

6-1 Non-Destructive Observation of Air Hydrates by Phase-Contrast X-Ray Imaging

Air hydrate is a clathrate hydrate containing air (N_2 , O_2 , etc.) in cage structures formed by water molecules, and is only stable under the conditions of low temperature or high pressure. Measurements of natural air hydrates in Antarctica are essential for reconstructing the climates over the last several hundred thousand years because gas concentrations obtained from the air hydrate in deep ice cores are an important source of data on the paleoatmosphere. However, identification of a gas hydrate with ice using conventional X-ray transmission imaging techniques is difficult because both lattice structures are formed by water molecules and their densities are almost the same.

Light elements have phase-shift cross sections that are approximately 1000 times larger than their absorption cross sections, so phase-contrast X-ray imaging may be able to identify a gas hydrate with ice. In this study, a cryo-system was designed (see Fig. 1) and arranged in a two-crystal X-ray interferometer to expand the use of phase-contrast X-ray imaging at BL-14C1 [1] that could only be performed at room temperature [2, 3]. This technique can be applied for *in-situ* observations under various temperature conditions from 190 K to room temperature.

A three-dimensional phase-contrast X-ray computed tomography (X-ray CT) image of the air hydrate in a hexagonal ice core drilled from Dome Fuji in Antarctica, which was sampled by the Japan Antarctic Research Expedition (JARE), is shown in Fig. 2. The average density of the air hydrate is estimated to be 937 mg/cm^3 at 233 K, which is 13.6 mg/cm^3 higher than that of the surrounding ice. The density difference of each air hydrate crystal within 6 mg/cm^3 was also measured, which would be caused by a crystallographic difference of the air hydrate such as the lattice constant or the cage occupancy as reported in previous studies using the X-ray diffraction method [4].

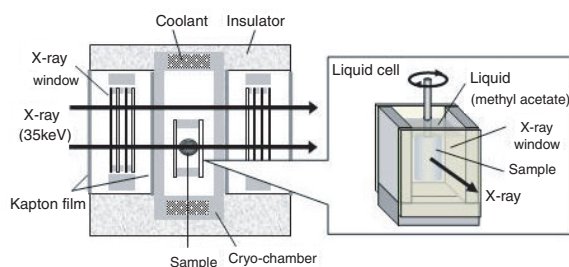


Figure 1
Schematic view of the sample chamber.

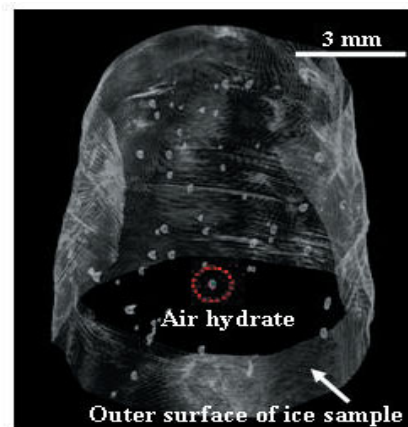


Figure 2
Three-dimensional image of the spheroid-shaped ice sample including air hydrate crystals. The red dotted circle indicates one of the air hydrate crystals in the ice sample. One part of the ice surface was made transparent to show the air hydrate more clearly.

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6-2 Experimental Investigation on the Kinetics of the Pyroxene-Garnet Transformation Using an *in-situ* X-Ray Diffraction Method

The oceanic plate descends into the Earth's mantle, and its constituent minerals transform to their high pressure phases with increasing pressure. Pyroxene gradually dissolves into the garnet structure under high pressure, with complete transformation at a depth of around 500 km in the equilibrium state. On the other hand, untransformed low-pressure metastable minerals are believed to exist in the mantle, especially in the subducting plates, because these transformations are kinetically inhibited due to the low temperatures present

in these plates. At 500 km, the temperature within the subducting plates (~600-1200°C) are estimated to be much lower than the surrounding hot mantle (~1600°C). Presence of the metastable minerals has a great influence on the overall mineralogical constitution of the plate, and consequently on the dynamics due to varying density, rheology, and mechanical structure. In order to clarify the conditions of metastable mineral formation, extensive kinetic studies have been previously carried out. However, most studies in the transition zone conditions have been limited to high-pressure transformations in the olivine component. We report new experimental results on a study of the kinetics of the pyroxene-garnet transformation in the multi-component system of CaO-MgO-Al₂O₃-SiO₂. The in-situ X-ray diffraction method was employed to elucidate the intermediate stages of the transformation.

