Formation of a metastable hollandite phase from amorphous plagioclase: A possible origin of lingunite in shocked chondritic meteorites

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ABSTRACT

We conducted high-pressure experiments in plagioclase with different anorthite contents at 18–27 GPa and 25–1750 °C using both a laser-heated diamond anvil cell and a Kawai-type multi-anvil apparatus to clarify the formation conditions of the hollandite phase in shocked chondritic and Martian meteorites. Lingunite ($NaAlSi_3O_8$-rich hollandite) was found first to crystallize from amorphous oligoclase as a metastable phase before decomposing into the final stable state. This process might account for the origin of lingunite found along with maskelynite in shocked chondritic meteorites. Metastable lingunite appeared at ∼20–24 GPa and ∼1100–1300 °C in laboratory tests lasting tens of minutes; however, it might also form at the higher temperatures and shorter time periods of shock events. In contrast, the hollandite phase was not observed during any stage of crystallization when using albite or labradorite as starting materials. The formation process of (Ca,Na)-hollandite in the labradorite composition found in Martian shergottites remains unresolved. The orthoclase contents of the hollandite phase both in shocked meteorites (2.4–8.2 mol%) and our oligoclase sample (3.9 mol %) are relatively high compared to the albite and labradorite samples (0.6 and 1.9 mol%, respectively). This might critically affect the crystallization kinetics of hollandite phase.

1. Introduction

Lingunite ($NaAlSi_3O_8$-rich hollandite), a high-pressure mineral of the plagioclase series, has been found in heavily shocked meteorites such as L6 chondrites (e.g., Gillet et al., 2000; Tomioka et al., 2000; Liu and El Goresy, 2007). The presence of this phase provides important evidence for shock metamorphism; however, establishing the pressure and temperature conditions of its formation is not straightforward because the stability field of this phase has not been experimentally determined. Its presence in maskelynite (dense plagioclase glass formed by shock metamorphism) has been identified by Raman spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD) (e.g., Gillet et al., 2000; Tomioka et al., 2000; Ohtani et al., 2004; Xie and Sharp, 2007). The albite ($NaAlSi_3O_8$, Ab), anorthite ($CaAl_2Si_2O_8$, An), and orthoclase ($KAlSi_3O_8$, Or) contents of lingunite in chondritic meteorites are $Ab_{81-83}An_{11-13}Or_{5-8}$, similar to those in maskelynite. Hollandite-phase with a Ca-rich plagioclase composition ($Ab_{46-52}An_{45-51}Or_{2-4}$, hereafter (Ca,Na)-hollandite) has also been found in heavily shocked achondrites such as Martian shergottites (e.g., Langenhorst and Poirier, 2000; Beck et al., 2004, 2007). This phase is also present in maskelynite regions along with other high-pressure minerals. Quenching from shock-induced melt and solid-state reactions have been proposed as the formation pathways of these hollandites.

While natural lingunite and (Ca,Na)-hollandite clearly exist in nature, experimental investigations of their formation conditions have not yielded clear results. Laser-heated diamond anvil cell (LHDAC) experiments (Liu, 1978) revealed that following the decomposition of albite into jadeite ($NaAlSi_2O_6$) plus silica (SiO_2) at 2–3 GPa, these phases recombine to form lingunite at pressures between 21 and 24 GPa, before decomposing again into calcium ferrite- (CF-) type $NaAlSiO_4$ (CF phase) plus stishovite at pressures above 24 GPa. Similarly, Tutti (2007) observed lingunite at 21–23 GPa and 2000 °C using LHDAC. Both these previous LHDAC experiments used pure albite as the starting material, and lingunite was observed as a minor phase

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coexisting with jadeite, CF phase, and stishovite.

On the other hand, experimental results from using multi-anvil type apparatus have been inconsistent with those from LHDAC experiments. Pure albite composition shows no stability field of linguunite between jadeite + stishovite and CF-phase + stishovite assemblages up to 2000 °C (e.g., Akaogi et al., 2010). The maximum solubility of the $NaAlSi_3O_8$ component in the $KAlSi_3O_8$ hollandite structure (liebermannite) was thought to be limited to ~50 mol% at 14–25 GPa and 800–2400 °C (Yagi et al., 1994; Liu, 2006), although the stability field of $NaAlSi_3O_8$-rich hollandite was also suggested to exist at still higher temperatures (Liu, 2006; Liu and El Goresy, 2007; Akaogi et al., 2010). Recently, Zhou et al. (2017) revealed that both pressure and temperature greatly affect the solubility of Na in hollandite, and synthesized hollandite with a $NaAlSi_3O_8$ content of 79 mol%—similar to natural linguunite in terms of Na content—at 22 GPa and 2000 °C in the $KAlSi_3O_8$–$NaAlSi_3O_8$ system. However, the orthoclase and anorthite contents of hollandite synthesized in the laboratory are still different from those of the natural hollandites in chondritic and Martian meteorites.

Given that the formation conditions of linguunite and (Ca,Na)-hollandite have not been experimentally clarified, our understanding of the presence of these minerals in shocked meteorites is incomplete. Although most previous studies have focused on the pressure–temperature (P–T) stability field of linguunite in the $KAlSi_3O_8$–$NaAlSi_3O_8$ system, anorthite is also an important component of both chondritic and achondritic meteorites. It is also necessary to investigate the time-dependent formation process of high-pressure phases, because the shock durations might be too short to reach equilibrium. We previously examined the crystallization kinetics from amorphous albite and labradorite at high pressures and described some non-equilibrium behaviors such as the first crystallization of jadeite (Kubo et al., 2010). However, the hollandite phase was not observed at any stage of crystallization. In the present study, we further investigate the crystallization process in amorphous plagioclase with varying anorthite contents, and confirm the formation conditions of hollandite. Based on the results, we discuss the metastable origin of linguunite in shocked meteorites.

