

## Variation in concentrations of gases dissolved in groundwater at Toyohashi station in Tokai area, Japan and neighboring seismic activity

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Based on the assumption that preseismic hydrological and geochemical changes in groundwater is caused by crustal deformation (Koizumi et al., 1999), since 1998, Geological Survey of Japan, AIST (National Institute of Advanced Industrial Science and Technology) and Nagoya University have observed levels and temperatures of groundwater, gases dissolved in the groundwater, crustal strain and crustal tilt at the observation well and tunnel in Toyohashi station of Nagoya University, which is near the western end of the impending Tokai earthquake zone. Using the system composed of a quadrupole mass spectrometer and a gas permeable membrane (Igarashi et al., 1997), we measure concentrations of the dissolved gases such as H<sub>2</sub>, He, CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub> every two minutes. After starting the observations, two earthquakes of magnitude 4.7 occurred around Toyohashi City on May 7, 1999 and November 29, 1999. Before these two earthquakes, H<sub>2</sub>/Ar ratio in the groundwater of the observation well changed anomalously. At the presentation, we will discuss about these changes in comparison with crustal deformation observed at the same station.

### References

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## Raman spectroscopy and heat capacity measurement of calcium ferrite type MgAl<sub>2</sub>O<sub>4</sub> and CaAl<sub>2</sub>O<sub>4</sub>

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Recent high-pressure and high-temperature experiments have reported the presence of Al-rich phases in high-pressure phases of mid-ocean ridge basalt (MORB) at the lower mantle conditions. In particular, a calcium ferrite type phase is expected as one of possible candidates for the Al-rich phases. In this study, heat capacity (Cp) measurement of CaAl<sub>2</sub>O<sub>4</sub> calcium ferrite was performed. Also Raman spectroscopy of MgAl<sub>2</sub>O<sub>4</sub> and CaAl<sub>2</sub>O<sub>4</sub> calcium ferrites were made. The obtained Raman data were applied to the estimation of Cp and lattice vibrational entropy of MgAl<sub>2</sub>O<sub>4</sub> calcium ferrite by the Kieffer model calculation.

MgAl<sub>2</sub>O<sub>4</sub> and CaAl<sub>2</sub>O<sub>4</sub> calcium ferrites were synthesized by heating MgAl<sub>2</sub>O<sub>4</sub> spinel at 27 GPa and 2273 K for 8 minutes and CaAl<sub>2</sub>O<sub>4</sub> stuffed tridymite at 15 GPa and 1873 K for 1 hour, respectively, with Kawai-type multianvil high-pressure apparatus at Gakushuin University. Heat capacity measurement of CaAl<sub>2</sub>O<sub>4</sub> calcium ferrite was made in the range of 155-733 K by using a differential scanning calorimeter (DSC) at Gakushuin University. Raman spectroscopy of both calcium ferrites was performed by using micro-Raman spectroscopy system at National Institute of Advanced Industrial Science and Technology with the 514.5 nm line of an argon ion laser.

In the DSC measurement, 79 Cp data of CaAl<sub>2</sub>O<sub>4</sub> calcium ferrite were obtained. When the Cp data are fitted to the Berman and Brown's Cp equation, it is represented as Cp(T) = 190.6 x 1.116x~10<sup>7</sup>T<sup>-2</sup> + 1.491x~10<sup>9</sup>T<sup>-3</sup> above 250 K. In the Raman spectroscopic measurement, 34 Raman peaks were observed for both calcium ferrites. The Kieffer model calculation for MgAl<sub>2</sub>O<sub>4</sub> calcium ferrite based on the Raman data gave the estimated Cp represented as Cp(T) = 223.4 x 1352T<sup>-0.5</sup> x 4.181x~10<sup>6</sup>T<sup>-2</sup> + 4.300x~10<sup>8</sup>T<sup>-3</sup> and lattice vibrational entropy at 298 K of 97.6 J/mol.K. The estimated entropy of MgAl<sub>2</sub>O<sub>4</sub> calcium ferrite was applied to a phase equilibrium boundary calculation between MgO+Al<sub>2</sub>O<sub>3</sub> and MgAl<sub>2</sub>O<sub>4</sub> calcium ferrite. A calculated boundary shows a negative slope which is consistent with the result of high-pressure experiments.