As starting materials for the transformation experiments we synthesized polycrystals of pyroxenes (enstatite + diopside) + garnet from a glass corresponding to the simplified olivine-free mantle composition of 52.6 wt% SiO₂, 11.9 wt% Al₂O₃, 25.9 wt% MgO, and 9.7 wt% CaO. The starting glass was kept at 3.5 GPa and 1180°C for 180 min using the MAX-90 multi-anvil high-

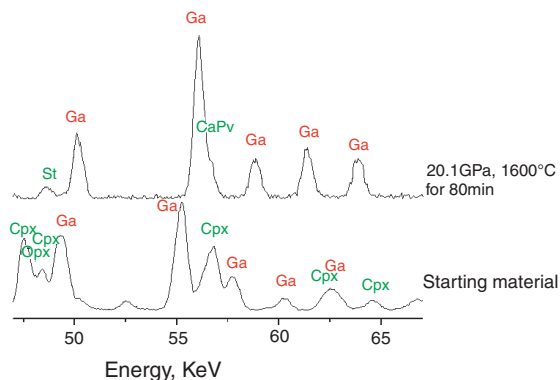


Figure 3
X-ray diffraction patterns of the starting material and following treatment at 20.4 GPa and 1600°C for 80 min. The observed phases are garnet (Ga), ortho pyroxene (Opx, enstatite), clino pyroxene (Cpx, diopside), stishovite (St), and Ca-perovskite (CaPv).

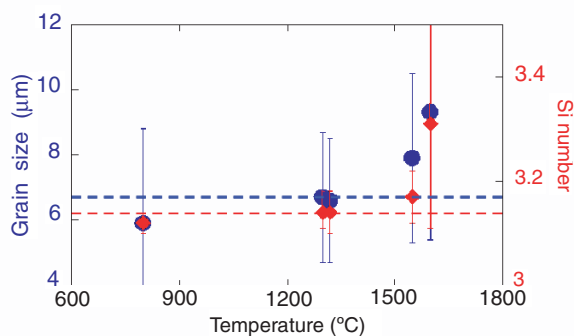


Figure 4
Atomic numbers of Si relative to 12 oxygens (red diamonds) and grain sizes of recovered garnets (blue circles) as a function of temperature. The Si number and grain size of the starting material garnet (with small enstatite inclusions) are 3.13 and 6.7 µm, shown as the red and blue dashed lines.

pressure apparatus at Kyushu University, and uniform pyroxenes + garnet polycrystals were obtained.

In situ X-ray diffraction experiments were performed using the MAX-III multi-anvil high-pressure apparatus installed at BL-14C2. The high pressure conditions were generated by a double-stage method, using a sintered diamond and seven WC cubes with 14 mm edge lengths as the second-stage anvils. The temperature was monitored with a W3%Re-W25%Re thermocouple located in the furnace, and pressure calculated based on the equation of state of MgO [1]. We were successful in obtaining X-ray diffraction data during the pyroxene-garnet transformation (Fig. 3).

The diffraction profiles obtained following 80 min at 20.4 GPa and 1600°C are shown in Fig. 3. The results suggest that the pyroxenes rapidly decompose to their high-pressure phases (Stishovite + wadsleyite + Ca-perovskite), and were significantly dissolved in garnet (Fig. 3). The back-scattered electron images show a clear increase in the average grain size of the recovered garnet. From these observations, the pyroxene-garnet transformation was considered to have proceeded by overgrowth of the original garnet with absorption of the pyroxene components. Figure 4 shows the Si numbers and grain sizes of recovered garnet as a function of the run temperatures. An increase in Si number is a useful indicator of the progression of the pyroxene-garnet transformation. Changes in the Si number and grain size of garnet were only observed at high temperatures, 1550-1600°C.

