

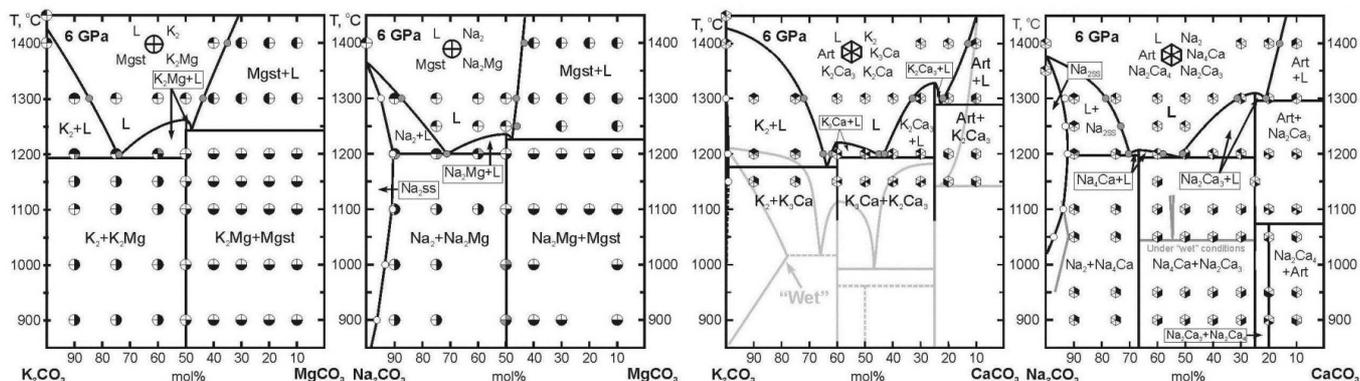
Phase diagrams of binary carbonate systems at 6 GPa and 900-1400C

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In this study we conducted HP-HT experiments at 6 GPa and 900-1400oC in binary carbonate systems K₂CO₃-MgCO₃, K₂CO₃-CaCO₃, Na₂CO₃-MgCO₃, Na₂CO₃-CaCO₃ using multi-anvil apparatuses at Tohoku University (Sendai, Japan) and IGM SB RAS (Novosibirsk, Russia). Based on obtained results we plotted phase diagrams for studied systems which shown in Fig. 1.

Keywords: Phase diagram, Carbonate, Binary system, High pressure and temperature



Solubility of Carbon in metallic liquid under high pressure in the natural carbonaceous chondrite system

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In order to explain of the density deficit of the core of the earth, the core is considered to contain some amounts of light elements. Oxygen, sulfur, silicon, carbon, and hydrogen are the possible candidates. It has been considered that the core composition was established by chemical differentiation processes in the magma ocean on the early stage of the earth. To clarify the core composition, the partitioning behavior between silicate- and metallic-liquids of the candidate elements; oxygen, sulfur, and silicon, has been investigated by many workers. However, there are not so many studies on carbon and hydrogen because of the difficulty of chemical analyses. The volatile depleted primitive materials similar to carbonaceous chondritic group have been considered as the building blocks of the earth. We choose Allende meteorite (CV3) as a model composition of primitive earth and investigated partitioning behavior of carbon together with sulfur and oxygen between silicate- and metallic-liquids.

We used natural Allende meteorite as the starting material. The sample was crushed and grounded to fine powder for high pressure experiments. High pressure experiments were performed using 3000 ton Kawai-type multianvil apparatus installed at Tohoku University. WC-anvils with truncation edge length of 12 mm were used. Semi-sintered zirconia was used as the pressure medium, and graphite was used for a sample container and a cylindrical heater. In each experiment, the sample was first compressed to the desired pressure, then, the temperature was raised to the target temperature at a rate of 85 K/min. Recovered sample was cut with a diamond blade and polished for electron microprobe analyses. Microfocused X-ray diffractometry and electron microprobe analysis were used for phase identification and compositional analysis of run products.

The experiments were performed at the conditions of 5 GPa and 2073 K. We will present experimental results and discuss about core-mantle chemical differentiation processes on early planets.

Keywords: Carbon, carbonaceous chondrite, high pressure, solubility, high temperature

Sound velocity of liquid Fe-Ni-C alloy at high pressure and temperature

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Sound velocity is important to understand the composition of the Earth's and lunar core because it can be directly compared with seismological data.

