Abstract—The identification of hydrogen in a range of lunar samples and the similarity of its abundance and isotopic composition with terrestrial values suggest that water could have been present in the Moon since its formation. To quantify the effect of water on early lunar differentiation, we present new analyses of a high-pressure, high-temperature experimental study designed to model the mineralogical and geochemical evolution of the solidification material equivalent to 700 km deep lunar magma oceans first reported in Lin et al. (2017a). We also performed additional experiments to better quantify water contents in the run products. Water contents in the melt phases in hydrous run products spanning a range of crystallization steps were quantified directly using a secondary ion mass spectrometry (SIMS). Results suggest that a significant but constant proportion (68 ± 5%) of the hydrogen originally added to the experiments was lost from the starting material independent of run conditions and run duration. The volume of plagioclase formed during our crystallization experiments can be combined with the measured water contents and the observed crustal thickness on the Moon to provide an updated lunar interior hygrometer. Our data suggest that at least 45–354 ppm H$_2$O equivalent was present in the Moon at the time of crust formation. These estimates confirm the inference of Lin et al. (2017a) that the Moon was wet during its magma ocean stage, with corrected absolute water contents now comparable to estimates derived from the water content in a range of lunar samples.

INTRODUCTION

The Moon is thought to have formed in a giant impact between a Mars-sized impactor and the proto-Earth (e.g., Čuk and Stewart 2012; Canup 2012; Lock et al. 2018). Its early differentiation was likely accompanied by the presence of a global silicate magma ocean, referred to as the lunar magma ocean (LMO; e.g., Smith et al. 1970; Wood et al. 1970; Warren 1985; Shearer et al. 2006). Estimates for the initial LMO depth range from 400 km based on Snyder et al. (1992) to 1350 km (equivalent to whole Moon melting) based on pressure–temperature (P–T) conditions derived from models of core formation in the Moon (e.g., Righter and Drake 1996; Rai and Van Westrenen 2014; Steenstra et al. 2016). Crystallization of the LMO is thought to have created a series of concentric cumulate layers with different chemical compositions and mineralogical assemblages in the lunar interior, and a ferroan anorthosite primary crust via flotation of low-density plagioclase-rich cumulates (e.g., Warren 1985; Snyder et al. 1992; Shearer et al. 2006; Elardo et al. 2011; Elkins-Tanton et al. 2011).

The crystallization sequence and composition of these cumulate layers and plagioclase-rich crust are of primary importance for understanding subsequent events in lunar evolution, including a proposed density-driven overturn in the mantle (e.g., Hess and Parmentier 1995; Stegman and Richards 2003; Zhang et al. 2013; Li et al. 2019; Pernet-Fisher et al. 2019; Zhao et al. 2019) leading
to decompression mantle melting and mare basalt volcanism. Recently, several experimental studies of the crystallization sequence of deep, nominally anhydrous LMOs were published (Lin et al. 2017b; Charlier et al. 2018; Rapp and Draper 2018). Lin et al. (2017b) found that (1) the cumulates formed during the first ~50% of LMO crystallization characterized by dense olivine (Ol) and orthopyroxene (Opx), (2) plagioclase first appeared after 68 vol% solidification (PCS), (3) ilmenite and β-quartz formed toward the end of crystallization, and (4) the last percent of magma remaining was extremely iron-rich (>26 wt% FeO). Lin et al. (2017b) showed several differences with the models of dry LMO crystallization (Snyder et al. 1992; Elardo et al. 2011; Elkins-Tanton et al. 2011; Charlier et al. 2018; Rapp and Draper 2018), in part due to its incorporating explicitly the effect of variable pressure within a deep magma ocean on crystallization.

Over the past 10 years, the classical view of an anhydrous, volatile-poor Moon has been challenged by the discovery of water and other volatiles in lunar pyroclastic glass (Saal et al. 2008, 2013; Füri et al. 2014; Hauri et al. 2015; Wetzel et al. 2015), apatites (e.g., McCubbin et al. 2010; Greenwood et al. 2011; Tartèse and Anand 2013; Tartèse et al. 2013, 2014; Barnes et al. 2014, 2016; Boyce et al. 2015; Potts et al. 2018; see review by Lin and van Westrenen 2019), melt inclusions hosted in olivine (Hauri et al. 2011; Saal et al. 2013; Chen et al. 2015; Wetzel et al. 2015; Füri et al. 2017; Ni et al. 2019), and plagioclase crystals believed to be remnants of the solidification of the LMO (Hui et al. 2013, 2017). Water could therefore play an important role in the evolution of the Moon, including perhaps during the cooling and crystallization of an early LMO. The presence and abundance of water affect chemical and physical properties of both magma and minerals, including changing the liquid line of descent of melt, suppressing the crystallization of plagioclase relative to olivine and clinopyroxene in mid-ocean ridge basalts (Sisson and Grove 1993; Danyushevsky 2001), and changing mineral and melt viscosities (e.g., Hirth and Kohlstedt 1996; Hui and Zhang 2007; Giordano et al. 2008).

To better understand the evolutionary history of a water-bearing LMO, including its crystallization sequence, the chemical compositions of cumulates, corresponding residual LMO during progressive solidification, and the quantitative differences between dry and wet LMO solidification scenarios, we performed a series of experiments at high $P-T$ conditions that are directly relevant to the evolution of the lunar interior. The crystallization sequence of these experiments was previously described in Lin et al. (2017a), but the full chemical compositions of minerals and melts were not discussed previously. In addition, the water contents in the experiments of Lin et al. (2017a) were not determined quantitatively, but were estimated indirectly from deficiencies in the totals of electron microprobe analyses (which cannot detect water) of experimental melt phases, assuming these deficiencies were fully due to the presence of water.

Here, we provide secondary ion mass spectrometry (SIMS) data for a subset of our experiments enabling quantitative assessment of the water content of our experiments. A representative subset was obtained by selecting samples from a wide range of crystallization steps, as these should cover a wide range of water contents. Our results, indicating less hydrogen was present in the experimental run products than originally estimated, prompted an additional set of experiments which were also analyzed by SIMS, aimed at elucidating the reason and timing of the water loss. Final results are compared to results of the crystallization of a nominally dry LMO of the same major element composition (Lin et al. 2017b), to better quantify the effect of water, and to provide constraints on the likely range of LMO water content.

**METHODS**

**Experimental Approach**

Our experimental approach is identical to that outlined in our study focusing on the evolution of a nominally dry LMO (Lin et al. 2017b), slightly adjusted to be able to quantify the effect of water. We assume water does not significantly affect the Ol/Opx ratio during early LMO crystallization steps, because the olivine-pyroxene-plagioclase piercing point in the olivine-clinopyroxene-plagioclase ternary moves toward plagioclase, nearly perpendicular to the olivine-clinopyroxene join, with increasing water (Sisson and Grove 1993). Water-bearing experiments were therefore performed starting from the fifth crystallization step of our nominally dry LMO solidification model (Lin et al. 2017b), which was the first step in which plagioclase formed, at 68% solidification (PCS) of the LMO. We simulated two hydrous LMO scenarios with different water contents by adding Mg(OH)$_2$ to produce the equivalent of 0.5 and 1 wt% H$_2$O in the residual liquid composition calculated from the fourth step of the dry LMO solidification series (the step before plagioclase first formed in the nominally dry experiments; Lin et al. 2017b). We refer to these two series as low-H (with sample names given as LBS$n$H, with $n$ denoting a specific number in the sequence of crystallization steps) and high-H (with sample names given as LBS$n$H, with $n$ the step number), respectively. If all hydrogen in our
experiments remained in the silicate materials, this approach would be equivalent to adding 1575 (low-H) and 3150 (high-H) ppm (by weight) H₂O equivalent in the initial LMO. These numbers are based on neglecting the very small amounts of hydrogen incorporated in the nominally anhydrous minerals olivine (<3 ppm) and orthopyroxene (<25 ppm) based on their low mineral-melt partition coefficients for water of 0.0015–0.0016 and 0.0046–0.0142, respectively (Adam et al. 2016). The water concentrations in subsequent starting materials were calculated based on mass balance and the percentage of the residual liquid of the previous crystallization step after removal of the corresponding crystal assemblage. For simplicity, we assumed here that no water degassing occurred and that separation between mineral and melt was very efficient during progressive LMO crystallization, which is undoubtedly an oversimplification (e.g., Elkins-Tanton and Grove 2011; Barnes et al. 2016).