The present study demonstrates that on the laboratory time and grain size scales (10⁵ s, 10⁻⁵ m) the pyroxene-garnet transformation requires much higher temperatures (1550-1600°C) than the major mantle mineral Mg₂SiO₄ olivine-wadsleyite transformation (850-1100°C) [2]. Temperatures within the subducting plates are estimated to be as low as 600°C even at depths of 500 km, corresponding to 16 GPa. It has been proposed that metastable olivine survives to depths of 500 km or more

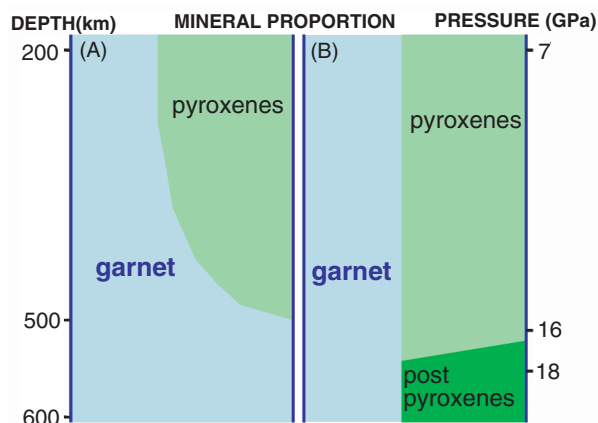


Figure 5
Mineral proportions of pyroxenes and garnet for depths of 200 to 600 km for the cases where the pyroxene-garnet transformation (A) proceeds in equilibrium; (B) does not proceed due to kinetic effects.

in the subducting slabs [3]. Our experimental results show that the pyroxene-garnet transformation is much more kinetically inhibited than the transformation of olivine to wadsleyite in such low temperature regions. This suggests that the phase distribution in the subducting plate is different to the equilibrium distribution, and that the transformation of pyroxenes to their high-pressure phases (post pyroxenes; wadsleyite, stishovite and Ca-perovskite), may occur (Fig. 5). These non-equilibrium phases could be present in the subducting plate for significant periods of time.

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6-3 High-Pressure Phase of KAISi_3O_8 as a Carrier of Potassium into the Earth's Lower Mantle

The high-pressure behavior of potassium deep inside the Earth can have a significant influence on thermal evolution due to the presence of the radiogenic isotope ^{40}K , which is an important heat source. The host mineral of potassium in the deep regions remains unknown, and there are thus no exact estimation for the amounts of potassium, particularly in the lower mantle. Potassium feldspar KAISi_3O_8 is an abundant mineral in the Earth's crust, and, when carried from the surface through subduction, is likely to become the host mineral of potassium in the mantle (Fig. 6). The high-pressure

polymorph of KAISi_3O_8 , which is stable above 9-10 GPa and at 1000-1500 K, has an ideal hollandite structure with large open tunnels that can accommodate the potassium atom, which has a large ionic radius (Fig. 7) [e.g., 1, 2]. Recently, a new high-pressure phase of KAISi_3O_8 hollandite II has been discovered above 20 GPa, and this new phase has the same structure as the natural hollandite $\text{BaMn}_8\text{O}_{16}$ and is distorted from the ideal hollandite structure [3, 4]. The stability of the KAISi_3O_8 hollandite II phase in the whole lower mantle needs further investigation since the phase could provide a profound effect on heat production in the Earth's mantle as a reservoir of potassium. Here, we report a high-pressure *in situ* X-ray diffraction study of natural potassium feldspar KAISi_3O_8 at BL-13A and BL-18C.

