

Copyright

by

Caitlin Moeller

2023

The Thesis Committee for Caitlin Moeller

Certifies that this is the approved version of the following Thesis:

**Water solubility in evolved lunar melts with implications for lunar degassing
history**

**APPROVED BY
SUPERVISING COMMITTEE:**

Chenguang Sun, Supervisor

James Gardner

John Lassiter

Water solubility in evolved lunar melts with implications for lunar degassing history

by

Caitlin Moeller

Thesis

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Masters of Science in Geosciences

The University of Texas at Austin

December 2023

Dedication

For my family and friends that supported me throughout my academic journey, who showed me patience, compassion, and encouraged my personal and intellectual growth.

Acknowledgements

My advisor, Chenguang Sun, for his continued support, guidance, and kindness. He has made me a better writer, presenter, and coder.

James Gardner, for his guidance and continuous help. He was always receptive to my drop-ins with various questions and patient as I learned laboratory operations.

John Lassiter for guidance, advice, and constructive criticism. Working under him as a teaching assistant improved my skills as a teacher and fueled my continued passion for planetary geology.

Kenny Befus, for his aid and guidance. He taught me so much in just one semester and was immensely helpful in navigating the final stages of my thesis.

My friends and colleagues, Nicholas Montiel and Lucia Bellino, for unwavering emotional and intellectual support, encouragement, and generosity. Sharing ideas, workspaces, and helping each other improve has been crucial to my success.

Abstract

Water solubility in evolved lunar melts with implications for lunar degassing history

Caitlin Moeller, M.S. GEO.SCI

University of Texas at Austin, 2023

Supervisor: Chenguang Sun

Constraint of lunar water budgets is vital to understanding the evolution of the rocky body. A wide variety of water abundances have been measured in lunar samples, leading to a large range of initial water budget estimates. This study targets evolved late-stage Lunar Magma Ocean (LMO) melts trapped at the base of the crust, which are enriched in volatiles. Synthesized samples are saturated, experimentally placed at relevant P-T conditions, and quenched into glass. The measured water contents represent the water capacity of this composition as a function of pressure. Comparing measurements against six previous models, I evaluate their ability to reproduce the observed data and suggest a best fit model for this unique composition. Furthermore, at reduced conditions H_2 becomes a more dominant fluid species, reducing the partial pressure and consequently the solubility of H_2O . Previous models do not include the effects of oxygen fugacity or H-volatile speciation. I provide a thermodynamic framework to calculate H_2O/H_2 speciation as a function of oxygen fugacity. With the best fit model and thermodynamic framework, the last 1% of LMO liquid (urKREEP) is found to have a maximum capacity of 0.43 wt.% water at IW-2 and a crustal thickness of 40 km. Using previous bulk LMO water contents, it is concluded that urKREEP could exceed the saturation limit in many scenarios. Excess water was therefore likely degassed through the lunar crust, effectively reducing the observable water budget of the lunar mantle.

Table of Contents

Abstract	6
Table of Contents	7
List of Tables	9
List of Figures	11
Introduction	13
Background	16
Lunar magma ocean crystallization.....	16
Lunar water measurements.....	18
Thermodynamics.....	22
Previous solubility models.....	25
Methods	31
Sample Preparation.....	31
Experimental Setup.....	32
Analysis.....	33
Thermodynamic Modeling.....	36
Results	40
Solubility measurements.....	40
Model Comparisons.....	42
Speciation.....	44
Discussion	46

Saturation in urKREEP.....	46
Degassing history of the Moon.....	49
Future solubility model calibration.....	50
Conclusions.....	51
Appendix.....	52
References.....	63

List of Tables

Table 1: Summary of the estimated water contents for the bulk LMO, urKREEP, and lunar mantle from the literature.....	22
Table 2: Fit parameters for Moore et al. (1998) H ₂ O solubility model ($\pm$ error).....	27
Table 3: Fit parameters for Liu et al. (2005) H ₂ O-CO ₂ solubility model ($\pm$ error).....	28
Table 4: Hydrous coefficients of Iacono-Marziano et al. (2012) solubility model ($\pm 2\sigma$ error). Values are updated post-manuscript publication from the web-based application of the model...	29
Table 5: Target composition from Seddio et al. (2013), initial measured composition of synthetic sample powder ($\pm$ error), and EPMA measured compositions for each experimental run ($\pm$ error). Phosphorus is not measured with EPMA due to the low concentrations in the desired composition.....	35
Table 6: Experimental inputs and conditions. One standard deviation of each run's pressure conditions is given in parentheses.....	36
Table 7: FTIR measured total water contents from the 1630 cm ⁻¹ , 3570 cm ⁻¹ , and the 5230 cm ⁻¹ + 4520 cm ⁻¹ features, all expressed in wt.% ($\pm 1\sigma$ error). These values are averages around several analyzed spots on the glass piece. The full table can be seen in the appendix (Table A.3).....	42
Table 8: Water solubility predictions from existing solubility models for a range of pressures ($\pm$ error). All calculations are assumed to be at terrestrial fO_2 conditions ($\sim IW+4$). Input compositions are those measured by EPMA. Percent error from this study's measured water solubilities are shown for each pressure.....	44
Table 9: Estimations of water available in the initial bulk urKREEP derived from varying $X_i^{H_2O}$ [LMO] and remaining liquid fractions using Eq. (21).....	46