Starting Materials

Target starting material compositions are listed in Table 1. With the exception of the addition of water, synthesis of the starting materials used the same approach as in Lin et al. (2017b) and is repeated here for completeness. The major element composition of our starting material was based on a model of lunar mantle composition derived from geophysical data (Khan et al. 2007) in the simplified chemical system Fe-Ca-Mg-Al-Ti-Si-O to enable direct comparison with our results in the nominally dry system. Starting materials were prepared by mixing appropriate amounts of high purity (99.5–99.99%, Alfa Aesar) powdered (hydr)oxides (MgO, Mg[OH]₂, Fe₂O₃, Al₂O₃, Al[OH]₃, TiO₂, SiO₂) and CaCO₃ (99.95–100.05%, Alfa Aesar). The oxides MgO, Al₂O₃, TiO₂, and SiO₂ were fired overnight at 1000 °C and then stored at 110 °C prior to use. The other oxides, hydroxides, and calcium carbonate were dried at 110 °C overnight prior to use. Starting material preparation involved two stages. In the first stage, after mixing nominally dry starting materials under ethanol in an agate mortar for 1 h, they were dried in air and decarbonated in a Pt crucible in a box furnace by gradually raising the temperature from 650 to 1000 °C in approximately 7 h. The Pt crucible had previously been iron saturated to minimize iron loss. The resulting mixtures were melted in air for 20 min at 1500 °C to promote homogeneity, and to reduce most of the iron in the starting material to 2+. The homogenized glass was quenched by immersing the bottom of Pt crucible in water. Small fragments of all resulting glasses were embedded in ClaroFast acrylic resin (Struers), polished, carbon coated, and analyzed for homogeneity by electron microprobe. The glasses were subsequently crushed, dried, and reground under ethanol in an agate mortar for 1 h and then kept at 110 °C until use. In the second stage of starting material preparation, water was added to dry glass using Mg(OH)₂ or Al(OH)₃. In all starting material batches, the Mg or Al added as oxides in the first stage was lowered to quantitatively account for the Mg or Al added subsequently in hydroxide form in the second stage.

High-Pressure Experiments

A total of 24 high-pressure, high-temperature experiments initially reported in Lin et al. (2017a), as well as one new experiment at 0.4 GPa and 1180 °C in the “low-H” series, were performed in a piston cylinder press using a half inch (12.7 mm) diameter tälle-pyrex cell assembly, using the pressure calibration of Van Kan Parker et al. (2011). For these experiments, a hand-machined graphite bucket, with an inner diameter (ID) of 0.7 mm, outer diameter (OD) of ~1.7 mm, and a length of 3–4 mm, was filled with starting material, closed with a graphite lid, and inserted in a gold-palladium (Au₈₀Pd₂₀) capsule, with an ID of 1.7 mm, OD of 2 mm, and a length of 5–7 mm. The bottom of the Au₈₀Pd₂₀ capsule was triple crimped, flattened, and welded shut at one end. After inserting the graphite capsule, the other end was crimped and welded shut. Graphite was added to ensure that iron in the experiments remained predominantly divalent, as is the case in the Moon.

An additional set of three experiments at identical P–T conditions of 0.4 GPa and 1200 °C focused on the effect of run duration from 2 to 24 h on the run products (referred to in the rest of the manuscript as “leak test experiments”). SIMS data for the water contents of the silicate glass in these run products were used to identify when water is lost from the silicate portion of the charges. For this additional set, the prepared, sealed capsules were weighed three times before and after running to assess hydrogen loss from the capsules (Table S1 in Data S1 of supporting information). Before performing these additional experiments, the welded capsules were weighed before and after putting in ethanol for 30 min, and then weighed again after heating for 1 h in a 110 °C oven. Only capsules showing no weight loss were selected. After experiments, the samples were weighed again in the same processes. In general, the capsule masses after experiments are slightly larger than before the experiments, because the MgO rod surrounding the capsules could not be completely removed. Temperature was monitored using a W₅Re–W₁₈Re (type C) thermocouple and Omega CN76000 programmable
### Table 1. Summary of experimental conditions and results.

| Wet exp. | Conditions | Results |
|----------|------------|---------|
|          | Starting composition | Duration (h) | Phase | SiO₂ | TiO₂ | Al₂O₃ | FeO | MgO | CaO | Total mass | Phase proportion (modal %) | Mg# |
|          | T (°C) | P (GPa) |          |      |      |      |      |      |      |            |                          |     |
| High-H   |        |        |          |      |      |      |      |      |      |            |                          |     |
| LBS5H    | 1240   | 0.8    | 4        | 0.18  | 0.01 | 0.16 | 0.75 | 0.47 | 0.38 | 0.31       | 89.0          | 92  |
|          |        |        |          | 0.22  | 0.04 | 0.17 | 0.65 | 0.47 | 0.38 | 0.31       | 89.0          | 92  |
|          |        |        |          | 0.40  | 0.10 | 0.16 | 0.75 | 0.50 | 0.55 | 0.02       | 90.0          | 91  |
| LBS6H    | 1220   | 0.8    | 8        | 0.38  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.38  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.47  | 0.12 | 0.15 | 0.75 | 0.50 | 0.55 | 0.02       | 90.0          | 91  |
| LBS7H    | 1200   | 0.7    | 12       | 0.51  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.38  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.47  | 0.12 | 0.15 | 0.75 | 0.50 | 0.55 | 0.02       | 90.0          | 91  |
| LBS8H    | 1180   | 0.6    | 20       | 0.51  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.38  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.47  | 0.12 | 0.15 | 0.75 | 0.50 | 0.55 | 0.02       | 90.0          | 91  |
| LBS9H    | 1160   | 0.4    | 24       | 0.51  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.38  | 0.04 | 0.08 | 0.15 | 0.36 | 0.65 | 0.03       | 88.0          | 89  |
|          |        |        |          | 0.47  | 0.12 | 0.15 | 0.75 | 0.50 | 0.55 | 0.02       | 90.0          | 91  |
| Oxygen fugacity buffer | Log ($\log_f O_2$) | Olivine $K^O_0$ | Olivine $K^O_0$ | Pyroxene $K^O_0$ | Pyroxene (EnFsWo) | Mineral assemblage (vol%) | Global crystallization proportion | PCS | Depth (km) | Floating crustal thickness (100% plagioclase) (km) |
|------------------------|------------------|----------------|----------------|----------------|----------------|--------------------------|---------------------------------|-----|-----------|-----------------------------------------------|
| Graphite–COH (C–COH)   | –9.2             | 0.30           | 0.32           |                |                | Olivine (Fo83)           | 1.1                             | 69.6| 154       | 0                                             |
|                        | –9.7             | 0.29           | 0.32           |                |                |                          |                                 |     |           |                                               |
|                        | –10.1            |                |                |                |                |                          |                                 |     |           |                                               |
|                        | –9.4             | 0.30           |                | En75Fs18Wo7    | Pyroxene (En75–75Fs18–17Wo7–4) | 3.7                     | 73.3                           | 134 | 0         |                                               |
|                        | –9.8             | 0.30           |                | En78Fs18Wo4    |                |                          |                                 |     |           |                                               |
|                        | –10.3            |                |                |                |                |                          |                                 |     |           |                                               |
|                        | –9.7             | 0.28           |                | En77Fs19Wo4    | 20% Olivine (Fo81) + 60% pyroxene (En76–77Fs19–18Wo4) + 20% plagioclase | 3.5                     | 76.8                           | 119 | 3.2       |                                               |
|                        | –10.0            | 0.27           | 0.32           | 0.27           | En78Fs18Wo4    | plagioclase              |                                 |     |           |                                               |
|                        | –10.5            |                |                |                |                |                          |                                 |     |           |                                               |
|                        | –10.0            | 0.31           |                | En63Fs25Wo12   | 60% Pyroxene (En66–65Fs25–24Wo12–18) + 40% plagioclase | 5.8                     | 82.6                           | 101 | 14.1      |                                               |
|                        | –10.2            | 0.29           |                | En66Fs24Wo10   |                |                          |                                 |     |           |                                               |
|                        | –10.7            |                |                |                |                |                          |                                 |     |           |                                               |
|                        | –10.4            | 0.29           |                | En60Fs28Wo12   | 62% Pyroxene (En60–61Fs28–27Wo12–17) + 38% plagioclase | 5.9                     | 88.5                           | 80  | 24.9      |                                               |
Table 1. Continued. Summary of experimental conditions and results.