Carbon is a plausible candidate as a light element in the core due to its high cosmic abundance and high affinity to liquid Fe [e.g., Wood, 1993]. However, the effect of carbon on the sound velocity (V_P) of liquid Fe-Ni alloy has not been investigated. In this study, we have measured the V_P of liquid (Fe-10wt.%Ni)-4wt.%C alloy at around 4.7 GPa and 1563-1788 K.

High-pressure experiment was performed using a 1500-ton multi-anvil apparatus (SPEED-1500) installed at BL04B1 of the SPring-8 synchrotron radiation facility. Experimental pressure was determined from the lattice constants of MgO and hBN. We have used a cylindrical graphite heater and temperature was monitored using a W5%Re-W26%Re thermocouple. V_P measurements were carried out by the pulse-echo-overlap method using a LiNbO₃ transducer for generating and receiving P-wave signals. Used frequencies of the wave signal were 37 and 21 MHz. The sample length was measured from an X-ray radiography image of the sample.

The observed V_P of liquid Fe-Ni-C decreases with increasing temperature. Comparing the V_P of Fe-C calculated from the previously reported densities and bulk moduli of liquid Fe and Fe-C [Anderson & Ahrens, 1994; Shimoyama et al., 2013; Terasaki et al., 2010], V_P of liquid Fe-C or Fe-Ni-C decrease with increasing carbon content.

Keywords: Carbon, Earth's outer core, Light element

In-situ determination of NOHD species in coexisting silicate melt and fluid

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In-situ measurements of solubility and speciation of N-O-H-D volatiles in coexisting fluid and melt were made at high pressure and temperature to estimate the effect of N-O-H-D volatiles on physical properties of magma. The experiment was performed using a Bassett-type hydrothermal diamond anvil cell with Raman spectroscopy as a structural probe. Silicate composition was (Na₂O-4SiO₂)₉₀(Na₂O-4NaAlO₂)₁₀. Water is a liquid mixture of H₂O and D₂O (H₂O:D₂O=50:50 in volume ratio). Nitrogen was supplied from Ag(14/15=0.7/0.3)N₃. Pressure was measured with one-phonon Raman shift of carbon-13 diamond [1]. The in-situ measurements were conducted in the pressure and temperature range of 425-800 °C and 100-1300 MPa, respectively. Temperature was initially raised up to 800 °C and then decreased to the desired values. Experiments were conducted in two different redox conditions. Oxidizing conditions were obtained by using no buffer and reducing condition controlled with the Mo-MoO₂ buffer based on the reaction $Mo+2H_2O=MoO_2+2H_2$. In the reducing condition, fO₂ was near that of the iron-wustite buffer. In the experiments under oxidizing conditions, only molecular N₂ was observed in coexisting silicate melt and NOH fluid. The ¹⁴N₂ and ¹⁵N₂ can be clearly distinguished. However, the isotope partitioning between fluid and melt is uncertain because of the low nitrogen solubility in the melt. For experiments under reducing conditions, nitrogen in the fluid was reduced to NH₃ coexisting with H₂O+H₂(+D₂O+D₂). In coexisting melt, both molecular NH₃ and NH₂ groups were observed in the pressure and temperature range investigated. The ammine groups bonded directly to Si⁴⁺ to Si-NH₂ bonding. In the spectra of fluid, there is evidence for both NH₃ and probably ND₃ in addition to H₂O, D₂O, H₂, and D₂. Partitioning of D and H between the coexisting phases was determined spectroscopically. SiNH₂ groups were also detected in melt and probably generated by the reaction, $Si-O-Si+NH_3=Si-NH_2+H-O-Si$. This reaction depolymerizes the network of SiO₄ tetrahedra and will affect, therefore melt properties that depend on silicate polymerization (melt viscosity, diffusion, mineral/melt partitioning).

From these data, it is clear that nitrogen in the Earth's interior cannot be modeled simply as a N₂ molecule, whether in melt or fluid. The reduced nitrogen species have a different solubility, different solution mechanisms and probably different nitrogen and hydrogen isotopic behaviors. These results do, therefore affect modeling of earth degassing based on assumed behavior of nitrogen.

[1] Mysen, B. O., Yamashita, S., (2010). *Geochimica et Cosmochimica Acta* 74, 4577-4588

Keywords: fluid, speciation, distribution, silicate melt, diamond anvil cell, in-situ