Table 10: Estimations of water contents necessary to saturate urKREEP.....	47
Table A.1: An Apollo KREEP basalt composition (KB; Ryder & Bower, 1976) was also tested. Rhyolite-MELTS (Ghiorso & Gualda, 2015; Gualda et al., 2012) predicted the liquidus for the KB composition to be 1125 °C. A KB sample was run at 1200 °C and held at a pressure of ~100 MPa for ~5 hrs. It was with a different method than the LG samples. The pressure vessel was flipped so that the sample dropped from the heated end to the water cooled end. The difference in quenching methods was in anticipation of the known higher rate of crystallization characteristic of basalts. Unfortunately, even with the rapid quench, crystallization of small microlites made it unusable for FTIR. The composition was not explored further. Below are the compositions of published KREEP basalt, composition of synthesized KB sample ($\pm$ error), measured EPMA KB composition.....	55
Table A.2: EPMA glass standard compositions.....	56
Table A.3: Full FTIR measurements. Abs. is the uncorrected absorbance peak height.....	57

List of Figures

Figure 1: Crystallization of lunar magma ocean. Stages include (a) completely molten, (b) crystallization of mantle cumulates, (c) crystallization of flotation FAN crust, (d) crystallization of ilmenite to begin forming the ilmenite-bearing-cumulate (IBC), (e) urKREEP defined as the last 1% of melt, and (f) the completely solidified and overturned Moon, prior to lunar volcanism. Solidified Fe-rich and KREEP-containing material primarily remained at the base of the lunar crust and later initiated remelting due to the concentration of heat-producing elements, leading to volcanism.....	17
Figure 2: Speciation of H-volatile species in the fluid and melt phases.....	25
Figure 3: Experimental setup. 2mm AuPd capsule loaded with KREEP-y composition powder and water. One run utilized a 3mm capsule instead with the same setup.....	32
Figure 4: Spectra for each LG-05kb-1.2 (top), LG-1kb-8.1 (middle), LG-15kb-1.4 (bottom) at multiple spots across each glass piece. Absorbance is normalized by the thickness at each individual location. Average thicknesses for each spot are listed in appendix (Table A.3). Cut out to the left shows a magnified view of the 5230 cm^{-1} and 4520 cm^{-1} features. A CO_2 peak is present at 2350 cm^{-1} , likely due to incomplete decarbonation of CaCO_3 and K_2CO_4	41
Figure 5: Comparison of tested models to this study's measured data. The blue line is the line of equality for this study's data.....	43
Figure 6: Speciation of H volatiles in the fluid phase with change in $f\text{O}_2$. H_2 is scaled to account for the difference in weight between the two species.....	45
Figure 7: urKREEP saturation lines as a function of initial LMO water content and overhead pressure, corresponding to crustal thickness. Present day crustal thicknesses are indicated by the	

gray region. Saturation lines for three lunar relevant fO_2 conditions are shown, with solubility limits notated along each line. As fO_2 decreases, so does the water capacity of urKREEP.

Scenarios where urKREEEP would be below saturation lay to the left of the saturation line and above saturation to the right, as indicated by the red and blue arrows respectively..... 48

Figure 8: Degassing history of the Moon. (a) Outgassing from initial LMO. (b) LMO with steam atmosphere produced by outgassing. (c) 99% solidified LMO. Degassing from crust breaching impacts exposing that liquid and degassing through the lunar crust due to oversaturation of urKREEP are both shown. (d) Magmatism and volcanic degassing after complete LMO solidification and subsequent remelting due to enrichment of heat-producing elements in the upper mantle.....50

Figure A.1: Sample LG-05kb-1.2 under cross-polarized light (a and c) and imaged via Scanning Electron Microprobe (SEM; b and d)..... 52

Figure A.2: Sample LG-1kb-8.1 under cross-polarized light (a and c) and imaged via SEM (b and d)..... 53

Figure A.3: Sample LG-15kb-1.4 under cross-polarized light (a and c) and imaged via SEM (b and d)..... 54

1. Introduction

Water is an important volatile affecting the chemical and dynamic evolution of rocky planetary bodies, including Earth's Moon, as it can significantly change the mantle rheology and melting conditions (e.g. Hirschmann, 2006; Hirth et al., 1998). The Moon was originally thought to be nearly devoid of water (Estep et al., 1972), a consequence of volatile removal during the giant impact from which it formed (Canup & Asphaug, 2001). The discovery of water-bearing lunar glasses (e.g. Hauri et al., 2015; Saal et al., 2008) and minerals (Boyce et al., 2010; Greenwood et al., 2011; McCubbin et al., 2007, 2008, 2009, 2010) as well as polar ice deposits in permanently shadowed craters (Binder, 1998; Feldman et al., 1998; S. Li et al., 2018) with predicted magmatic origins (Wilcoski et al., 2022) indicate that water plays a complex role. Recent work suggests the Giant Impact could have created an envelope of vaporized gasses to prevent the water from escaping during lunar accretion (Hauri et al., 2015), and consequently leave a non-negligible amount of water in the initial lunar magma ocean (LMO). That remaining water could thus impact the chemical differentiation of the Moon after LMO crystallization by moderating the style of magmatic and volcanic processes (Milliken & Li, 2017; Morgan et al., 2021). Therefore, determination of the water budget in the initial LMO is critical to understanding the formation and evolution of the Moon.

