

NEW HIGH-PRESSURE FORM OF KAlSi_3O_8 HOLLANDITE UNDER LOWER MANTLE CONDITIONS

We have developed an *in situ* X-ray diffraction technique for the precise determination of phase transitions and the P-V-T relations of high-pressure phases under lower mantle conditions ($P = 25\text{--}130$ GPa), combining sintered diamond (SD) anvils for a multianvil apparatus with synchrotron radiation. As a result, we are now able to conduct routine-basis *in situ* X-ray diffraction measurements at simultaneous high pressures up to 45 GPa and high temperatures up to 2100°C with markedly improved accuracy and on a sample volume significantly larger than those available in a diamond anvil cell (DAC). Here, we report the formation of a new high-pressure form of KAlSi_3O_8 [1], as an example of the recent experimental results based on this technique.

KAlSi_3O_8 -rich feldspar is a major mineral in continental crust, which is known to transform to the hollandite structure at approximately 9 GPa via a mixture of $\text{K}_2\text{Si}_4\text{O}_9$ wadeite + Al_2SiO_5 kyanite + SiO_2 coesite. The K-rich hollandite was shown to be stable at pressures up to 95 GPa and temperatures up to 2300°C using a laser-heated DAC (LHDAC) [2], but no *in situ* X-ray diffraction studies have been carried out under simultaneous high-pressure and high-temperature conditions.

We used both synthetic K-hollandite and glass starting materials in our *in situ* X-ray diffraction study. The cell assembly was basically the same as that used in our earlier studies (e.g. [3]), as shown in Fig. 1,

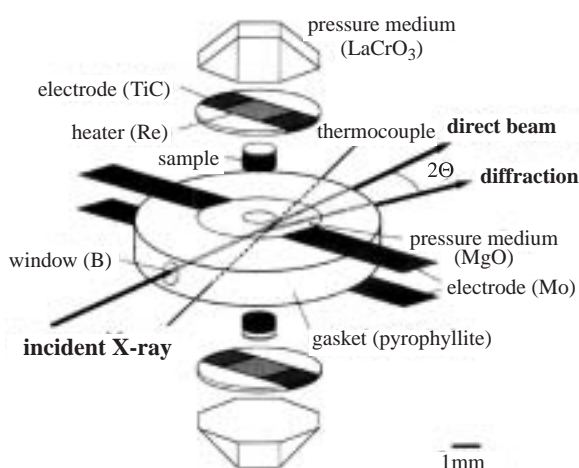


Fig. 1 Illustration of the cell assembly used for *in situ* X-ray diffraction measurements using sintered diamond anvils.

and sintered diamond cubes of 14 mm edges with truncations of 1.5 mm (TEL=1.5) were used as the second-stage anvils. An energy-dispersive method was adopted for X-ray diffraction measurements with a white X-ray beam of $\sim 50\ \mu\text{m}$, and a new 1500 ton MA (SPEED-Mk.II [4]) constructed at beamline **BL04B1** was used for high-pressure experiments with SD anvils.

Pressure was first increased, and diffraction data were acquired for every ~ 2 GPa upon compression. We found that some of the diffraction peaks of K-hollandite (Fig. 2(a)) became significantly broader at pressures above 22–23 GPa in the course of compression, which partially split at pressures greater than ~ 25 GPa (Fig. 2(b,c)). Upon increasing temperature at a maximum press load, at ~ 35 GPa, the diffraction peaks became sharper and completely split into several peaks at more than $\sim 800^\circ\text{C}$ (Fig. 2(d)). The new phase was preserved after quenching under pressure (Fig. 2(e)), but was converted back to K-hollandite upon release of pressure (Fig. 2(f)). The diffraction pattern of the new high-pressure form of K-hollandite, named hollandite II, was reasonably indexed on the basis of a monoclinic symmetry with the $I2/m$ space group, and yielded a density of $4.39\ \text{g/cm}^3$ under a pressure of 27.5 GPa at room temperature.

The P-T conditions of the present study and the plausible phase boundary between K-hollandite and hollandite II is shown in Fig. 3. The formation of hollandite II was confirmed when we used a glass starting material, and was also demonstrated by independent experiments using DAC with a helium pressure medium by Prof. T. Yagi's group of ISSP, University of Tokyo [5]. The present result of the transformation of K-hollandite to hollandite II is inconsistent with the results of earlier studies, which concluded that hollandite is stable at pressures up to 95 GPa, equivalent to depths of almost the entire lower mantle. However, the latter results are based mainly on the quench experiments, and the present results demonstrated the superiority of *in situ* measurements over the traditional quench experiments in the identification of a truly stable phase under high pressure and temperature.

