at 14.5 GPa and 19.5 GPa respectively. After heated at 29.4 GPa, Mg-perovskite and magnesiowustite were observed. These phase transitions of olivine are similar to those observed in the conditions without the fluid and with only water [10]. Methane-water fluid was considered dominant phase of C-O-H fluids in the deeper part of the mantle [9]. The present results suggest that phase transition of olivine might occur and that wadsleyite and ringwoodite and Mg-perovskite, magnesiowustite might form even under the existence of methane-water fluid in the deeper part of the mantle.

References

[1] Dasgupta R and Hirschmann M M 2006 Nature 440 659-662
[2] Taylor W R and Green D H 1988 Nature 332 349-352
[3] Woodland A B and Koch M 2003 Earth Planet. Sci. Lett. 214 295-310
[4] McCammon C and Kopylova MG 2004 Contrib. Mineral. Petrol. 148 55-68
[5] Ballhaus C 1995 Earth Planet. Sci. Lett. 132 75-86
[6] Ballhaus C and Frost B R 1994 Geochem. Cosmochim. Acta. 58 4931-4940
[7] Rohrbach A, Ballhaus C, Golka-Schinedler U, Ulmer P, Kaffenetsky V S and Kumin D V 2007 Nature 449 456-458
[8] Frost D J 2004 Nature 428 409-412
[9] Frost D J and McCammon C A 2008 Annu. Rev. Earth Planet. Sci. Lett. 36 389-420
[10] Ohtani E and Litasov K D 2006 Rev. Mineral. Geochemistry 62 397-420
[11] Saxena S X 1989 Geochem. Cosmochim. Acta 53 89-95