Previous studies have utilized highland samples (e.g. Hui et al., 2013; Liu et al., 2012; McCubbin et al., 2015; Mills et al., 2014), mare basalt samples (e.g. Greenwood et al., 2011; Tartèse et al., 2013), and phase equilibria experiments (Lin et al., 2017) to estimate the initial lunar water budget. These estimates vary greatly, ranging from as low as 3 ppm (McCubbin et al., 2015) to as high as 500 ppm (Lin et al., 2017). Such a large variation may result from sample choices (e.g., anorthosite, picritic glass, apatite) in addition to analytical or experimental

approaches. As these lunar samples formed under different conditions, from LMO solidification to crustal magma differentiation to mantle melting, they may have recorded a wide range of magmatic processes involving volatile degassing. During solidification, the LMO first crystallized ultramafic cumulates, such as olivine and pyroxene, followed by a flotation crust of anorthite starting at ~78% solidification (Elkins-Tanton & Grove, 2011; Snyder et al., 1992). Because these cumulates are nominally anhydrous, it is expected that water will become increasingly concentrated in evolved LMO melts. If the evolved LMO melt reached water saturation, the total water budget of the Moon would inevitably become reduced through degassing and yield a more water-depleted state post LMO solidification. In this case, previous estimations of lunar mantle water contents, especially the higher end, likely indicate the maximum capacity of water in the highly evolved LMO melt. It is also possible that the evolved LMO melt never underwent substantial water degassing, which allows the lunar mantle to preserve the initial water budget.

A key to constraining the initial water budget of the Moon is understanding the solubility of water in highly evolved LMO melts. Many models have been developed to quantify water solubility in terrestrial magmas of rhyolitic to basaltic compositions (e.g. Gualda et al., 2012; Iacono-Marziano et al., 2012; Liu et al., 2005; Moore et al., 1998; Newman & Lowenstern, 2002; Shishkina et al., 2014). As demonstrated by these models, water solubility in silicate melt is controlled by H_2O partial pressure, melt composition, temperature, and total pressure. Because these previous models were calibrated for different compositions, pressures, and temperatures, their predictions of water solubilities can be inconsistent (Iacovino et al., 2021; Wieser et al., 2022). Using the Aluto rhyolite composition from Wieser et al. (2022) as an example, solubility predictions vary from 1.85 to 3.89 wt.%. Whether these models would work for evolved lunar

melts is unknown because of the Fe- and Al-rich composition. Furthermore, these models only consider the oxidized H species H_2O , which is the primary H species in terrestrial magmatic gasses for their relatively oxidized conditions. This is not the case for the Moon. The lunar mantle is a highly reduced environment, at an oxygen fugacity (f_{O_2}) between Iron-Wüstite (IW) to IW-2, $\sim 4\text{--}5$ orders of magnitude lower than that of Earth's depleted upper mantle. Considering that lower f_{O_2} increases H_2 partial pressure and decreases H_2O partial pressure, the highly reduced redox state can suppress the solubility of H_2O of late stage LMO melts and thus allow water degassing at higher pressures than terrestrial conditions, assuming H_2 solubility in the melt is negligible. The total water budget of the lunar mantle upon the completion of LMO solidification is therefore limited by the capacity of water in the highly evolved LMO melt depending on its water solubility and redox conditions. In this project, I will *i*) run high P-T experiments using an evolved lunar composition and compare experimental solubility data with current models to provide suggestions for a more accurate model, and *ii*) using the best fit model, provide a theoretical framework to access lunar water capacity considering $\text{H}_2/\text{H}_2\text{O}$ speciation and the effects of f_{O_2} .

2. Background

2.1 Lunar magma ocean crystallization

Soon after the Moon's formation via giant impact (Canup & Asphaug, 2001), the high energy of the system created the Lunar Magma Ocean (LMO). According to petrological modeling, the LMO first crystallized nominally anhydrous cumulates (olivine + pyroxene), followed by plagioclase at ~78% solidification (Fig. 1; Elkins-Tanton & Grove, 2011; Snyder et al., 1992). The less dense plagioclase floated to form the ferroan anorthosite (FAN) crust, which likely sealed off volatiles in the remaining melt due to their incompatibility in the preceding cumulates. After 95% solidification, a dense ilmenite-bearing cumulate (IBC) began crystallizing (Hess et al., 1978). Ilmenite is ~1.4 times denser than the forsterite and enstatite, the Mg-rich phases of olivine and pyroxene that represent the primitive mantle cumulates. This creates a density instability that would eventually cause an overturn of the mantle, likely after majority or full solidification. The last 1% LMO melt that once resided at the base of the FAN crust is referred to as urKREEP and was enriched in incompatible elements including K, rare-earth elements (REE), and P (Elkins-Tanton & Grove, 2011; Warren & Wasson, 1979; Fig. 1). Because the mantle cumulate and crustal mineral phases are dominantly anhydrous minerals, water and other volatiles should be enriched in the urKREEP layer (e.g. Elkins-Tanton & Grove, 2011). After complete solidification of the LMO, the concentration of heat-producing elements in urKREEP caused remelting of the material that then erupted on the surface.