K-hollandite is the major host for geochemically important trace elements, such as K, Ba, La, Pb, Sr, etc. in subducted crust and marine sediments, and is

believed to play a fundamental role in the fractionation of these elements in the deep mantle. It follows that chemical fractionation due to partial melting in the presence of K-hollandite should introduce some distinctive geochemical signatures in the deep mantle, which may be related to the origin of the enriched mantle reservoirs for EMI, EMII, and HIMU ocean island basalts. The present finding of the new phase transition of K-hollandite to hollandite II may significantly affect the partitioning behavior of these elements and thereby lead to a reconsideration of the origin of such reservoirs in the deep mantle.

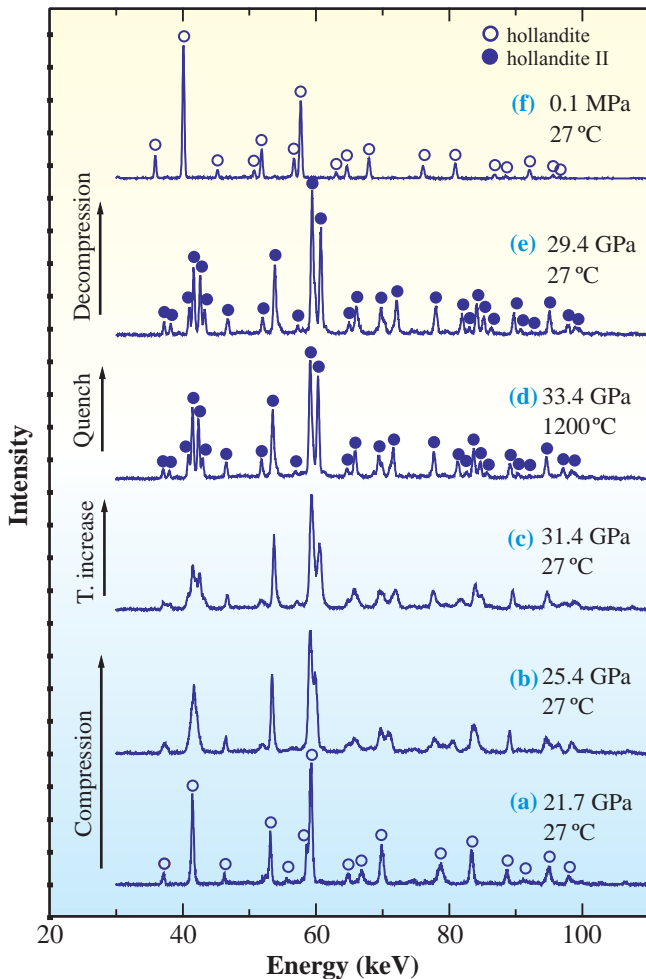
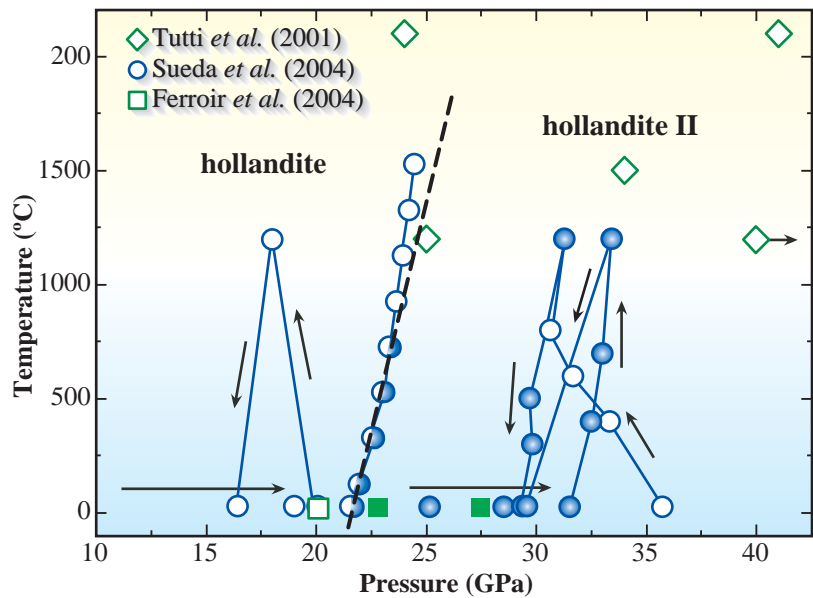


Fig. 2 Variations of X-ray diffraction profile of $KAlSi_3O_8$ with increasing pressure (a-c), and at high temperature under fixed load (d). Hollandite II was quenchable under pressure (e), but converted back to hollandite upon release of pressure (f).

Fig. 3 P-T conditions of *in situ* X-ray diffraction measurements of the present study (circles). Squares denote those of a corresponding study with DAC at room temperature [5]. Diamond symbols denote the P-T conditions where hollandite was reported to be stable in an earlier study based on DAC [2].

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