| Wet exp. | Starting composition | $T$ ($^\circ$C) | $P$ (GPa) | Duration (h) | Phase | $n$ | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO | MgO | CaO | Total mass (modal %) | Mg# |
|----------|---------------------|----------------|------------|-------------|-------|-----|--------|--------|-------------|-----|-----|-----|---------------------|-----|
| LBS10H   | 1130                | 0.4            | 48         | Cpx         | 8     | 45.49 | 4.66   | 6.21   | 17.30       | 10.90 | 14.77 | 98.9 | 30                  | 53  |
|          |                     |                |            | Spinel      | 5     | 5 66  | 5.64   | 61.03  | 23.49       | 6.94  | 2.24  | 99.9 | 6                  | 34  |
|          |                     |                |            | Ilmenite    | 5     | 1.07  | 50.63  | 0.63   | 45.60       | 1.37  | 0.72  | 100.0 | 4                 | 5   |
|          |                     |                |            | $\beta$-Quartz | 7    | 96.92 | 0.30   | 0.28   | 0.59        | 0.04  | 0.12  | 98.2  | 9                | 12  |
|          |                     |                |            | Liquid      | 6     | 48.01 | 1.09   | 13.57  | 16.16       | 4.24  | 13.65 | 96.7  | 46                | 32  |
| Low-H    | LBS5H-              | 1240           | 0.8        | 4           | Opx   | 7     | 53.48  | 0.36   | 5.15        | 10.81 | 29.04 | 100.7 | 17                | 83  |
|          |                     |                |            | Liquid      | 9     | 46.61 | 1.80   | 16.30  | 12.77       | 9.70  | 1.60  | 100.3 | 10               | 83  |
|          |                     |                |            | Liquid      | 8     | 47.08 | 1.74   | 15.31  | 12.89       | 9.27  | 11.35 | 98.2  | 87                | 56  |
|          |                     |                |            | Liquid      | 5     | 48.11 | 1.59   | 14.29  | 12.93       | 13.20 | 16.29 | 99.4  | 100              | 63  |
|          |                     |                |            | Cpx         | 7     | 53.97 | 0.36   | 5.08   | 12.67       | 7.29  | 14.68 | 99.8  | 10                | 79  |
|          |                     |                |            | Cpx         | 5     | 52.65 | 0.54   | 4.81   | 12.37       | 25.93 | 3.51  | 99.8  | 86                | 52  |
|          |                     |                |            | Liquid      | 6     | 47.58 | 1.94   | 16.82  | 12.00       | 7.57  | 11.68 | 98.2  | 87                | 56  |
|          |                     |                |            | Liquid      | 6     | 48.72 | 2.33   | 16.62  | 12.68       | 7.26  | 11.44 | 99.1  | 100              | 63  |
|          |                     |                |            | Liquid      | 5     | 47.54 | 1.70   | 15.25  | 12.88       | 10.53 | 10.98 | 98.9  | 100              | 59  |
|          |                     |                |            | Liquid      | 6     | 47.82 | 2.33   | 16.62  | 12.68       | 7.26  | 11.44 | 99.1  | 100              | 59  |
|          |                     |                |            | Cpx         | 7     | 54.64 | 0.40   | 2.94   | 12.62       | 27.07 | 2.08  | 99.8  | 10                | 79  |
|          |                     |                |            | Cpx         | 5     | 52.65 | 0.54   | 4.81   | 12.37       | 25.93 | 3.51  | 99.8  | 86                | 52  |
|          |                     |                |            | Liquid      | 6     | 47.58 | 1.94   | 16.82  | 12.00       | 7.57  | 11.68 | 98.2  | 87                | 56  |
|          |                     |                |            | Liquid      | 5     | 47.75 | 2.69   | 15.11  | 14.51       | 8.44  | 12.00 | 98.9  | 86                | 46  |

Olivine $K_D^{Fe-Mg} = K_D^O[X_{FeO-Olivine}]X_{MgO-Liquid} - X_{FeO-Liquid}X_{MgO-Olivine}$; Olivine $K_D^{Fe-Mg}$ was calculated and corrected after Toplis (2005). Phase abundances calculated using least squares mass balance and area percentage. Compositions from EMPA in wt% oxides. 1 sigma standard deviations (1SD) based on multiple analyses for each phase are shown in italic. At PCS = 99.0, the calculated crustal thickness is 42 km (SD = 1.13) at 1575 ppm H$_2$O (Low-H) equivalent, and 40 km (SD = 1.28) at 3150 ppm H$_2$O (High-H) equivalent, respectively. PCS = per cent solid by volume. *Including quartz. n, number of analyses.
| Oxygen fugacity | Log $\left( f_{O_2} \right)$ | Olivine $K_D$ | Olivine $K_D$ | Pyroxene $K_D$ | Pyroxene $(\text{EnFsWo})$ | Mineral assemblage (vol%) | Global crystallization proportion | Residual LMO Depth (km) | Floating crustal thickness (100% plagioclase) (km) |
|----------------|-------------------------------|---------------|---------------|-----------------|--------------------------|---------------------------|-------------------------------|----------------|----------------------------------|
| −10.8          | −10.8                         | 0.42          |               |                 | En35Fs31Wo34            | 6.2                       | 94.7                         | 57.5           | 32.2²                             |
|                |                               |               |               |                 |                          | 56% Pyroxene $(\text{En35Fs31Wo34})$ + 9% plagioclase + 7% ilmenite + 1% quartz + 11% spinel |                               |                               |                               |                   |
| −9.2           | −9.2                          | 0.28          |               |                 | En80Fs17Wo3             | 10% Olivine $(\text{Fo83})$ + 90% pyroxene $(\text{En81-80Fs17-16Wo4-3})$ | 3.1                         | 71.6                        | 144             | 0                                |
|                |                               |               |               |                 | En81Fs16Wo3             |                          |                               |                               |                   |
| −9.7           | −9.7                          | 0.27          | 0.31          | 0.26            | En73Fs20Wo7             | 32% Olivine $(\text{Fo76-75})$ + 45% pyroxene $(\text{En73-71Fs22-21Wo7-6})$ + 23% plagioclase | 4.2                         | 75.8                        | 125             | 4.5                              |
|                |                               |               |               |                 | En76Fs20Wo4             |                          |                               |                               |                   |
| −10.1          |                               |               |               |                 | En71Fs22Wo7             | 59% Pyroxene $(\text{Fo73-72Fs20-19Wo7-6})$ +41% plagioclase | 5.2                         | 81.0                        | 107             | 14.6                             |
| −9.7           | −9.7                          | 0.25          |               |                 | En73Fs21Wo6             |                          |                               |                               |                   |
| −10.3          |                               |               |               |                 |                          | 64% Pyroxene $(\text{En68Fs25Wo7})$ +36% plagioclase | 2.7                         | 83.7                        | 99              | 19.0                             |
| −10.2          |                               |               |               |                 |                          | 64% Pyroxene $(\text{En68Fs25Wo7})$ +36% plagioclase | 2.7                         | 83.7                        | 99              | 19.0                             |
controller. The center of the sample was located in the hot spot of the assembly, 2 mm away from the thermocouple tip end, so that sample temperatures were within 10 °C of the thermocouple reading (Watson et al. 2002). Experiments were pressurized cold and then heated while maintaining pressure. Pressures range from 0.4 to 0.8 GPa and temperatures from 1130 to 1240 °C (e.g., Tonks and Melosh 1990; Elkins-Tanton et al. 2011). Additional experiments at 1 atm were run in a high-temperature box furnace (temperatures between 1180 and 1240 °C), using capsule setups that were identical to the high-pressure experiments. These experimental temperature ranges cover conditions in which our samples are partially molten, as required to be able to study the magma ocean crystallization process. Experiment duration varied between 4 and 48 h depending on the melting degree and temperature. 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 Techniques

Electron Microprobe Analysis

Experimental run products were mounted in resin epoxy and polished to a <1 μm finish and carbon coated. Backscattered electron image was used to assess the texture and mineralogy. The major element chemical compositions of the run product phases (minerals and quenched melts) were determined with electron microprobe analysis (EMPA) using a JEOL JXA-8800M electron microprobe at Utrecht University, and checked for contamination and iron loss. Analyses were conducted using an accelerating voltage of 15 kV and a beam current of 20 nA for Si, Ti, Al, Fe, Mg, and Ca. Analyses were calibrated against primary standards of diopside (Ca, Si), fayalite (Fe), ilmenite (Ti), forsterite (Mg), and orthoclase (Al). Peak areas were converted to concentrations using certified standard compositions. Peak count times were 20 s and background count time 10 s. We used three different beam diameters of 1, 10, and 20 μm for the mineral phases, glassy quenched melts nearly free of quench crystals, and quenched melts, respectively. In all cases, detection limits for these elements are less than 0.01 wt%. Compositions reported here are based on the average of 5–10 analyses. The mineral and melt proportions were determined by mass balance calculations using major cation abundances in the starting materials and run product phases obtained from EMPA analyses combined with area percentages derived from mapping of the charges with an EDAX-EDS system in imaging mode. The uncertainties on the mass balance calculations reported here are less than 2%.