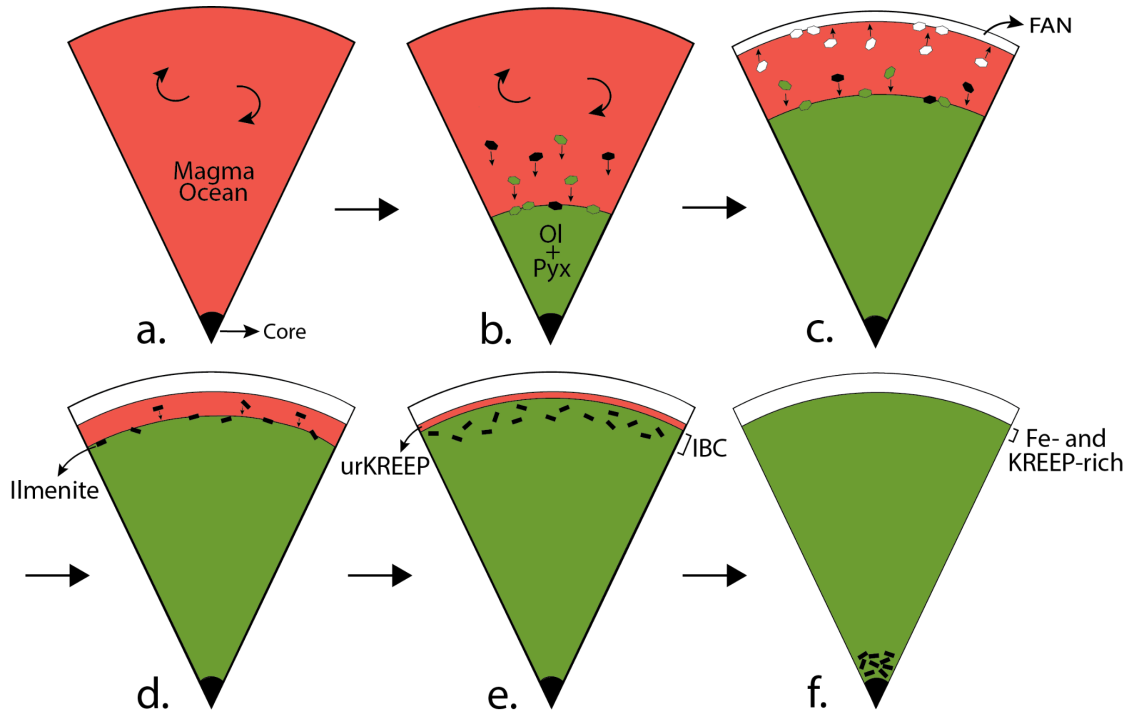


Figure 1: Crystallization of lunar magma ocean. Stages include (a) completely molten, (b) crystallization of mantle cumulates, (c) crystallization of flotation FAN crust, (d) crystallization of ilmenite to begin forming the ilmenite-bearing-cumulate (IBC), (e) urKREEP defined as the last 1% of melt, and (f) the completely solidified and overturned Moon, prior to lunar volcanism. Solidified Fe-rich and KREEP-containing material primarily remained at the base of the lunar crust and later initiated remelting due to the concentration of heat-producing elements, leading to volcanism.

Magma oceans are hypothesized to outgas volatiles, which could have produced an atmosphere early in lunar history (Elkins-Tanton, 2008). The Moon is massive enough to have a gravitationally bound atmosphere that contains H_2O or H_2 (Ikoma et al., 2018). If saturation is not reached during LMO evolution, then volatiles do not exist in the melt in excess and can effectively remain dissolved. The presence of a steam atmosphere would aid in maintaining a temperature above the solidus at the surface, prolonging the duration of the magma ocean (Abe & Matsui, 1985). The atmosphere is eventually lost via photoionization and gravitational escape

(Killen & Ip, 1999; Stern, 1999), the rate of which can be increased by any impacts. A lunar atmosphere is estimated to have a lifespan of ~ 70 Myr, or longer depending on values of atmospheric density (Needham & Kring, 2017). During late-stage solidification of the magma ocean, the saturation of ilmenite (i.e. an Fe-Ti oxide) could also provide energy efficient bubble nucleation sites (Hurwitz & Navon, 1994). It has been previously thought that it is highly unlikely for late-stage LMO melts, such as urKREEP, to reach saturation (Elkins-Tanton & Grove, 2011).

Early-degassing due to crust-breaching impacts exposing the urKREEP liquid has been suggested to occur prior to complete LMO complete solidification (Barnes et al., 2016). Evidence for this process comes from Cl, another volatile species that should be enriched in urKREEP. The elevated $\delta^{37}\text{Cl}$ value observed in lunar basalts, glasses, and apatites is thought to be inherited from urKREEP and is attributed to fractionation of ^{35}Cl to ^{37}Cl due to degassing (Boyce et al., 2015; McCubbin et al., 2015).

2.2 Lunar water measurements

The Moon has always been assumed to be “dry”. Over the last decade, however, an increasing number of “wet” lunar glasses have been discovered displaying water in concentrations comparable to Earth’s depleted mantle (Boyce et al., 2010; Hauri et al., 2015; McCubbin et al., 2015; Saal et al., 2008). Dissolved water content has been measured for a variety of lunar lithologies, including apatite grains (e.g. Barnes et al., 2013, 2014; Boyce et al., 2010; Greenwood et al., 2011; Hu et al., 2021; McCubbin et al., 2010; Tartèse et al., 2013, 2014), plagioclase grains (e.g. Hui et al., 2013, 2017), pyroclastic glass beads (Saal et al., 2008), and

olivine hosted melt inclusions (e.g. Chen et al., 2015; Hauri et al., 2011; Ni et al., 2019; Stephant et al., 2020). Mantle water abundances have been extrapolated from several types of lunar samples (apatite, mare basalt, volcanic glasses, etc.) and vary greatly from parts per billion to ~100 ppm (McCubbin et al., 2015). It can be assumed that mare basalts and volcanic glasses underwent additional degassing processes because they were generated from magmatism in the mantle over an extended period after LMO solidification, including magma generation from heat-producing element derived re-melting, eruptive volatile loss, and fractional crystallization. Apatite grains from a variety of lunar rock types, correcting for the secondary processes, as well as FAN plagioclase grains have been used by previous authors to extrapolate urKREEP and bulk LMO water contents.