The crystal structure and stability of KAISi_3O_8 were studied at pressures up to 128 GPa, corresponding to the lowermost mantle conditions, in a laser-heated diamond-anvil cell (DAC) [5]. The X-ray diffraction patterns show that the hollandite II phase was stable at pressures between 28 and 128 GPa. The observed diffraction peaks at all conditions can be reasonably assigned to the hollandite II phase, as reported in previous work (Fig. 7). The pressure-induced structural distortion lowers the tetragonal symmetry of the ideal hollandite structure to the monoclinic, resulting in a splitting of the diffraction lines for the tetragonal phase into those for the monoclinic phase. For instance, the $200\text{-}020$ and $2\bar{2}0\text{-}220$ doublets and $3\bar{1}0\text{-}310\text{-}1\bar{3}0\text{-}130$ quadruplet in the hollandite II phase split from the 200 , 220 , and 130 lines in the hollandite phase, respectively. The splitting of $h00$ and $hk0$ reflections in the hollandite phase with tetragonal symmetry is associated with the separation of the a axis of the tetragonal phase into the a and b axes of the monoclinic symmetry of the high-pressure phase. The interval of splitting observed in the monoclinic phase results from a degree of structural distortion, corresponding to a change in the internal angle of the unit cell. Pressure induces the distortion of the framework of (Si, Al) O_6 octahedra which form a tunnel structure, lead-

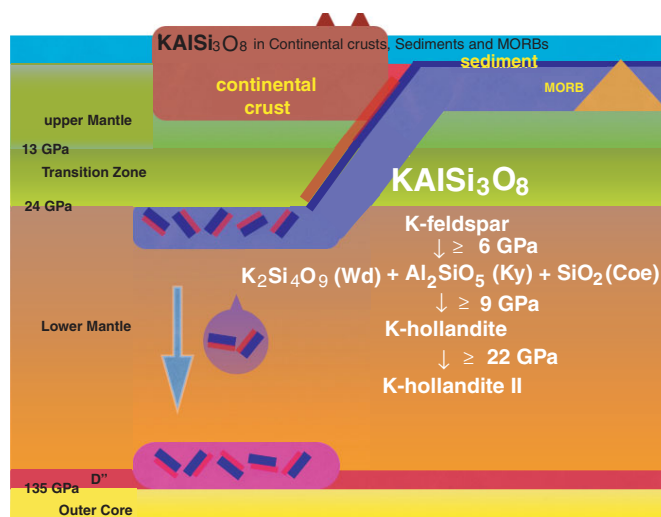


Figure 6 Schematic model of the subduction slab and the pressure-induced phase transition of KAISi_3O_8 . The subduction slab transports mid-ocean ridge basalts (MORB) and continental and marine sediments from the surface to the Earth's deep mantle.