Secondary Ion Mass Spectrometry

It was not feasible to analyze all experimental charges by SIMS due to limitations in terms of available analytical time, coupled with the challenges of analyzing experimental samples with low glass volumes (making it undoable to obtain glass-only analytical spots using SIMS). We selected samples so that they covered both experimental series (low H and high H) and hence a broad range of added water contents, as well as a range of temperature and pressure conditions, and run durations (see Table 3). Selected experimental run products in which the surface exposures of quenched silicate melts showed large areas of homogeneous glass (8 of 27 experiments) were removed from their ClaroFast epoxy holders, enclosed into tin-based alloy, and reground with sand paper (2000 grit silicon carbide) and polished by a diamond polishing medium (0.5 μm polycrystalline diamond suspension). All mounts were dried in an oven for several days before coating with gold for SIMS analysis. The Cameca IMS 1280-HR ion microprobe at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences was used for all of the SIMS measurements (Zhang et al. 2018; Xia et al. 2019). To minimize hydrogen backgrounds, the instrument was baked for 24 h and samples were kept in the sample storage chamber (<5 × 10⁻⁸ mbar) for several days prior to analyses. The vacuum of the analysis chamber with an automatic liquid nitrogen refilling system working during analyses was regulated to less than 5 × 10⁻⁸ mbar. We followed analytical procedures developed specifically for hydrogen measurements with this instrument (Xia et al. 2019). Analyses were made using a Cs⁺ primary beam with a beam current of 4.0–4.4 nA with an accelerating voltage of 10 kV. The size of the analytical area was about 30 × 30 μm (15 μm spot size + 15 μm rastering; Xia et al. 2019). ¹⁶O⁻ and ¹⁸O¹H⁻ were collected simultaneously and ¹⁶O¹H⁻/¹⁶O⁻ ratios were calibrated to yield estimates of water content for each spot analysis. ¹⁶O¹H⁻ was resolved from ¹⁷O at a mass resolving power of approximately 7000. The hydrogen background during the analyses is on the order of 10 ppm (Xia et al. 2019), which is more than two orders of magnitude lower than the lowest water content in our calibration standards and samples. The reproducibility of an individual measurement, based on repeated standard measurements of six standards (Li et al. 2015), is about ±10%. The H₂O content of glass was determined from the measured ¹⁶O¹H⁻/¹⁶O⁻ ratios and a calibration curve of H₂O (wt%) versus ¹⁸O¹H⁻/¹⁶O⁻ determined using six well-characterized hydrous glass standards synthesized at high pressure and high temperature, with independent measurements.
of water contents obtained using FT-IR, with H$_2$O abundances (based on SIMS measurements) between ~0.2 and ~0.6 wt% (Li et al. 2015). Full calibration data are given in the supporting information, as is the calibration curve. Reported H$_2$O contents represent averages of 5–15 individual measurements and reported uncertainties are the standard deviation of these measurements based on counting statistics. All original SIMS measurement data of the standards and samples are given in Tables S2 and S3 of Data S1 in supporting information, respectively.

RESULTS

Demonstration of Equilibrium

Tables 1 and 2 provide the overviews of our experiments: 14 in the “high-H” LMO series, and 10 for the “low-H” series, simulating solidification processes up to 95 and 84 PCS, respectively. All experiments contained quenched liquid with a glassy texture, with most experiments containing two or more mineral phases. The quenched melt phase did not show any other texture than glassy, and did not contain any bubbles suggesting the melts were all fluid-undersaturated. Some typical examples of experimental charges are shown in Fig. 1 (with additional charges shown in subsequent figures). Compositional measurements of all phases and associated errors are presented in Table 1. Texturally, mineral-melt contacts are straight without resorption textures, suggesting equilibrium.

Mineral grains and melt areas are homogeneous in composition, as seen from the small 1 sigma standard deviations reported in Table 1. Olivine–liquid Fe–Mg exchange coefficients, $K_D$($[X_{FeO-Olivine}] [X_{MgO-Liquid}] / [X_{FeO-Liquid}] [X_{MgO-Olivine}]$), range from 0.27 to 0.30 in the olivine-bearing experiments (Table 1). Correcting these values for the effects of temperature, pressure, and composition using the parameterization of Toplis (2005) yields $K_D^0$ values of 0.31–0.32 (Table 1), well consistent with the equilibrium value range of the terrestrial compositions (e.g., Filiberto and Dasgupta 2011; Matzen et al. 2011; Fig. 2). Figure 3 shows the measured calcium and aluminum abundances in experimental olivines, similar to literature data including ~17,000 olivine grains with Mg$\#$ of ~75–85 from terrestrial samples including mid-oceanic ridges basalts, ocean islands, and large igneous provinces (e.g., Sobolev et al. [2007] and references therein). The Ca and Al abundances are very low (0.27–0.35 wt% CaO and 0.07–0.22 wt% Al$_2$O$_3$) and fall within the ranges found for terrestrial magmatic olivines, suggesting olivine-melt equilibrium in our experiments.

In the pyroxene-bearing experiments, average $K_D^{Fe-Mg}$ values for pyroxene with a wide range of aluminum contents (2.94–6.28 wt% Al$_2$O$_3$) range from 0.24 to 0.31, with one experiment at 1130 °C showing the highest value (0.42; Table 1). This is broadly consistent with the equilibrium value range of 0.20–0.40 (e.g., Grove and Bryan 1983; Kinzler and Grove 1992; Sisson and Grove 1993; Fig. 2). Taken together, textural and chemical evidence suggest that equilibrium was reached in our experiments.

Water Contents in Experiments

High-temperature experiments can suffer from water loss through fast solid-state hydrogen diffusion through the graphite inner capsule and noble metal.
outer capsule (e.g., Truckenbrodt and Johannes 1999; Freda et al. 2001). Graphite and water can also react to form COH fluid phase (e.g., Ulmer and Luth 1991). It is therefore important to ascertain the water budget of our experiments. Qualitatively, EMPA analyses of glasses in all experiments shown in Table 1 yield totals that are significantly lower than 100%, consistent with the presence of dissolved hydrogen (that cannot be