2.2.1 Picritic glasses and melt inclusions

Volcanic picritic glasses sampling KREEP-poor compositions contain 0.4 to 46 ppm H₂O across a range of Ti glass contents (orange, yellow, and green glass beads). These samples would have been produced by fire-fountain eruptions, where one of the main volatile drivers is likely H₂ (e.g. McCubbin et al., 2015; Newcombe et al., 2017). Modeling of diffusive volatile loss during eruption showed that lunar glasses lost up to 98% of their original magmatic water content, estimating pre-eruptive contents of ~745 ppm, with a minimum estimate of at least 260 ppm H₂O (Saal et al., 2008). This can be extrapolated to source regions of 2-12 ppm (Elkins-Tanton & Grove, 2011). Within the same regions, olivine hosted melt inclusions within high-Ti orange glass beads were found to have 615 to 1410 ppm H₂O (Hauri et al., 2011). The lunar mantle is

assumed to be heterogeneous; extrapolated water abundances range between 9-130 ppm (McCubbin et al., 2015).

2.2.2 Apatite

Apatite is the most main volatile bearing mineral found on the Moon, always appearing as a trace mineral. This mineral phase has undergone many processes that could alter the water available prior to the mineral formation, including magma generation, eruption volatile loss, and preceding melt crystallization. Apatite has been identified in mare basalts, lunar granites, Mg-suite rocks, alkali suite rocks, KREEP-rich impact melts, and KREEP basalts. Mare basalt apatites contain the largest range of H₂O contents of up to 7000 ppm (Greenwood et al., 2011; Tartèse et al., 2013), whereas Mg-suite rocks, alkali suite rocks, KREEP-rich impact melt apatites contain up to 1600 ppm H₂O (Barnes et al., 2014). KREEP basalts, thought to be derived from remelted urKREEP material, typically contain apatites with 40 ppm to 2500 ppm H₂O (McCubbin et al., 2010; Tartèse et al., 2014).

Water content measurements from apatites were used in two different methods to extrapolate both urKREEP and LMO water contents using various lunar rock types: lunar soils and highlands apatite (LSHA) and chondritic F and highlands apatite (CFHA). McCubbin et al. (2015) first employed an LSHA composition combined with both apatite-melt partitioning data and metasomatism derived F estimates to infer volatile concentrations in urKREEP and the bulk mantle. Assuming 0.5% trapped interstitial liquid, the bulk mantle is estimated to have 0.15 to 0.61 ppm H₂O, urKREEP to contain 300 to 1250 ppm, and the bulk LMO to contain 3.1 to 13.1 ppm (McCubbin et al., 2015). The LSHA estimates may be underestimates because of the

observed depletion in F relative to those estimated for the mantle. McCubbin et al. (2015) also utilized a CFHA composition, where the primordial bulk Moon F abundance was assumed to be that of CI carbonaceous chondrites, allowing the derivation of F abundances for the bulk LMO. This value along with the relative abundances of F, Cl, and H₂O in the CFHA composition were used to infer H₂O bulk mantle and urKREEP. Again assuming 0.5% trapped interstitial liquid in the cumulate mantle during LMO solidification, the bulk mantle is estimated to have 1.2 to 5.3 ppm H₂O, urKREEP to have 0.26 to 1.09 wt.%, and the bulk LMO to have 27–114 ppm (McCubbin et al., 2015).

2.2.3 Plagioclase Feldspar

Plagioclase is a nominally anhydrous mineral (NAM) that makes up a majority of the FAN crust as well as brecciated rocks and soils in the lunar highlands. FAN plagioclase grains have been found to contain up to 6 ppm H₂O, while grains from a Mg-suite troctolite contain up to 2.7 ppm (Hui et al., 2013). Feldspar grains derived from a brecciated granitoid clast contain up to 1000 ppm H₂O (Mills et al., 2014).

Water content measurements from plagioclase have been used to extrapolate both urKREEP and LMO water contents. Liu et al. (2012) measured from 27 ppm H₂O in an agglutinate glass from a lunar soil plagioclase grain, which is often taken as a lower bound estimate of bulk LMO contents (McCubbin et al., 2015). Hui et al. (2013) measured water contents of FAN feldspar grains and used a plagioclase mineral-melt partition coefficient of 0.004 to extrapolate the water contents of the source melt. The resulting estimates are 320 ppm H₂O in the bulk LMO and up to 1.4 wt.% H₂O in urKREEP.

2.2.4 Phase Equilibrium Estimates

Lin et al. (2017) performed high P-T phase equilibria experiments simulating LMO solidification for a range of lunar hydration conditions, from dry to wet. The dry conditions allowed for earlier nucleation of plagioclase, leading to a thicker crust than is observed on the Moon. Estimates of initial LMO depth range between 400-1000 km (Elkins-Tanton et al., 2011). To explain GRAIL observed crustal thicknesses (Wieczorek et al., 2013), Lin et al., (2017) predicts at least 500 ppm for a shallow magma ocean, but > 1800 ppm for a deep magma ocean. For the purposes of this project, the CFHA, Hui et. (2013), and Lin et al., (2017) ranges are explored.

