

**A LUNAR HYGROMETER BASED ON PLAGIOCLASE-MELT PARTITIONING OF HYDROGEN.**

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**Introduction:** The classic view of a dry lunar interior has been challenged by recent discoveries of hydrogen (H, often reported as equivalent amounts of OH or H<sub>2</sub>O) in lunar samples [1-4]. Sample-based inferences about water in the Moon are complemented by experimental studies of lunar magma ocean crystallization, that suggest the presence of water in the early Moon is required to explain the observed thickness of the lunar crust [5]. Converting measured hydrogen abundances in samples or experiments to quantitative estimates of the abundance of water in the Moon and its temporal and spatial evolution is, however, far from straightforward [6]. As a result, estimates of lunar interior water contents vary by several orders of magnitude from <10 ppm to >1000 ppm.

This study focuses on improving constraints on the water content in the Moon specifically during the lunar magma ocean (LMO) stage. Nominally anhydrous plagioclase is thought to have crystallized and floated to the surface during the later stages of LMO cooling, forming the primary lunar crust [5,7,8]. This indicates that lunar plagioclase from ferroan anorthosite, a direct product of the LMO [9], could be our best candidate for estimating the water content of the LMO [10].

To link plagioclase water contents to the water contents in the LMO from which these crystals grew, plagioclase-melt partition coefficients for hydrogen are required, with  $D_{\text{water}}^{\text{plag-melt}} = C_{\text{OH}}^{\text{plag}} / C_{\text{OH}}^{\text{melt}} = C_{\text{H}}^{\text{plag}} / C_{\text{H}}^{\text{melt}}$ . Unfortunately, to date, no plagioclase-melt partitioning data for water are available under lunar conditions. In this study,  $D_{\text{water}}^{\text{plag-melt}}$  was measured for the first time at lunar-relevant pressure-temperature-composition-oxygen fugacity conditions using high-pressure and high-temperature experiments and Fourier-transform infrared (FTIR) spectroscopy. The main purpose of this study is to offer further constraints on the LMO content of the Moon at the time of plagioclase formation.

**Experimental:** The composition of our starting material and the experimental pressure-temperature conditions were based on our recent experimental study of lunar magma ocean crystallization [5]. High-pressure, high-temperature experiments were performed in a piston cylinder press using a half-inch diameter talc-pyrex cell assembly. For these experiments a hand-machined graphite bucket was filled with starting material, closed with a graphite lid and inserted in a gold-palladium (Au<sub>80</sub>Pd<sub>20</sub>) capsule. Experiments were pressurized cold and then heated to a superliquidus temperature of 1280 °C in

20 mins. Subsequently, samples were cooled to the temperature of interest at a rate of 10 °C per hour while maintaining target pressure, followed by 14–22 hours at target temperature. Pressure was 0.4 GPa in all experiments performed to date, and final target temperatures ranged from 1160 to 1200 °C. At completion of an experiment, runs were quenched by cutting power to the heater and the temperature typically dropped below the glass transition in < 10 s.

**Analytical:** Experimental run products were mounted in epoxy and polished for back-scattered electron (BSE) imagery (Fig. 1) to assess texture and mineralogy, and then carbon coated for electron microprobe analysis (EMPA). After EMPA analysis, hydrogen concentrations in minerals and coexisting glass in our samples were analyzed at the State Key Laboratory for Mineral Deposits Research, Nanjing University, using a Nicolet IS50 Fourier Transform Infrared Spectrometer equipped with Continuum microscope, liquid nitrogen cooled MCT/A detector and KBr beam splitter.

**Results:** Experiments produced plagioclase crystals in equilibrium with quenched melt (Figure 1).

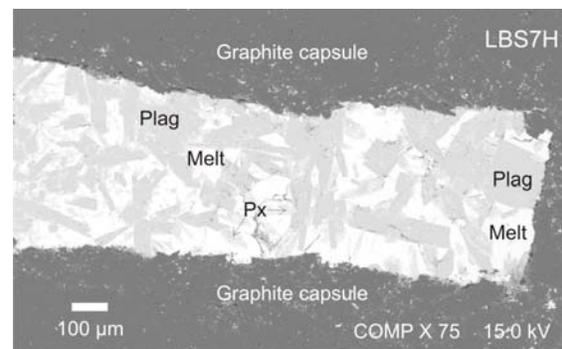


Figure 1: Back scattered electron (BSE) image of a representative experimental run product (LBS7H, 0.4 GPa – 1200 °C). Px = pyroxene; Plag = plagioclase.

The hydrogen concentrations of our samples range from 58±18 to 99±36 ppm OH in plagioclase and from 0.24±0.09 to 1.03±0.16 wt.% OH in glass. The corresponding partition coefficients range between 0.006±0.002 and 0.04±0.01. Water partitioning values decrease with increasing abundance of water in coexisting glass. The lowest  $D$  value in our experiments is still higher than almost all previously published data ( $D_{\text{water}}^{\text{plag-melt}} = 0.001–0.006$  based on Hamada et al. [11]). Our highest partition coefficient

is ~10 times higher than previously reported values. The possible reason for this major difference is likely oxygen fugacity, consistent with previous observations about the dependence of H solubility in feldspars on oxygen fugacity [12].

**Discussion and Conclusions:** The only study published to date of the water content of lunar plagioclase reported 6.4 ppm water (H<sub>2</sub>O equivalent) in ferroan anorthosite sample 60015 [10], thought to be a primary crystallization product of the LMO [9,13]. Our experiments constrains  $D_{\text{water}}^{\text{plag-melt}}$  to 0.006–0.04 under lunar conditions. Based on the above constraints, the amounts of water (in terms of equivalent H<sub>2</sub>O) in the residual LMO after ~75 per cent solidification of the initial magma ocean is calculated to be 160–1130 ppm. We previously showed that the minimum amount of water in the initial LMO was 500–1800 ppm (with the lower minimum linked to a shallow (400 km) initial magma ocean and the higher minimum linked to a deep (1000 km) initial magma ocean) [5]. If no H degassing from the LMO had occurred until sample 60015 was formed, the water content of the LMO at the time of plagioclase formation should have been 0.2–0.72 wt.%. The much lower estimates of the amount of water remaining in the LMO by the time of formation of 60015, derived from our plagioclase-based hygrometer, indicate that the early Moon experienced extensive degassing during the LMO stage, with ~45–98 per cent of the initial water lost during the first three quarters of LMO crystallisation.

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