# Phase transformation in $Fe_2SiO_4$ at high pressure and high temperature

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Olivine, $(Mg,Fe)_2SiO_4$, 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 $Fe_2SiO_4$ end-member is important for precise modeling of the $Mg_2SiO_4$-$Fe_2SiO_4$ system. With pressure and temperature increase, $Fe_2SiO_4$ 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 $Fe_2SiO_4$ needs to be determined.

The starting material was $Fe_2SiO_4$ fayalite, synthesized from a starting mixture composed of finely powdered $Fe_2O_3$ and $SiO_2$. 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 $Fe_2SiO_4$, 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.

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

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.

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# Clumped Methane Isotopologue ($^{13}CH_3D$) Thermometry of Geological Methane by Tunable Mid-Infrared Laser Spectroscopy

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We have developed a tunable laser mid-infrared spectroscopy instrument to measure four isotopologues of methane including clumped isotopologue, $^{13}CH_3D$. Precise measurements of $^{13}CH_3D$ 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 $\mu$m wavelength region. One laser measures absorption lines for $^{12}CH_3D$, $^{12}CH_4$, and $^{13}CH_3D$, and the other $^{12}CH_4$ and $^{13}CH_4$. Precisions ($1\sigma$) are 0.1‰ for the ratio $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$, and 0.3 ‰ for the ratio $^{13}CH_3D/^{12}CH_4$, evaluated by comparing two methane cylinder samples. Accuracy of the technique is assured by comparing $\delta^{13}C$ and $\delta D$ values measured by a conventional isotope-ratio mass spectrometer.

The abundance of $^{13}CH_3D$ is expected to reflect the temperature at which methane is thermally equilibrated, according to the isotope exchange reaction:

$$^{13}CH_4 + {}^{12}CH_3D \leftrightarrow {}^{13}CH_3D + {}^{12}CH_4$$

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 be biased when mixing of two or more sources of methane occur due to some non-linearity in the ratio $^{13}CH_3D/^{12}CH_4$ 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.

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