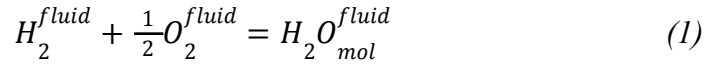
Table 1: Summary of the estimated water contents for the bulk LMO, urKREEP, and lunar mantle from the literature.

H₂O Estimate Source	LMO	urKREEP	Mantle
LSHA (McCubbin et al., 2015)	3.1-13.1 ppm	300-1250 ppm	0.15 to 0.61 ppm
CFHA (McCubbin et al., 2015)	27-114 ppm	0.26-1.09 wt.%	1.2 to 5.3 ppm
Hui et al. (2013)	320 ppm	≤1.4 wt.%	-
Lin et al. (2017)	500-1800 ppm	-	-

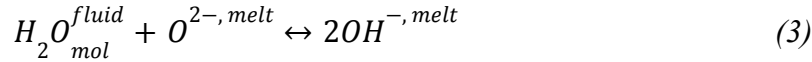
2.3 Thermodynamics

The solubility of a volatile species in the melt describes the maximum concentration of a volatile species dissolved in the liquid at certain conditions. In this project, only H volatile species are considered. As the main focus of this thesis is on the water budget of the Moon, we only consider the volatile species of H with two different valence states (i.e., H₂ and H₂O). Other

volatile elements such as Cl, F, C, and S are ignored here because they are either highly depleted in lunar interior (e.g., C and S; McCubbin et al., 2015) or much more soluble in the melt than water (e.g., F; Aiuppa et al., 2009). In a fluid-melt equilibrium system with H as the only volatile element, the fluid phase includes two H redox species, H_2 and H_2O , following the redox reaction:



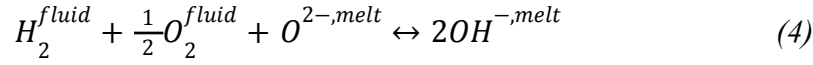
Both H species could dissolve in the melt following the dissolution reactions (Stolper, 1982b):



where O^{2-} and OH^- are the oxygen anion and hydroxyl, respectively, associated with cations in the melt. At higher, terrestrial relevant f_{O_2} conditions, H_2O is the primary fluid species. At reducing conditions, OH^- becomes more relevant as a dissolved volatile species in the melt phase (Hirschmann et al., 2012; McMillian, 1994). Because overall solubility is controlled by the partial pressure of a species in the fluid phase, OH^- can be used directly as a proxy for H_2O in the melt (e.g. Saal et al., 2008).

H_2O could dissolve in the melt as molecular H_2O and OH^- anion complex (Stolper, 1982a); OH^- , however, is the primary H^+ species dissolved in high-temperature melts with low to moderate water contents (Zhang et al., 1997). H_2 could be a major component in the gas during lunar magmatism or magma ocean solidification for the highly reduced conditions; however, the dissolved H_2 in lunar melts is likely negligible in lunar melts unless its partial pressure could go above ~ 300 MPa (e.g., Hirschmann et al., 2012). Hence, the direct dissolution of molecular H_2 in

the melt will not be considered in this thesis. Combining Eq. (1) and (4), we consider H_2 solubility through the following reaction:



A similar reaction has also been proposed previously as the driver for the fire-fountain eruptions of lunar pyroclastic glass (e.g. McCubbin et al., 2015; Newcombe et al., 2017).

In lunar magmatic systems, the degassing of H can then be described by Eqs. (1), (3) and (4) and particularly requires knowledge of *a*) redox equilibria between H_2 and H_2O in the gas and *b*) H_2O solubility in the silicate melts. As redox equilibria in the gas has been extensively investigated in many previous studies, the former can be quantified using existing thermodynamic data and equation of states for the lunar relevant redox conditions. Notably, several water solubility models are also available in the literature (e.g. Gualda et al., 2012; Iacono-Marziano et al., 2012; Liu et al., 2005; Moore et al., 1998; Newman & Lowenstern, 2002; Shishkina et al., 2014). All previous water solubility models follow similar thermodynamics as described by Eq. (3). The equilibrium constant for Eq. (3) can be expressed by:

$$K = \frac{(a_{OH}^{melt})^2}{f_{H_2O}^{fluid} a_{O^{2-}}^{melt}} \quad (5)$$

where a is activity and f_{H_2O} is the fugacity of molecular water. Given that $a = X\gamma$, where X is the mole fractions and γ is the activity coefficient:

$$K = \frac{(X_{OH}^{melt} \gamma_{OH}^{melt})^2}{f_{H_2O}^{fluid} X_{O^{2-}}^{melt} \gamma_{O^{2-}}^{melt}} \quad (6)$$

The equilibrium coefficient can also be expressed by:

$$\ln K = \frac{-\Delta G}{RT}, \quad (7)$$

Accordingly, one can obtain a generic thermodynamic expression from Eq. (6):

$$2 \ln X_{OH}^{melt} = \ln f_{H_2O} + \ln a_{O^{2-}} - \ln \gamma_{OH}^{melt} + \frac{\Delta G}{RT} \quad (8)$$

It is important to note that melt composition impacts the solubility of water. In Eq. (8), uncertainty stems from the $\ln a_{O^{2-}}$ and $\ln \gamma_{OH}^{melt}$ terms because both are compositionally dependent. Given that previous water solubility models were mainly calibrated for terrestrial magma compositions and f_{O_2} conditions, it remains unclear whether they are suitable for evolved LMO magmas. In the following section, we will briefly review the commonly used water solubility models from the literature.

