In Situ High Pressure X-Ray Measurements of a Low Symmetry Hydrous Silicate: High Pressure Stability of Phlogopite

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Introduction

Hydrous silicates receive a great deal of attention in the Earth sciences due to their importance for water transport and storage in the solid Earth [e.g. 1, 2, 3]. The critical role of water in the generation of arc volcanism is well uderstood [4], and key subduction zone related minerals have been investigated to determine their high pressure and temperature stability [e.g. 1, 5, 6-9]. Notably, it is estimated that more water is currently subducted into the mantle than is released by volcanic outgassing [e.g. 10]; this has accordingly generated broad interest in hydrous mineral phases.

Layered silicates, such as $Mg_2Si_4O_{10}(OH)_2$-talc, $KAl_3Si_3O_{10}(OH)_2$-muscovite and $KMg_3AlSi_3O_{10}(OH)_2$-phlogopite are common in metamorphic rocks and as such are likely important for water storage in the crust. Furthermore, it has been shown that phlogopite may be stable up to 6-7 GPa at temperatures between 1000 – 1300°C [11], and is therefore likely an important phase for metasomatic reactions in mantle wedges. However, few *in situ* measurements have been made to determine the structural response of such relatively low symmetry mineral phases to pressure. This is largely a result of the challenge inherent in collecting high-pressure data of high enough quality to accurately determine equations of state. Prior to the widespread use of synchrotron sources for *in situ* high pressure x-ray measurements of Earth minerals, Faust and Knittle [12] and Hazen and Finger [13] studied muscovite and phlogopite, respectively, using conventional x-ray sources. It is anticipated that these pioneering studies can be enhanced by the high quality data that can be quickly gathered using a dedicated high-pressure beamline at a modern synchrotron facility. Specifically, we are interested in producing more well-constrained equations of state and to make detailed observations of the pressure-induced modifications to these layered structures.

Methods and Materials

The phlogopite sample for the present measurements is from the IUSB mineral collection and is of unknown provenance. Electron microprobe analyses are in progress to determine the major element composition. The sample was ground under acetone using a corundum mortar and pestle to a mean grain size of ~5 μm in the largest dimension; due to the layered nature of the sample it is expected that preferential orientation will occur along the c direction.

High pressures were achieved using a diamond anvil cell equipped with 500 μm type I diamonds. A pre-indented and drilled spring steel gasket was used with a hole of 100 μm. The standard ruby fluorescence technique was used to monitor the pressure from three ~5 μm ruby grains both before and after each pressure measurement. A pressure medium of 16:3:1 methanol:ethanol:water by volume was used, and is expected to maintain a hydrostatic pressure environment over the range of pressure investigated (<10 GPa).

Experiments were conducted at beamline ID-B of Sector 16 (HPCAT) using the MAR345 imaging plate system. Monochromatic x-rays with a wavelength of 0.4157 Å were collimated and passed through a 20 μm diameter pinhole with a sample to detector distance of 428 mm. Exposure times of 60 seconds produced high quality diffraction patterns.

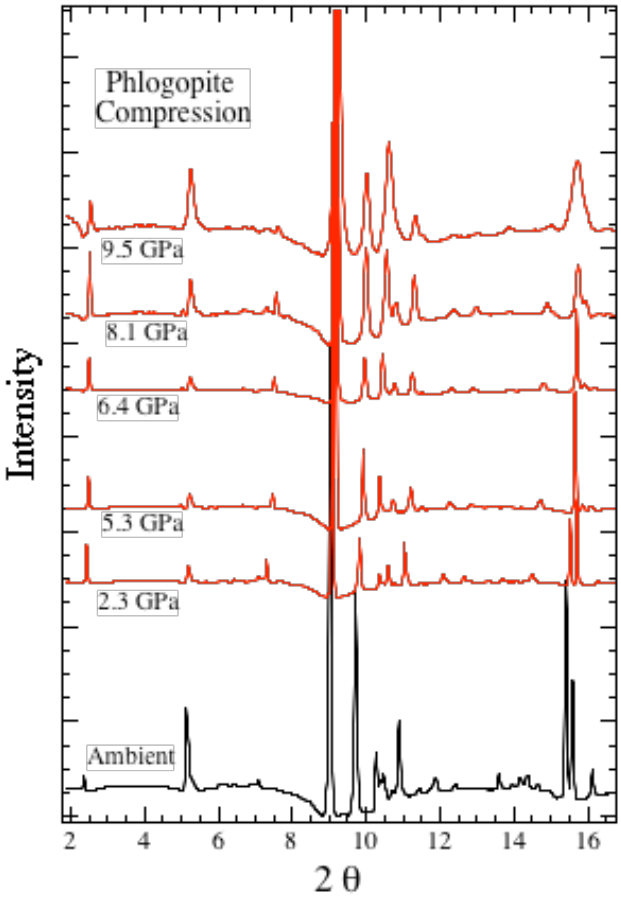

Fig. 1. X-ray spectra of phlogopite taken during compression to 9.5 GPa. Modifications are observed near 10 and 15°, but the ambient pressure spectrum is reproduced after decompression.