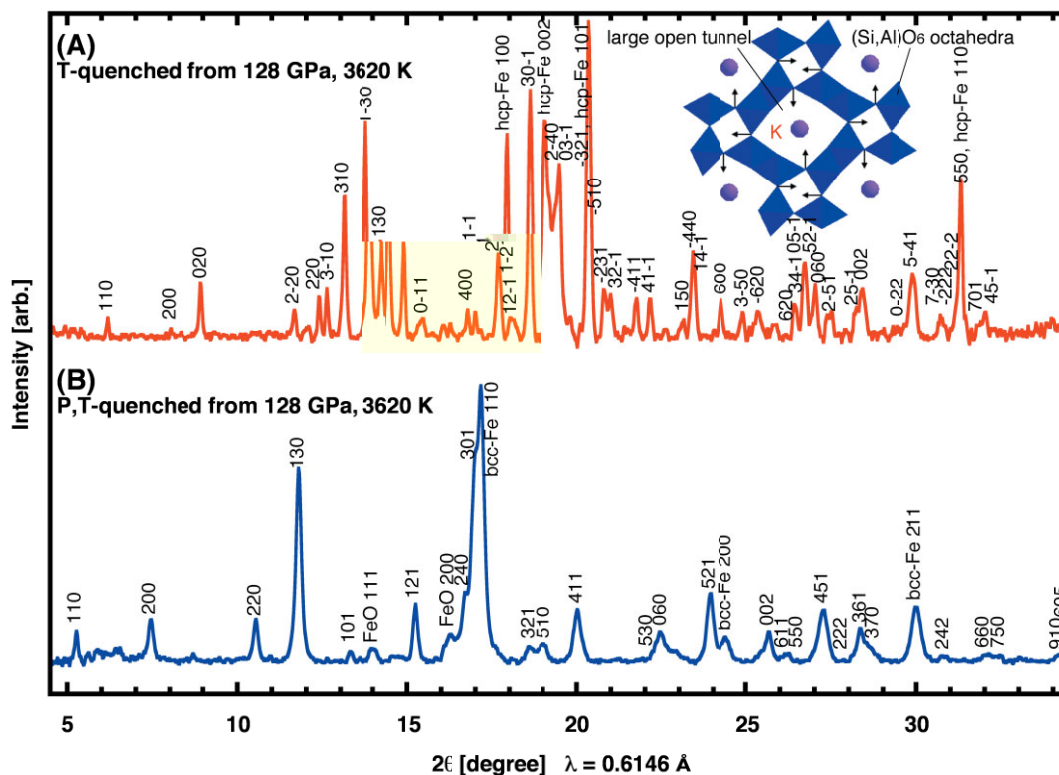


Figure 7
 Representative X-ray diffraction patterns of (A) KAlSi_3O_8 hollandite II phase with monoclinic symmetry (space group $I2/m$) at 128 GPa and 300 K after heating at 3620 K and (B) the sample with tetragonal symmetry (space group $I4/m$) recovered to ambient conditions on the same run. Inset: crystal structure of the KAlSi_3O_8 hollandite II phase in the $[010]$ projection. Hollandite structures have large open tunnels that are formed by double-chains of edge-sharing $(\text{Si, Al})\text{O}_6$ octahedra. The arrows represent the direction of displacement of atom positions from those in the ideal hollandite phase.

ing to compaction of the tunnel, but the potassium atom can still be accommodated in the hollandite II phase up to 128 GPa. This result shows that, if potassium feldspar KAlSi_3O_8 is transported further into the lower mantle by subduction slabs, the high-pressure polymorph of KAlSi_3O_8 hollandite II phase could become the prime candidate for a potassium host mineral, providing a reservoir of ^{40}K in the Earth's lower mantle. Thus, the stability of the KAlSi_3O_8 hollandite II phase in the Earth's lower mantle may have significant influence in the geochemical and isotopic constraints on the formation and evolution of the solid Earth and its atmosphere.

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6-4 Speciation Study of Sulfate-Containing Size-Fractionated Aerosol Particles Using Sulfur K-Edge X-Ray Absorption Near-Edge Structure Spectroscopy (XANES)

Sulfate ions are a major constituent of aerosols (suspended airborne particles) in the atmosphere, and can lead to various environmental problems related to radiative forcing, respiratory health, and the acidification of soils and natural water. In the evaluation of the influence of sulfate aerosols, it is necessary to determine which sulfate ions are present. Electron microscopy and X-ray diffraction are frequently employed physicochemical methods for the speciation of elements in aerosols, but it is difficult to determine the ratio of each sulfate species quantitatively using these methods. Therefore, the establishment of new methods for speciation will contribute to the better characterization of sulfate species and related chemical processes in aerosols.

In this study, X-ray absorption near-edge structure (XANES) measurements at the sulfur K-edge were used to determine the sulfate species present in 9 different size-fractionated aerosol particles. In particular, it was found that post-edge structure at higher energies than the main absorption peak in the XANES region can