| Exp. Phase       | SiO₂ | TiO₂ | Al₂O₃ | FeO  | MgO  | CaO  | Total | Mg# |
|------------------|------|------|-------|------|------|------|-------|-----|
| **High-H**       |      |      |       |      |      |      |       |     |
| LBS5H Olivine    | 39.32| 0.04 | 0.08  | 16.04| 44.29| 0.28 | 100.06| 83  |
| Cumulate (Ol)    | 39.32| 0.04 | 0.08  | 16.04| 44.29| 0.28 | 100.06| 83  |
| Liquid (LMO₆₅₆) | 47.90| 1.62 | 14.65 | 12.80| 11.06| 10.43| 98.48 | 61  |
| LBS6H Cpx        | 52.01| 0.34 | 5.12  | 11.46| 27.95| 2.81 | 99.68 | 81  |
| Cumulate (Cpx)   | 52.01| 0.34 | 5.12  | 11.46| 27.95| 2.81 | 99.68 | 81  |
| Liquid (LMO₃₃₄) | 47.41| 1.76 | 15.16 | 12.64| 10.15| 11.07| 98.19 | 59  |
| LBS7H Olivine    | 40.20| 0.12 | 0.22  | 17.23| 40.96| 0.35 | 100.60| 81  |
| Cpx              | 53.64| 0.45 | 4.88  | 11.76| 27.82| 2.05 | 100.60| 81  |
| Cumulate (Ol+Cpx)| 50.28| 0.37 | 3.72  | 13.13| 31.11| 1.62 | 100.22| 81  |
| Plagioclase      | 44.97| 0.07 | 34.51 | 0.83 | 0.67 | 19.21| 100.25| 59  |
| Liquid (LMO₆₅₆) | 47.77| 1.95 | 15.74 | 12.22| 8.74 | 11.61| 98.19 | 59  |
| **Low-H**       |      |      |       |      |      |      |       |     |
| LBS5H- Olivine   | 39.39| 0.05 | 0.08  | 16.40| 44.15| 0.29 | 100.37| 83  |
| Opx              | 53.66| 0.36 | 4.66  | 10.75| 29.34| 1.75 | 100.52| 83  |
| Cumulate (Ol+Opx)| 52.24| 0.33 | 4.20  | 11.32| 30.82| 1.60 | 100.50| 83  |
| Liquid (LMO₆₅₆) | 47.51| 1.70 | 15.24 | 12.87| 10.52| 10.98| 98.82 | 60  |
| LBS6H- Olivine   | 39.49| 0.04 | 0.08  | 16.46| 44.15| 0.29 | 100.37| 83  |
| Opx+Cpx          | 53.65| 0.47 | 3.88  | 12.50| 26.50| 2.80 | 99.79 | 79  |
| Cumulate (Ol+Opx+Cpx)| 47.82| 0.29 | 2.31  | 15.36| 32.35| 1.78 | 99.91 | 79  |
| Plagioclase      | 45.11| 0.15 | 33.31 | 1.23 | 0.89 | 18.37| 99.42 | 57  |
| Liquid (LMO₃₃₄) | 47.88| 1.95 | 16.15 | 12.73| 8.64 | 11.34| 98.70 | 55  |
| LBS7H- Cpx       | 52.66| 0.47 | 4.62  | 13.77| 25.66| 3.13 | 100.30| 77  |
| Cumulate (Cpx)   | 52.66| 0.47 | 4.62  | 13.77| 25.66| 3.13 | 100.30| 77  |
| Plagioclase      | 44.23| 0.06 | 34.16 | 0.88 | 0.42 | 19.70| 99.46 | 46  |
| Liquid (LMO₆₅₆) | 47.58| 2.45 | 15.48 | 13.83| 7.50 | 11.52| 98.37 | 49  |
| LBS8H- Cpx       | 51.99| 0.58 | 3.98  | 15.65| 24.06| 3.71 | 99.96 | 73  |
| Cumulate (Cpx)   | 51.99| 0.58 | 3.98  | 15.65| 24.06| 3.71 | 99.96 | 73  |
| Plagioclase      | 40.52| 0.13 | 37.84 | 0.89 | 0.53 | 20.59| 100.50| 52  |
| Liquid (LMO₃₃₄) | 47.75| 2.69 | 15.11 | 14.51| 6.84 | 12.00| 98.91 | 46  |

Calculations of the overall crystallizing mineral assemblage in each step, and of the composition of the overall liquid remaining, take into account the different volumes of material present at different depths in the Moon. The crystals and evolving LMO compositions in each step are weighted to account for different volumetric contributions from different pressure regimes during the different stage, respectively. All values except Mg# and PCS (per cent solid by volume) are in wt%.
measured by EMPA) at the end of the experiments. Differences from perfect 100 wt% totals in EMPA analyses can be due to the presence of H2O and/or OH species, but also due to the presence of other volatiles such as CO2 or CH4, the presence of ferric iron, and/or errors introduced in the microprobe measurement.

In a previous paper on the effect of water on LMO crystallization (Lin et al. 2017a), we assumed that all hydrogen added to the starting materials remained in the silicate melt phase of the experimental charges, because deviations from EMPA totals were close to expected values if no water had been lost. In this study, we measured water concentrations in the silicate melt phase in eight samples (five representative samples of the original Lin et al. [2017a] study covering a wide range of added water contents, and three additional samples from new experiments) by SIMS to quantify water contents (Table 3).

In Table 3 and Fig. 4, a comparison is provided between the water content of the experimentally produced melts measured by SIMS, the water abundances expected (assuming water behaves perfectly incompatibly) on the basis of the amount of hydrogen added to each starting material, and the water abundances derived from deficiencies in EMPA totals (as used in our previous study). Our SIMS data suggest that hydrogen in the experimental charge was lost significantly and systematically. The slope of the correlation line in Fig. 4 is 0.33 ($R^2 = 0.90$), suggesting that 68 ± 5% of the water added is not present anymore in the silicate sections of the charges, independent of run temperature. The true water contents in our hydrous experiments are therefore approximately a factor of three lower than assumed in Lin et al. (2017a).

Our time series results from the leak test experiments are consistent with these observations. Figure 5a indicates that a steady state in terms of sample hydrogen contents is reached within 2 h, and that the proportion of water left in the silicate glass of the assemblies is constant at ~33%, within error of the proportion left in the original data set covering a range of temperatures and pressures (Fig. 5b). Rapid achievement of steady state is confirmed by spatial analyses of water contents of silicate melt of sample LBS6H- (Fig. 6). Melt water contents are identical within error throughout the sample, independent of location in the sample, arguing for a homogenous distribution of water throughout the experiments (and arguing against the presence of a compositional gradient that would be expected in the case of continuous water loss throughout the experiments). Continuous water loss would also have caused progressive sample oxidation that would have led to zonation of growing mineral phases. No such zonation occurred in our experiments.

![Image](https://example.com/image1.png)

**Fig. 2.** Ranges of $K_{D(Sol-liq)}^{Fe-Mg}$ of experimental olivine and pyroxene versus FeO+MgO of experimental melts. The $K_0$ (red and green diamonds) and corrected $K_0^{'}$ (red and green triangles) of olivine from our experiments overlap with the equilibrium value range of the terrestrial basalts. The terrestrial basalts’ data are from the literature (Filiberto and Dasgupta [2011] and the references therein). The lunar literature data are from recent experimental studies (Elardo et al. 2011; Lin et al. 2017b; Charlier et al. 2018; Rapp and Draper 2018). Pyroxene data in red and green squares are consistent with the range of 0.2–0.4 (Grove and Bryan 1983; Kinzler and Grove 1992; Sisson and Grove 1993). $K_{D(Sol-liq)}^{Fe-Mg}$ represents the corrected $K_{D(Sol-liq)}^{Fe-Mg}$ based on Toplis (2005). (Color figure can be viewed at wileyonlinelibrary.com.)

![Image](https://example.com/image2.png)

**Fig. 3.** The CaO and Al2O3 contents in olivine versus Mg# of olivine from our experiments. The light green and gray bars represent the CaO and Al2O3 contents of ~17,000 olivine grains with Mg# of ~75 to 85 from terrestrial samples including mid-oceanic ridges basalts, ocean islands, and large igneous provinces, showing ~0.14–0.42 wt% CaO and ~0.03–0.13 wt% Al2O3 (Sobolev et al. 2007). (Color figure can be viewed at wileyonlinelibrary.com.)
Table 3. Summary of concentrations of water (H₂O equivalent) in experimental glass

| Conditions | $T$ (°C) | $P$ (GPa) | $t$ (h) | High-H exp. | Glass proportion (modal %) | Starting OH content | Water (H₂O) in the residual melt | Exp. measured by SIMS | Percentage lost (%) |
|------------|----------|-----------|---------|-------------|----------------------------|---------------------|---------------------------------|------------------------|---------------------|
|            |          |           |         |             |                            |                     |                                 |                        |                     |
|            |          |           |         |             |                            |                     |                                 |                        |                     |
|            |          |           |         |             |                            |                     |                                 |                        |                     |
| 1240       | 0.8      | 4         |         | LBSSH       | 95                         | 2.00                | 1.06                           | 1.11                   | 12                  |
|            | 0.4      | 4         |         |             |                            |                     |                                 |                        |                     |
| 1220       | 0.8      | 8         |         | LBS6H       | 79                         | 2.08                | 1.10                           | 1.39                   | 8                   |
|            | 0.4      | 8         |         |             |                            |                     |                                 |                        |                     |
| 1200       | 0.7      | 12        |         | LBS7H       | 86                         | 2.36                | 1.25                           | 1.45                   | 12                  |
|            | 0.4      | 12        |         |             |                            |                     |                                 |                        |                     |
| 1180       | 0.6      | 20        |         | LBS8H       | 65                         | 2.72                | 1.44                           | 2.40                   | 8                   |
|            | 0.4      | 20        |         |             |                            |                     |                                 |                        |                     |
| 1160       | 0.4      | 24        |         | LBS9H       | 66                         | 3.63                | 1.92                           | 2.91                   | 13                  |
|            | 0.4      | 48        |         | LBS10H      | 46                         | 5.50                | 2.91                           | 6.33                   | 13                  |
| 1200       | 0.4      | 2         |         |             |                            |                     |                                 |                        |                     |
|            | 0.4      | 4         |         |             |                            |                     |                                 |                        |                     |
|            | 0.4      | 24        |         |             |                            |                     |                                 |                        |                     |

