Kinetics of decomposition reaction in pyrope $Mg_3Al_2Si_3O_{12}$

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Introduction

The subducted oceanic lithosphere is mainly composed of basaltic crust and the underlying peridotite layer, in which garnet and silicate spinel are the major constituent minerals, respectively, at the depth of ~500-600 km. As the slab descends into the lower mantle, garnet and spinel decompose to perovskite plus aluminous phase (post-garnet transformation) and perovskite plus ferro-periclase (post-spinel transformation), respectively. Metastability in these transformations under subduction zone conditions greatly affect on dynamics of the slab in the deep mantle. Mechanisms and kinetics of the post-spinel transformation has been examined before [1]. Here we report results of the post-garnet transformation kinetics in pyrope $Mg_3Al_2Si_3O_{12}$. We performed high-pressure *in-situ* X-ray diffraction experiments combined with microstructural observations of the recovered sample using SEM and TEM.

Experimental

In-situ X-ray diffraction experiments were carried out using sintered-diamond multi-anvil apparatus "MAX-III" installed at KEK-PF. White X-ray from synchrotron radiation was used as the incident X-ray beam and the diffracted beam was measured by the energy dispersive method. Pressure was evaluated from the equation of state of gold. The starting material is a sintered mixture of $Mg_3Al_2Si_3O_{12}$ pyrope (grain size is 3.2 μm) and gold. It was compressed to the desired pressure at room temperature, and then heated to the desired temperature at constant oil pressure. When the temperature reached to the desired value, it was kept constant and time-resolved X-ray diffraction profiles were taken every 10-200 seconds. In this way, we observed decomposition kinetics of pyrope into perovskite and corundum at 26.2-31.0 GPa and 1000-1400°C.

Results and Discussion

The post-garnet transformation occurred by grain-boundary nucleation and growth mechanisms. Perovskite and corundum grew with rectangular and granular shape, respectively, thus dissociated post-garnet assemblages do not show the lamellar texture as observed in the post-spinel assemblages [2]. This suggests that the growth requires long-range diffusion. Obtained kinetic data (Fig. 1) was analyzed based on the observed transformation mechanisms. The rate equation [3] is given by,

$$V = 1-\exp\{-2SX(t)\} \quad (1)$$

, where V is the transformed volume fraction, S is the area of the grain boundary, and $X(t)$ is the growth distance at time t. The area of grain boundary can be expressed by $3.35/d$, where d is the grain size of the parental phase. $X(t)$ is described by kt^n, where k and n are constants. The n-value was estimated to be very small and less than 1 in the post-garnet transformation, which means that the growth rate is time-dependent and significantly decreases with time contrary to the post-spinel transformation [1]. Consequently, the rate of post-garnet transformation is much slower than that of the post-spinel transformation. Differences in kinetics of these transformations might have important implications for buoyancy of the subducted oceanic crust and formation of the garnetite layer at the top of the lower mantle.

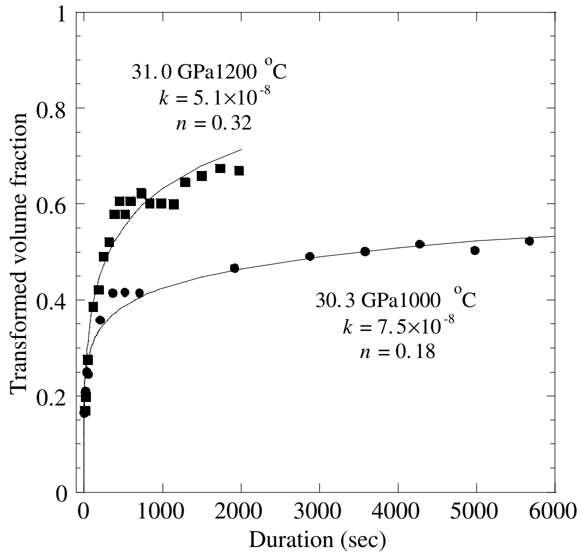

Fig. 1 Plots of transformed fraction with the heating duration at the desired temperature. Curves and kinetic parameters obtained by the least-square fits of equation (1) are also shown.

References

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