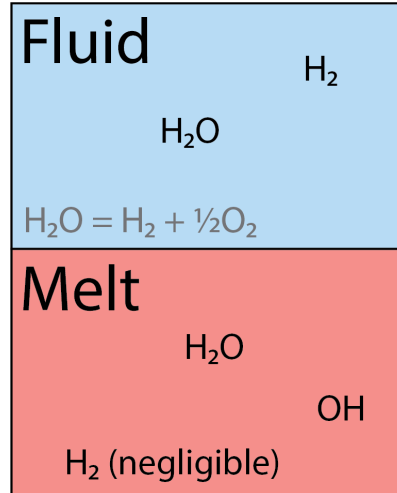


Figure 2: Speciation of H-volatile species in the fluid and melt phases.

2.4 Previous solubility models

2.4.1 Magmasat

The Magmasat thermodynamic solubility model is utilized for H₂O-CO₂ mixing systems or H₂O only systems (Ghiorso & Gualda, 2015), adapted from Rhyolite-MELTS (Gualda et al.,

2012). Calibrated from published experimental data, Magmasat covers a broad range of silicate compositions, from high Mg basalt to rhyolites. The only dissolved H-volatile species considered is OH, based on the assumption that the activity of molecular water is approximately equal to the mole fraction of molecular water dissolved in the melt squared ($a_{H_2O} \approx X_{H_2O}^2$). The model is based on the configurational entropy for dissolved water, derived from Ghiorso et al. (1983). An excess enthalpy term is included to account for any effects from the speciation assumptions (Gualda et al., 2012). For the H₂O only system, Magmasat covers pressures in the range 0-2000 MPa and temperatures in the range 550-1420 °C.

2.4.2 *VolatileCalc-Rhyolite*

VolatileCalc-Rhyolite is H₂O-CO₂ mixture model that can calculate degassing paths, saturation pressures, isobars, and isopleths for magmas of a rhyolitic composition (Newman & Lowenstern, 2002). The thermodynamic expressions that describe H₂O in the system are from Silver & Stolper (1989), with fitted parameters and dissolution driven enthalpy changes from Silver (1988) and Silver et al. (1990), respectively. H-volatile speciation is considered through molecular H₂O and OH for pressures up to 500 MPa and temperatures in range 600-1500 °C (Wieser et al., 2022). Unlike the basaltic version of VolatileCalc (Dixon, 1997; Newman & Lowenstern, 2002), VolatileCalc-rhyolite is independent of melt composition and highly sensitive to temperature. Redox conditions are kept stable, buffered at the Ni-NiO buffer (Newman & Lowenstern, 2002). VolatileCalc-Rhyolite is available through a macro-enabled Excel spreadsheet, from which the calculate degassing paths feature was utilized for this project.

2.4.3 Moore et al. (1998)

The Moore et al. (1998) thermodynamic pure H₂O solubility model covers pressures in the range 0-300 MPa and temperatures 700-1200 °C. A wide range of silicate magma compositions are used for calibration, including from basalts to rhyolites, calibrated from a mixture of study specific experimental and literature derived data. H-bearing speciation effects are considered in the model. All dissolved contents are assumed to be molecular H₂O. Redox effects are not considered (Wieser et al., 2022). The Moore et al. (1998) empirical expression for dissolution of water in magma is as follow:

$$\ln X_{H_2O}^{melt} = \frac{1}{2} \left(\frac{a}{T} + \sum_i b_i X_i \frac{P}{T} + c \ln f_{H_2O}^{fluid} + d \right) \quad (9)$$

where X is mole fraction, i is oxide phase, f is H₂O fugacity, T is temperature in Kelvin, P is pressure in bars, and a , b , c , and d are calibrated fit parameters listed below in Table 2. The model is available through the Volatile Equilibria and Saturation Identification calculator hosted in python (VESIcal; Iacovino et al., 2021; Wieser et al., 2022).

Table 2: Fit parameters for Moore et al. (1998) H₂O solubility model ($\pm$ error).

Coefficient	a	$b_{Al_2O_3}$	b_{FeO}	b_{Na_2O}	c	d
Value (error)	2565 (362)	-1.997 (0.706)	-0.9275 (0.394)	2.736 (0.871)	1.171 (0.069)	-14.21 (0.54)

2.4.4 Liu et al. (2005)

Liu et al. (2005) solubility model is for H₂O-CO₂ mixtures and pure H₂O systems, based on study specific experimental and literature data. Experiments were conducted for haplogranites and rhyolite compositions, spanning pressures up to 500 MPa and temperatures in the range 700-1200 °C. The empirical model does not consider melt compositional effects, H-volatile

speciation effects, or redox effects (Wieser et al., 2022). The model is described by the following expression:

$$[H_2O]_{wt.\%} = [a_1(P_{H_2O}/10)^{0.5} + a_2(P_{H_2O}/10) + a_3(P_{H_2O}/10)^{1.5}] / T + a_4(P_{H_2O}/10)^{1.5} + P_{CO_2}(a_5(P_{H_2O}/10)^{0.5} + a_6(P_{H_2O}/10)) \quad (10.1)$$

$$[H_2O]^{wt.\%} = [a_1(P_{H_2O}/10)^{0.5} + a_2(P_{H_2O}/10) + a_3(P_{H_2O}/10)^{1.5}] / T + a_4(P_{H_2O}/10)^{1.5} \quad (10.2)$$

Where T is temperature in Kelvin and P_{H_2O} is partial pressure of H₂O and is equivalent to the mole fraction of H₂O in the fluid multiplied by the total pressure ($P_{H_2O} = X_{H_2O}^f P$), with P in bars.