All values except phase proportion are in wt%. Values in parentheses are 1σ SD.
The water content in italic shown in the LBS7H- step at 1200 °C and 0.4 GPa is converted by the proportion of the expected water contents (≈0.57 × 1.09/1.69).
No. = the numbers of SIMS analyses.
Our SIMS analyses also enabled us to identify one experiment that appears to have suffered anomalously large loss of water (LBS9H in the high-H series, Fig. 4). This sample still contains significant water, but has lost over 80% of the amount originally added to the experiment. Because the capsule was opened and polished for analysis, it is not possible anymore to assess whether this capsule suffered from a leak during the experiment. We have retained this experiment because it still provides valuable information about the final stages of crystallization of a hydrous LMO, but note that its water content may not be representative for simulating LMO crystallization without water degassing.

Our SIMS data are consistent with a literature compilation of the maximum Al$_2$O$_3$ content of hydrous silicate melts (denoting the point just before plagioclase begins to form) as a function of melt water contents (Fig. 7; Parman et al. [2011] and references therein). Our SIMS results are fully consistent with the linear trend between Al$_2$O$_3$$_{\text{max}}$ and H$_2$O-melt observed in previous work, as well as the nominally dry experiments of Lin et al. (2017b), Charlier et al. (2018), and Rapp and Draper (2018).

Our results indicate that approximately two-thirds of the water added to the experiments is consistently lost from the silicate section of the experiments. All of the melts are undersaturated in water, and there is no textural or compositional evidence of the presence of COH phase in any of our experiments. The solubility of water in basaltic melts is >6 wt% at our experimental conditions (e.g., Mitchell et al. [2017] and references therein), and even if no water had been lost from any of our experiments, the maximum water content in our melts would not have exceeded 3 wt%. Our time series shows that water loss occurs quickly, and then stops so that a steady state is reached within hours, after which no additional water loss occurs. This, together with the leak tests performed in the time series experiments, argues against capsule leaks as the cause. The absence of a trend where more water is lost as time progresses and the absence of a trend of overall capsule weight loss with time argue against progressive solid-state diffusive loss of hydrogen. The fact that the proportion of water lost from the starting material is independent of run duration suggests that either less water was added to the samples than thought (rapid dissociation of Mg[OH]$_2$ followed by water evaporation during welding of the capsules is considered unlikely) or that the same proportion of hydrogen is removed by reaction with the graphite capsule in every experiment. In a recent separate study of water partitioning between plagioclase and lunar melt, performed using identical sample preparation and experimental techniques (Lin et al. 2019), FT-IR analyses of silicate melts did not detect carbon species in the silicate melt, arguing against significant sample oxidation or the dissolution of significant amounts of COH components in the silicate melts. We therefore cannot provide a definitive answer as to the sink of hydrogen in our experiments at this stage. The systematic loss in the experiments allows us to still use our data set as a basis for inferences about the effect of water on crystallization of the LMO. Finally, we note that anomalously low totals in EMPA analyses of water-bearing silicate melts can be caused in part by performing such analyses at relatively high voltages and currents (as we did). Future EMPA analyses of these melts should be undertaken at lower voltages and currents than used in the present study. However, it is clear that the significant differences between SIMS-determined water contents and estimates from EMPA totals found in this study (e.g., for LBS9H) are too large to be explained by a non-ideal EMPA protocol.

Oxygen Fugacity

To calculate the oxygen fugacities in our experiments, based on our experimental assemblage with an outer-Au$_{80}$Pd$_{20}$ and inner graphite lining, we
use Equation 1 for the graphite–COH (C-COH) buffer (Ulmer and Luth 1991):

\[
\log f_O^2(C-COH \text{ buffer}) = (-22.324 + 189 \cdot P - 1.41 \cdot P^2)/T + 4.62
\]

(1)

where \( T \) is the temperature (K), and \( P \) is the pressure (kbar). The calculated \( \log f_O^2 \) values are shown in Table 1. Equation 1 is strictly valid only in the presence of a free COH phase. In our experiments, in which water saturation certainly did not occur, there is no free COH phase. In this case, the calculated \( \log f_O^2 \) values are maximum values as the fluid pressure has to be less than the experimental load pressure (Ulmer and Luth 1991). Our calculated maximum experimental \( \log f_O^2 \) values from 24 samples at the C-COH buffer range from \(-10.8\) to \(-9.2\), which is \( \approx-2 \) log units above the IW buffer (Table 1). This is consistent with the absence of iron metal blebs in these experimental charges, and consistent with previous data for this assembly (e.g., Médard et al. 2008; Lin et al. 2019). This suggests that iron is mainly present in the 2+ valence state in all samples. Calculations based on parameterizations of experimental data at high pressure indicate that the maximum \( Fe^{3+}/Fe^{2+} \) ratio in our samples is smaller than 0.1 (Kress and Carmichael 1991). The \( f_O^2 \) in our experiments is therefore not identical to that in the Moon, but for the purpose of this study, we consider our experiments sufficiently representative of those in the lunar interior (and closer in terms of \( f_O^2 \) than experiments focused on the terrestrial interior).

### Crystallization Sequence and Mineral Compositions

The mineralogy of the crystallizing hydrous LMOs is summarized graphically in Fig. 8. At the “low-H” and “high-H” series, plagioclase appears after 71 and 73 PCS, respectively, compared to 68 PCS in the nominally dry system. Ca-bearing pyroxene (referred to as Cpx if its wollastonite [Wo] content is >5 mole%, as Opx if Wo < 5 mole%) starts crystallizing between 70 and 73 PCS in the “high-H” experiments (72–76 PCS for the “low-H” experiments). The pyroxene compositions are shown in Fig. 9. The composition evolves toward more Fe-rich compositions as crystallization progresses, and the Ca content increases only slightly, from Wo4 to Wo7 between 68.5 and 76.8 PCS in the “high-H” system, and from Wo3 to Wo8 in the “low-H” system. After ~77 PCS in the “high-H” series, pyroxene compositions become more calcic. Olivine does not form beyond >77 PCS (>76 PCS for the “low-H” series). Plagioclase starts crystallizing at 1200 °C under the “low-H” and “high-H” series, 40 and 20 °C lower than in the nominally dry system (Lin et al. 2017b), respectively. From 89 to 95 PCS (step LBS10H in Table 1), spinel, ilmenite, and quartz appear and coexist with plagioclase and Cpx.

Olivine shows a near-constant composition of Fo83-81, and pyroxene shows a range of compositions En75-35Fs35-17Wo34-4 between 68 and 95 PCS, and Fo83-78 and En81-68Fs25-16Wo7-3 from 68 to 84 PCS, under the “low-H” and “high-H” experimental conditions, respectively (Table 1). Both show a gradual increase in FeO and TiO2 contents and decrease in
Fig. 6. H$_2$O in the quenched glass measured by SIMS as a function of the distance from the top to the bottom of the sample. The SIMS analysis data in the left panels (a, c, e, g, and i) correspond to sample locations in the right panels (b, d, f, h, and j). The error bar of individual measurements is based on the data shown in Table S3. There is no significant gradient in water concentrations, illustrating a homogeneous distribution of water in the charges. (Color figure can be viewed at wileyonlinelibrary.com.)
MgO content as crystallization progresses. In the “high-H” system, Al2O3 and CaO contents of olivine increase to maximum values of 0.22 and 0.35 wt%, respectively, at ~73 to 77 PCS when plagioclase appears as a liquidus phase. The CaO content of pyroxene increases from 2.0 to 14.8 wt%. As for plagioclase, there is a minor increase of FeO from 0.79 to 1.34 wt% and TiO2 from 0.06 to 0.15 wt% from 73 to 95 PCS. Spinel in step LBS10H has 61.0 wt% Al2O3 and 23.5 wt% FeO. In the “low-H” system, pyroxene increases in CaO content from 1.60 to 3.71 wt% between 69 and 84 PCS. Plagioclase shows minor variation of FeO from 0.87 to 1.23 wt% and TiO2 from 0.05 to 0.15 wt% between 72 and 84 PCS.