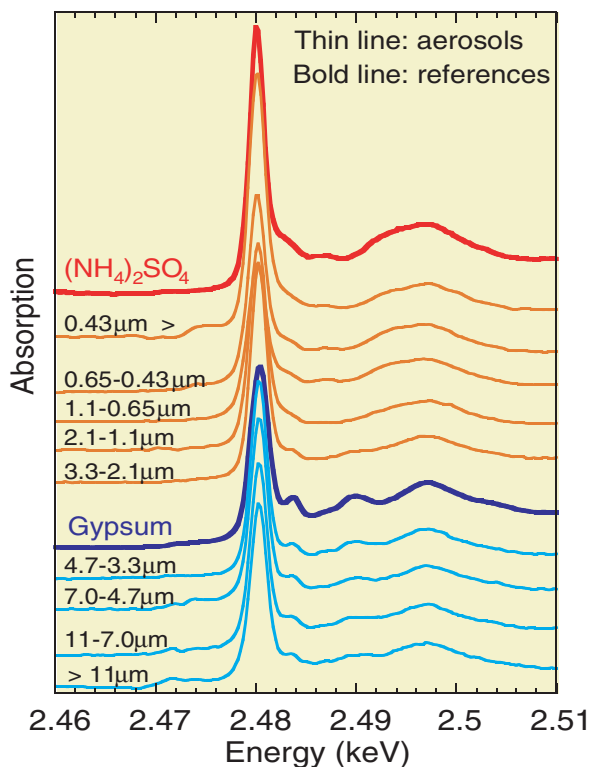


Figure 8
Sulfur K-edge XANES for the aerosol samples collected in April 2002 in Tsukuba. The thin lines show the spectra for the samples with the labelled particle diameters, and the spectra for gypsum and $(\text{NH}_4)_2\text{SO}_4$ are shown in bold for comparison.

be used to identify the sulfate species in solid materials (see Fig. 8). A comparison of the XANES spectra for reference sulfate materials and aerosol samples collected in Tsukuba, Japan, clearly showed that $(\text{NH}_4)_2\text{SO}_4$ was the main sulfur species in particles with small diameters, and that $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) was the main sulfur species in particles with larger diameters. It is well known that fine particles are produced from gaseous materials in the atmosphere, while coarser particles are directly transported as minerals. Thus, the present results suggest that $(\text{NH}_4)_2\text{SO}_4$ is produced in the air, while gypsum originates from the soil and desert. When comparing the samples collected during periods when Kosa (“yellow sand”) is known to be present in the atmosphere to samples collected at other times, the ratio of gypsum to $(\text{NH}_4)_2\text{SO}_4$ was high during the Kosa periods, showing that Kosa originating in dust storms in the arid and semi-arid areas of China increases the amount of mineral aerosols with mid-range particle sizes.

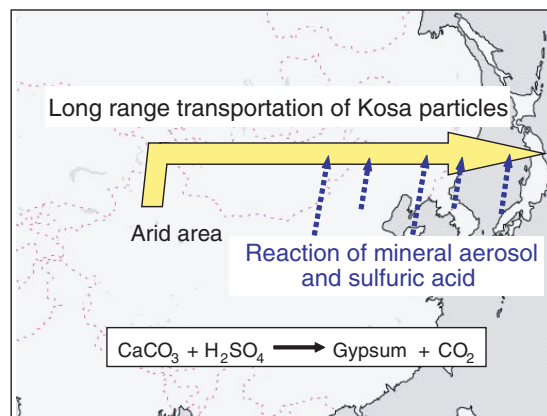


Figure 9
Schematic figure of the airborne reaction of calcite and sulfuric acid in mineral aerosol.

A simulation of the XANES spectra using spectra for reference materials allows us to obtain quantitative mixing ratios for the different sulfate species present in the aerosol samples. Such simulations along with a surface-sensitive conversion electron/He-ion yield XANES study suggest the presence of minor sulfur species other than $(\text{NH}_4)_2\text{SO}_4$ and gypsum at the surface of mineral aerosols. For example, aqueous SO_4^{2-} appears to be present as a second component in the coarser particles. This conclusion is consistent with transmission electron microscopy studies which revealed the presence of a “water crust” surrounding mineral particles and containing large amounts of sulfur.

In the absence of a contribution from a large dust event, the molar concentration of gypsum in mineral aerosol fractions with particle diameters of greater than $1 \mu\text{m}$, as determined from the XANES study, is similar to that of Ca determined independently using ion chromatography. This shows that Ca and sulfate in the mineral aerosols are present only as gypsum. Considering that calcite is the main Ca mineral in the original material arising from arid and semi-arid areas in China, it is strongly suggested that gypsum is formed by a reaction between calcite and sulfate ions within the aerosols during airborne transportation (see Fig. 9).

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