2. Experimental procedure

We conducted high-pressure transformation experiments in plagioclase using both LHDAC and Kawai-type multi-anvil (KMA) apparatus. Natural albite ($Ab_{99.4}An_{0.0}Or_{0.6}$) and pure albite glass powders were used in the LHDAC experiments as starting materials; the KMA experiments used natural oligoclase ($Ab_{74.1}An_{21.9}Or_{3.9}$) and natural labradorite ($Ab_{44.5}An_{53.5}Or_{1.9}$) powders. The natural albite and labradorite powders are the same as those used by Kubo et al. (2010), although the chemical composition was reanalyzed.

A lever-type diamond anvil cell was used for the LHDAC experiments. The culet was 450 μm in diameter. The starting albite powder, mixed with platinum black (3.9–11.9 wt%) as a laser absorber, was loaded directly into the hole (200–250 μm in diameter) of a Re gasket with a ruby chip. In one experiment, a platinum foil was used as the laser absorber instead of platinum black to increase the absorption efficiency. The samples were first compressed to the desired pressure and then heated from both sides of the anvils using a multimode Nd:YAG laser at Osaka University, Osaka, Japan. The focus size of the laser spot was about 50–80 μm in diameter. The temperature was measured spectroradiometrically and the pressure was determined by the ruby fluorescence method (Mao et al., 1978) at room temperature before and after the laser heating. Phases in the recovered samples were determined by angle-dispersive XRD measurements using synchrotron radiation and an imaging plate at the PFAR-NE1 beamline at the Photon Factory, KEK, Tsukuba, Japan. The incident X-ray beam was monochromatized to an energy of 30 keV and collimated to 15–30 μm. The exposure time was 10–30 min.

We performed high-pressure experiments using a KMA apparatus by

both the quenching method and in situ X-ray observations. The quenching experiments were conducted using a KMA apparatus (QDES) at Kyushu University, Fukuoka, Japan. The truncated edge length of the second-stage anvils was 3 mm. The sample assembly was composed of a sintered (Mg,Co)O pressure medium, a cylindrical $LaCrO_3$ heater, a Mo electrode, and a graphite sample capsule. The sample was first compressed at room temperature and then heated steadily to the desired temperature at 500 °C/s. The pressure was calibrated on the basis of the olivine-to-wadsleyite (Morishima et al., 1994) and wadsleyite-to-ringwoodite (Suzuki et al., 2000) transformations in Mg_2SiO_4 and the akimotoite-to-bridgmanite transformation in $MgSiO_3$ (Kato et al., 1995). Temperature was measured with W3%Re–W25%Re thermocouples. Phases in the recovered samples were determined by XRD measurements using a Rigaku RINT RAPID II microdiffractometer with a curved imaging plate. The incident beam was Cu Kα radiation generated at 40 kV and 30 mA, and collimated to 300 μm in diameter. The exposure time was 30–60 min.

In situ XRD experiments were carried out at the synchrotron radiation facilities of the Photon Factory (AR-NE7) and SPring-8 (BL04B1) using the KMA apparatus MAX-III and SPEED1500, respectively. The sample assembly was similar to that used in the quenching method. White X-rays from synchrotron radiation were used as the incident X-ray beam. The diffracted beam was measured in the horizontal direction between the second-stage anvils by the energy-dispersive method using a Ge solid-state detector. The glancing angle (2θ) of the solid-state detector was fixed at 5.0° or 6.0°. The pressure was calculated from the unit-cell volume of gold (Tsuchiya, 2003) mixed with the sample. The starting powders were first compressed at room temperature and then heated in 100–200 K steps at 500 °C/s with a constant load. The temperature was held constant for about 60 min at each step during the collection of diffraction patterns for the sample every 30–600 s. The recovered samples were also analyzed using the Rigaku RINT RAPID II microdiffractometer mentioned above.

3. Results and discussion

3.1. LHDAC and KMA experiments on albite

Four transformation experiments were conducted in natural albite using LHDAC by the quenching method at 22–27 GPa and 1250–1750 °C. Fig. 1 and Table 1 give the average values of pressures before and after the laser heating, and the temperature and XRD data obtained from hot spot regions in the sample. XRD patterns taken from several points in the focus area of the laser spot showed similar results. The temperature–time history is shown in Fig. S1. Heating at the maximum temperature lasted several minutes. XRD analysis of the recovered samples revealed that a CF phase + stishovite assemblage was the dominant phase under our experimental conditions (Fig. S2; Table 1). Jadeite was also present at the lowest pressure of 22 GPa (Run ABPT11). We did not observe any evidence of linguunite in the LHDAC experiments using albite, although a tiny amount of phase egg was present at relatively low temperatures. Tutti (2007) also reported the presence of phase egg, probably due to absorbed water in the powdered starting material.

Previous LHDAC experiments using pure albite powder showed that small amounts of linguunite formed with jadeite, stishovite, and CF phase at around 21 GPa and ~1000 °C (Liu, 1978), and at 19–23 GPa and ~2000 °C (Tutti, 2007), implying that the linguunite stability field exists between the jadeite + stishovite and CF-phase + stishovite assemblages. In contrast, phase equilibrium studies in albite using a KMA apparatus indicated no stability field of linguunite around the boundary between these assemblages at 21–23 GPa and 800–2000 °C (Yagi et al., 1994; Akaogi et al., 2010). These apparent contradictions might reflect differences in the experimental methods. Temperature and pressure gradients within the sample are usually larger during LHDAC experiments than KMA experiments, especially when not using a proper