Compositions of the Residual LMO and Corresponding Cumulate Pile

The weighted compositions of the residual LMO liquids and corresponding minerals, and bulk cumulate layer compositions for every crystallization step are listed in Table 2. The evolution paths of the major oxide concentrations and Mg# of the residual LMO are shown in Fig. 10 for the “high-H” system and Fig. 11 for the “low-H” system. Melt MgO content and Mg# decrease continuously from LBS5H (MgO = 12.52 wt%, Mg# = 63) to LBS10H (4.24 wt%, 32) for the “high-H” system (Fig. 10a). SiO2 is virtually constant at 48.0 ± 1.0 wt% in both experimental series, due to our approach to modeling LMO crystallization as a result of a polybaric isothermal process. Al2O3 increases steadily to maxima of 15.7 wt% (the “high-H” system) and 16.15 wt% (the “low-H” system), to the stage where plagioclase starts crystallizing. Melt CaO increases progressively throughout the crystallization sequence reaching 13.7 wt% at 95 PCS in the “high-H” system and 12.0 wt% at 84 PCS in the “low-H” system. The appearance of ilmenite affects significantly the shape of the curves for the TiO2 and FeO content in the residual melts. Before crystallization of ilmenite at 89 PCS (LBS9H), TiO2 gradually increases to 3.6 wt%, and FeO increases with minor fluctuations to 14.3 wt%. From this stage onward, FeO continues to be enriched in the melts up to 16.2 wt% at 95 PCS, while TiO2 in the melt sharply decreases to 1.09 wt%.

The evolution of the bulk chemical composition of the mantle cumulates is presented in Figs. 10b and 11b for the two water-bearing systems (compositions of the floating layers containing plagioclase are not shown). There is a significant drop in bulk mantle cumulate Mg# from 68 at 89 PCS to 44 at 95 PCS in the “high-H” system (Fig. 10b). The Mg# in the mafic cumulate pile remains higher than that of corresponding residual magma during LMO solidification (Figs. 10 and 11). When ilmenite appears at 89 PCS, both the MgO and SiO2 content of the cumulate layer decrease sharply (Fig. 10b). Simultaneously, TiO2 and FeO contents of the cumulates increase from 0.04 to 8.6 wt% and from 12.8 to 21.1 wt% (Fig. 10b), respectively. There is a clear increase in the Al2O3 content of the bulk mantle cumulate when spinel forms (Fig. 10b). The formation of high-Ca pyroxene (HCP; En35Fs31Wo34) in step LBS10H raises the CaO content of the cumulate pile.

DISCUSSION

Comparison with a Nominally Dry Moon

We first compare our results (summarized in Figs. 8a and 8b) with data from our nominally dry LMO crystallization study using the same bulk composition (Lin et al. 2017b), referred to as “dry model” hereafter, with the corresponding mineralogy of the solidified LMO shown in Fig. 8c. We also compare
our results with the results of the nominally dry LMO crystallization studies of Charlier et al. (2018) and Rapp and Draper (2018; Figs. 8d and 8e), which used different initial LMO compositions.

The dry model showed that plagioclase appears in a crystallizing assemblage with olivine and Cpx at 68 PCS, with olivine disappearing at 83 PCS, and ilmenite starting to crystallize at 91 PCS (Fig. 8c; Lin et al. 2017b). Charlier et al. (2018) and Rapp and Draper (2018) showed that plagioclase starts crystallizing together with pyroxene at 78 PCS (Fig. 8d) and with olivine and pyroxene at 74 PCS (Fig. 8e), respectively.

Fig. 8. Comparison of LMO crystallization sequences from this study after Lin et al. (2017a). a and b) Experimentally determined crystallization sequence in the “high-H” and “low-H” systems in an LMO with initial depth of 700 km; c, d, and e) Nominally dry experiments from Lin et al. (2017b), Charlier et al. (2018), and Rapp and Draper (2018), respectively. Two hydrous LMO scenarios with different water contents were simulated by adding amounts of 1 and 2 wt% OH (0.5 and 1 wt% H$_2$O equivalent) upon melting from the fourth step of the dry LMO solidification series (Lin et al. 2017b). If no water is lost during the experiments, this approach would be equivalent to adding 1575 (“low-H”) and 3150 ppm (“high-H”) H$_2$O equivalent in the initial LMO, neglecting the very small amounts of hydrogen incorporated in the nominally anhydrous minerals olivine and orthopyroxene. Therefore, we labeled the “high-H” and “low-H” to distinguish these two different series hydrous experiments. Opx = orthopyroxene; Cpx = clinopyroxene. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 9. Composition quadrilateral for experimentally produced pyroxene. It is summarized in the row of “Pyroxene (EnFsWo)” in Table 1. En = enstatite; Fs = ferrosilite; Di = diopside; Hd = hedenbergite; Wo = wollastonite. (Color figure can be viewed at wileyonlinelibrary.com.)
With a LMO solidification, the Mg\# of olivine and pyroxene vary from 91 to 79 and from 87 to 55 (Lin et al. 2017b), from 93 to 83 and from 92 to 23 (Charlier et al. 2018), and from 94.4 to 10.4 and from 88.1 to 20.4 (Rapp and Draper 2018), respectively. In the final step considered by Lin et al. (2017b) at 96 PCS, \(\beta\)-quartz coexists with Cpx, plagioclase, and ilmenite. Similarly, ilmenite and quartz start to crystallize at 95 PCS (Fig. 8d; Charlier et al. 2018) and at 97 PCS (Fig. 8e; Rapp and Draper 2018), respectively. In contrast, the hydrous models of this study show that only olivine ± Opx occurs at 68 PCS. Plagioclase does not crystallize until 71 and 73 PCS in the “low-H” and “high-H” systems, respectively. In the final step LBS10H from 89 to 95 PCS at the “high-H” system, \(\beta\)-quartz, spinel, and HCP coexist with plagioclase and ilmenite (Fig. 8a). These observations are consistent with prior experimental studies of terrestrial systems that showed that the addition of water delays crystallization of plagioclase relative to olivine and clinopyroxene in magmatic processes, inducing formation of HCP, and that Al can substitute into pyroxene and spinel in water-bearing crystallization experiments (e.g., Sisson and Grove 1993).

The implications of the presence of ilmenite and quartz were already discussed in Lin et al. (2017b). HCP has been observed by remote sensing in lunar craters with diameters larger than ~40 km (e.g., Yamamoto et al. 2015; Martinot et al. 2018a, 2018b), suggesting its presence in the shallow lunar crust. The presence of HCP...
is generally not linked to primary LMO crystallization processes, but Charlier et al. (2018) and Rapp and Draper (2018), using different bulk compositions of the initial LMO, showed that HCP with CaO of ~12–15 wt% and ~13.5 wt% could form in the LMO at 95 PCS and 74–88 PCS, respectively. In our study, HCP with at least 14.8 wt% CaO can form during late-stage crystallization in a water-bearing Moon.

To date, the formation of spinel has not been linked to primary LMO processes. However, previous studies (Prinz et al. 1973; Marvin et al. 1989) did indicate that a lunar rock rich in (Mg,Fe) alumina spinel would require extensive magmatic fractionation, as occurs during a late magma ocean stage. Magnesium-rich spinels have been observed in lunar meteorite ALHA81005 (Gross and Treiman 2011; Gross et al. 2014). The spinel from ALHA81005 (Gross and Treiman 2011) contains 63.23 wt% Al₂O₃ consistent with the one from our experiment (61.03 wt%). So-called “pink spinel” occurrences on the Moon, identified using remote sensing (Jackson et al. 2014; Pieters et al. 2014), point to the presence of very magnesian spinels in the crust of the Moon. Experiments have shown that such Mg-rich spinel likely formed through the interaction between Mg-suite parent magma and anorthositic crust (i.e., during processes that occurred after completion of LMO solidification, Prissel et al. 2014; Williams et al. 2016). Treiman et al. (2019) recently indicated that magnesium aluminate spinel on the walls and central peaks of impact craters results from rapid cooling and partial crystallization of superliquidus melts produced in the impacts by enthalpy constraints. Our experiments indicate that spinel (albeit of a more Fe-rich composition) can also be a product of LMO crystallization if water was present.