Results

The ambient pressure diffraction pattern agrees well with previous phlogopite measurements and peaks are readily indexed to a monoclinic unit cell (space group C 2/m) with **a** = 5.378±0.002, **b** = 9.289±0.004, **c** = 10.245±0.013 Å and **β** = 99.75±0.07°. During compression to 9.5 GPa there is an apparent convergence of two peaks that occurs near 15.5° between 2 and 5 GPa and a steady increase in amplitude of a feature initially at 10.5° over the entire pressure range studied (Fig.1). This is most likely associated with enhanced preferred orientation as the c-axis accommodates the majority of compression in this phase; yet, it may indicate the onset of a minor structural transformation. However, the ambient pressure

spectrum after decompression is essentially indistinguishable from the pre-compression spectrum (Fig. 2).

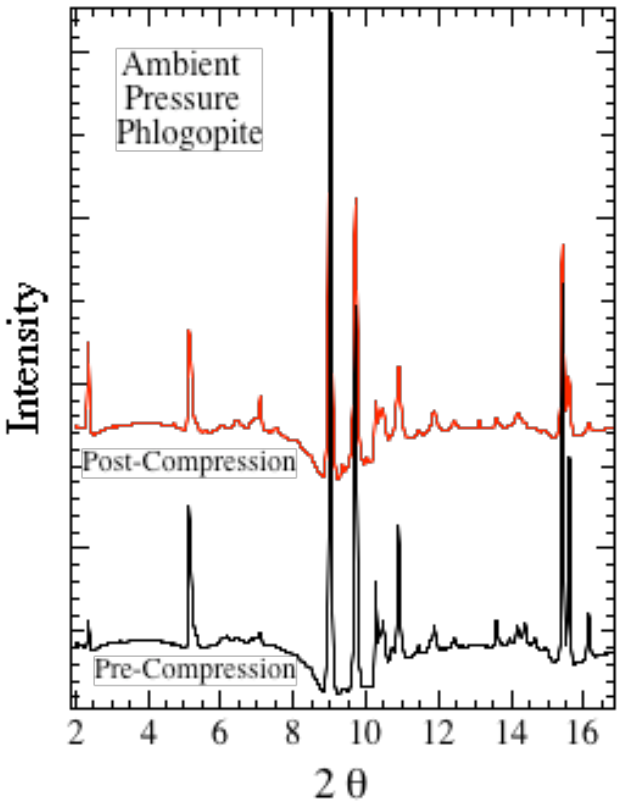

Fig. 2. X-ray spectra of phlogopite taken before and after compression to 9.5 GPa. Notably, although there are pressure-induced modifications to the diffraction patterns and peak broadening at the highest pressure measured, the pre-compression and post-compression spectra are essentially indistinguishable.

Discussion

Peak broadening is observed at the highest pressure of this study, however, which likely indicates that the structure is close to its maximum pressure stability at 300 K. Note that the previously-determined high pressure stability at high temperature was found to be 6-7 GPa [11]. As has been found for other silicate minerals [e.g. 8] it appears that at phlogopite can persist metastably at low temperatures well beyond its nominal stability field along a terrestrial geotherm.

The diffraction data from this study will be inverted for lattice parameters and unit cell volume to determine a 300 K equation of state. This result will be compared to the previous measurement of Hazen and Finger [13]. The data for the previous study were collected prior to the use of synchrotron x-rays for high-pressure studies, and the measurements were limited in pressure range (<5 GPa) and constrained by only 3 volumes at elevated pressure. The dedicated high-pressure beamlines of HPCAT have made it relatively quick and easy to collect closely spaced, high quality, diffraction data over a wide pressure range. Accordingly, it will now be possible improve the accuracy and availability of equation of state measurements; such thermodynamic data are necessary to calculate and model phase relations in an effort to fully understand the storage and transport of water in the deep Earth.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. We are grateful to the excellent support and facilities maintined by the HPCAT at Sector 16.

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