

Phase transformation in Fe₂SiO₄ at high pressure and high temperature

S. ONO¹

¹JAMSTEC., Yokosuka 237-0061, Japan
(sono@jamstec.go.jp)

Olivine, (Mg,Fe)₂SiO₄, is the most abundant mineral in the upper mantle. The iron content in olivine varies with depth because of chemical interactions with other mantle phases and determining the phase diagram of the polymorphs of the Fe₂SiO₄ end-member is important for precise modeling of the Mg₂SiO₄-Fe₂SiO₄ system. With pressure and temperature increase, Fe₂SiO₄ fayalite transforms into a spinel phase. The transition pressure from olivine to spinel phase has been confirmed to be around 5 GPa at high temperatures by previous experimental studies. However, the values of these dP/dT slopes scatter from 2.5 to 4.5 MPa/K. This phase boundary has been used as a pressure calibration point at high temperatures in high-pressure experiment. Therefore, the precise phase boundary of Fe₂SiO₄ needs to be determined.

The starting material was Fe₂SiO₄ fayalite, synthesized from a starting mixture composed of finely powdered Fe₂O₃ and SiO₂. High-pressure X-ray diffraction experiments were performed using a multi-anvil high-pressure apparatus, and was combined with a synchrotron radiation source located at the KEK and SPring-8 facilities in Japan. In our experiments, pressure was applied to the sample by generating a press load. The sample was then quickly heated until it reached the desired temperature for a given press load. After reaching the required temperature, we performed *in situ* measurements using the synchrotron X-rays and the heating temperature was maintained for 1-3 h. At the end of the experimental runs, the sample was quenched by cutting off the electrical power. This heating procedure was the same as that used in typical quench experiments.

We report on the disputed issue of the dP/dT slope of the olivine-spinel transition in Fe₂SiO₄, and establish the phase boundary with improved accuracy using our pressure and temperature data. We performed approximately 25 experimental runs to investigate the phase boundary between the olivine and spinel structures. The gradient of dP/dT of the phase boundary was positive.

$$P \text{ (GPa)} = 0.5(3) + 0.0034(3) \times T \text{ (K)}.$$

The boundary determined in this study is in general agreement with those reported in previous quench or *in situ* high-pressure experiments. However, the dP/dT slope was more positive than that in the previous *in situ* experiment.

Clumped Methane Isotopologue (¹³CH₃D) Thermometry of Geological Methane by Tunable Mid-Infrared Laser Spectroscopy

SHUHEI ONO¹, BARBARA SHERWOOD LOLLAR², ELIZA HARRIS¹, BARRY MCMANUS³, MARK ZAHNISER³
AND DAVID NELSON³

¹Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA.
(sono@mit.edu)

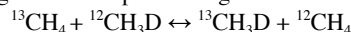
²Department of Earth Sciences, University of Toronto, Toronto, ON, Canada

³Center for Atmospheric and Environmental Chemistry, Aerodyne Research, Inc., Billerica, Massachusetts, USA

We have developed a tunable laser mid-infrared spectroscopy instrument to measure four isotopologues of methane including clumped isotopologue, ¹³CH₃D. Precise measurements of ¹³CH₃D abundance will add another critical dimension to resolve biogenic and abiogenic sources of methane in the marine and continental deep subsurface, and the atmosphere.

The new spectrometer houses two quantum cascade lasers that are tuned to a series of well resolved fundamental absorption lines in the 8 μm wavelength region. One laser measures absorption lines for ¹²CH₃D, ¹²CH₄, and ¹³CH₃D, and the other ¹²CH₄ and ¹³CH₄. Precisions (1σ) are 0.1‰ for the ratio ¹³CH₄/¹²CH₄ and ¹²CH₃D/¹²CH₄, and 0.3‰ for the ratio ¹³CH₃D/¹²CH₄, evaluated by comparing two methane cylinder samples. Accuracy of the technique is assured by comparing δ¹³C and δD values measured by a conventional isotope-ratio mass spectrometer.

The abundance of ¹³CH₃D is expected to reflect the temperature at which methane is thermally equilibrated, according to the isotope exchange reaction:



The equilibrium constant for this reaction approaches unity at very high temperatures (>1,000K). At low temperature, the above equilibrium constant deviates from unity, reaching values of 1.0066, 1.0050, 1.0011 at 0, 100 and 400 °C, respectively. Therefore, the precision of 0.3‰ would permit a temperature estimate of ±10°C for methane formed or scrambled at 25°C. The measured 'clumped isotope temperature', however, is expected to be biased when mixing of two or more sources of methane occur due to some non-linearity in the ratio ¹³CH₃D/¹²CH₄ upon mixing. We will discuss some preliminary data and the potential of this new approach to delineate deep subsurface methane sources and their role in the deep carbon cycle.