An Updated Lunar Crust Hygrometer

As first discussed in Lin et al. (2017a), our data can be used to constrain the water content in the early Moon by comparing the thickness of the lunar crust produced during hydrous LMO crystallization with the observed 34–43 km average lunar crustal thickness (Wieczorek et al. 2013). Our SIMS measurements allow us to improve this lunar hygrometer.

As discussed in the Comparison with a Nominally Dry Moon section, in hydrous experiments plagioclase crystallizes later than in a nominally dry system with the same bulk major element composition, with higher amounts of water leading to later crystallization of plagioclase (Fig. 8). Simultaneously, the proportion of plagioclase in the crystallizing assemblage of a water-bearing LMO is lower than the proportion of plagioclase in the crystallizing assemblage of a dry LMO. Our experiments show that, starting with a 700 km LMO, the crustal thickness assuming ideal segregation of plagioclase (~quartz) is 32.2 km at 95 PCS in the “high-H” system and 19 km at 84 PCS in the “low-H” system (Table 1), which translates to 40 ± 1 and 42 ± 1 km at 99 PCS, respectively (Lin et al. 2017a), consistent with the observed thickness of 34–43 km based on the most recent lunar gravity data (Wieczorek et al. 2013). This contrasts with the much higher crustal thickness at 99 PCS of 68 km in a nominally dry 700 km deep LMO (Lin et al. 2017b), again assuming 100% efficient extraction of low-density plagioclase and quartz from the magma ocean to the crust.

Four main factors affect the use of crustal thickness as a hygrometer, with the first three discussed below already assessed in Lin et al. (2017a, 2017b).

1. As previously suggested on the basis of trace element abundances (e.g., Snyder et al. 1992), a total ~5 wt% plagioclase (~quartz) and liquid could have been trapped in early LMO cumulates because of inefficient crystal-melt segregation. Removal of crustal material to the mantle would decrease the crustal thickness by <4 km.

2. None of our experiments contain chromium, sodium, or potassium, whereas the actual LMO did. If we assume all Cr₂O₃ (starting with 0.5 wt% according to Elardo et al. 2011) in the LMO is eventually locked up in Cr-spinel, ~0.4 wt% Al₂O₃ would be transferred into spinel (Lin et al. 2017b). This would lead to an additional lunar crustal thickness reduction of 5%. Rapp and Draper (2018) showed that plagioclase forming from a starting composition with an Na₂O content of 0.1 wt% is more sodic than lunar sample plagioclase, which means that the Na₂O concentration in the initial LMO bulk composition should be lower than 0.1 wt%, consistent with previous estimates (e.g., Warren 2005). The Na₂O (~0.05 wt%) and K₂O (~0.01 wt%) contents of the silicate Moon are about 54 times lower than the CaO content (~3.23 wt%) we used (Lin et al. [2017b] and the references therein). Also, the abundances of sodium and potassium in lunar plagioclase are very small (~0.2 wt% Na₂O and ~0.025 wt% K₂O; e.g., McGee 1993) compared with CaO content (~19 wt%). Therefore, the contributions of Na and K to lunar crustal thickness are negligible.

3. The effect of the initial depth of the LMO on crustal thickness can be modeled for a nominally dry magma ocean (Lin et al. 2017b), yielding crustal thicknesses of 52, 71.5, 60.6, and 61.6 km at initial LMO depths of 400, 1000, 1200, and 1350 km, respectively. This shows that initial LMO depth has a substantial effect on crustal thickness, with the
whole predicted thickness range (from 52 km for a 400 km deep LMO to 71.5 km for a 1000 km deep LMO) substantially larger than that observed (Wieczorek et al. 2013).

4. A factor that was not addressed previously is that the water contents in our experiments (both the nominally dry and the expectedly hydrous experiments) must be constrained accurately in order to quantitatively relate a given crustal thickness to an LMO water concentration. Our SIMS data indicate that approximately 66% of the water added to each experiment was lost (Fig. 5b). It was also shown recently that nominally anhydrous experiments of the type we describe in Lin et al. (2017b) can contain ~160 ppm water (Sarafian et al. 2017). Assuming this maximum amount of water, the nominally dry experiments of Lin et al. (2017b) would represent an LMO initially containing ~50 ppm water.

In Fig. 12, we use the above inferences to provide improved estimates of the effect of water to LMOs of 400, 700, 1000, 1200, and 1350 km initial depth on crustal thickness. As previously, we assume the same fractional decrease in plagioclase production with water content as measured in our experiments. Figure 12 shows that to yield the crustal thickness observed by GRAIL, we now estimate that the LMO could have contained at least 90, 325, 410, 220, and 240 ppm H₂O equivalent if it had an initial depth of 400, 700, 1000, 1200, or 1350 km, respectively.

Table 4. Summary of crustal thicknesses and estimated water (H₂O equivalent) contents in the Moon.

| Initial LMO depth (km) | Crust thickness (km) | Water (H₂O equivalent) content (ppm) |
|-----------------------|----------------------|-------------------------------------|
|                       | Nominal dry (~50 ppm water) | Expected in low-H system | Expected in high-H system | In the LMO constrained at 43 km thick | In the whole Moon | Corrected lunar water (y = 0.33x) |
| Ideal results (Lin et al. 2017b) | 400 | 52 | 32.4 | 30.8 | 520 | 283 |
|                        | 700 | 67.5 | 42.0 | 40.0 | 1400 | 1102 |
|                        | 1000 | 71.5 | 44.5 | 42.4 | 1800 | 1663 |
|                        | 1200 | 60.6 | 37.7 | 35.9 | 1030 | 1000 |
|                        | 1350 | 61.6 | 38.3 | 36.5 | 1100 | 1088 |
| Corrected results*    | 400 | 52 | 29.1 | 27.7 | 250 | 136 | 45 |
|                        | 700 | 67.5 | 37.8 | 36.0 | 930 | 732 | 242 |
|                        | 1000 | 71.5 | 40.0 | 38.1 | 1160 | 1071 | 354 |
|                        | 1200 | 60.6 | 33.9 | 32.3 | 640 | 621 | 205 |
|                        | 1350 | 61.6 | 34.5 | 32.9 | 680 | 672 | 222 |

*Correcting for the effects of inefficient segregation and Cr-spinel consuming Al (equivalent to a combined ~10 wt% reduction in crustal thickness).
Correcting for the effects of inefficient segregation and Cr-spinel consuming Al (equivalent to a combined ~10 wt% reduction in crustal thickness; Lin et al. 2017b), we conclude that the early Moon should have contained >~45 to 354 ppm water (Table 4), which is significantly lower than obtained previously with the indirect method based on EMPA totals in Lin et al. (2017a). Given that LMO crystallization and crust formation are among the first major differentiation stages in the Moon, this analysis suggests that the Earth–Moon system was not anhydrous at the time of the Moon-forming event.

The depletion of other volatiles, such as potassium and sodium, could be caused by the Moon-forming impact (>4000 K) and partially vaporized disk (Nakajima and Stevenson 2014), with incorporation into the lunar core being an additional sink for these elements (e.g., Steenstra et al. 2018). As for water as a vapor phase in the hot Moon-forming disk, it may not have hydrodynamically escaped due to this escape suppressed by heavy elements dominating the disk vapor (Nakajima and Stevenson 2018). Nakajima and Hauri (2017) modeled the evolution of Moon-forming silicate-vapor disk and finally yielded an average value of ~465 ppm as the initial water abundance in the bulk silicate Moon (BSM), which is quite consistent with our experimental estimate.

CONCLUSIONS

This study provides experimentally determined crystallization sequences for an LMO composition with two different initial water contents, with water contents in the experimental charges measured by SIMS. Comparison with results from crystallization of a nominally dry system with the same major element composition shows that water suppresses crystallization of plagioclase relative to olivine and clinopyroxene, and affects both mineral and residual melt compositions. A hydrous LMO can lead to the formation of HCP and spinel in the final crystallization steps. SIMS data enabled the development of an improved quantitative relation between lunar water content and resulting crustal thickness. This improved model can be used to calculate that the Moon contained at least 45–354 ppm H₂O equivalent during LMO crystallization, with the exact number depending on the initial depth of the LMO. This study illustrates the importance of incorporating the role of water in models of planetary magma oceans.

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**SUPPORTING INFORMATION**

Additional supporting information may be found in the online version of this article:

**Data S1.** Water content calibration.