The fit parameters a_1 , a_2 , a_3 , a_4 , a_5 , and a_6 are listed in Table 3. The Liu et al. (2005) model is available through VESICAL (Iacovino et al., 2021; Wieser et al., 2022).

Table 3: Fit parameters for Liu et al. (2005) H₂O-CO₂ solubility model ($\pm$ error).

Coefficient	a_1	a_2	a_3	a_4	a_5	a_6
Value	354.94	9.623	-1.5223	1.2439e-3	-1.084e-4	-1.362e-5
(error)	(4.55)	(0.923)	(0.0722)	(4.99e-5)	(4.06e-5)	(3.52e-6)

2.4.5 Iacono-Marziano et al. (2012)

The Iacono-Marziano et al. (2012) solubility model (IM2012) is for H₂O-CO₂ mixing and pure H₂O systems that is based on simplified melt-fluid thermodynamic expressions with parameterizations that account for the chemical composition and structure of the melt. Across 289 experiments, 44 different mafic compositions were tested, from subalkaline to alkaline

basalts and andesites. IM2012 for pure H₂O covers pressures in the range 16-607 MPa and temperatures 1000-1250 °C. No H-volatile speciation or redox sensitivity were considered in the model (Wieser et al., 2022). The model is described by the following series of equations for hydrous and anhydrous systems:

$$\ln[H_2O]_{wt.\%} = a \ln(P_{H_2O}) + b \frac{NBO}{O} + \frac{A}{T} + B + C \frac{P}{T} \quad (11.1)$$

$$\frac{NBO}{O}^{Anhyd} = \frac{X_{K_2O} + X_{Na_2O} + X_{CaO} + X_{MgO} + X_{FeO} - X_{Al_2O_3}}{(2X_{SiO_2} + 2X_{TiO_2} + 3X_{Al_2O_3} + X_{MgO} + X_{FeO} + X_{CaO} + X_{Na_2O} + X_{K_2O})} \quad (11.2)$$

$$\frac{NBO}{O}^{Hyd} = \frac{X_{H_2O} + X_{K_2O} + X_{Na_2O} + X_{CaO} + X_{MgO} + X_{FeO} - X_{Al_2O_3}}{(2X_{SiO_2} + 2X_{TiO_2} + 3X_{Al_2O_3} + X_{MgO} + X_{FeO} + X_{CaO} + X_{Na_2O} + X_{K_2O} + X_{H_2O})} \quad (11.3)$$

where T is temperature in Kelvin, P is pressure in bars, and NBO/O is non-bridging oxygen per oxygen. H₂O solubility was found to have negligible effects of melt composition and structure, and a weak correlation with NBO/O. To calculate the solubility of a hydrous melt, the anhydrous NBO/O equation with the hydrous coefficients is used because the water content is initially unknown. The model is available through a web application and VESIcal (Iacovino et al., 2021; Wieser et al., 2022).

Table 4: Hydrous coefficients of Iacono-Marziano et al. (2012) solubility model ($\pm 2\sigma$ error). Values are updated post-manuscript publication from the web-based application of the model.

Coefficient	<i>a</i>	<i>b</i>	<i>B</i>	<i>C</i>
Anhydrous (2σ)	0.54 (0.02)	1.24 (0.33)	-2.95 (0.17)	0.02 (0.02)
Hydrous (2σ)	0.521 (0.016)	2.116 (0.236)	-3.244 (0.106)	-0.022 (0.019)

2.4.6 Shishkina et al. (2014)

The Shishkina et al. (2014) model is a solubility model for H₂O-CO₂ and pure H₂O systems. For pure H₂O, the model was experimentally calibrated in the pressure range of 50-500 MPa and the temperature range 1200 to 1250 °C. Due to the narrow temperature range, the empirical model does not include the effect of temperature on solubility. The equation was tested for 1050-1400 °C, but found to be preferably consistent between 1150-1250 °C. Experiments were conducted across a range of mafic to intermediate composition, including subalkaline to alkaline basalt and andesite. The Shishkina et al. (2014) model is therefore viable for melt compositions with SiO₂ < 65 wt.%. No H-volatile speciation or redox effects were considered (Wieser et al., 2022). The model is described by the following expression:

$$[H_2O]_{wt.\%} = (3.36 \times 10^{-7}(\frac{P}{10})^3 - 2.33 \times 10^{-4}(\frac{P}{10})^2 - 0.0711\frac{P}{10} - 1.1309)(X_{Na} - X_K) \\ - 1.2 \times 10^{-5}(\frac{P}{10})^2 + 0.0196\frac{P}{10} + 1.1297 \quad (12)$$

where P is pressure in bars, and X_{Na} and X_K are mole fractions of the Na and K cations in the melt. The model is available through VESIcal (Iacovino et al., 2021; Wieser et al., 2022).

3. Methods

3.1 Sample Preparation

Known KREEP-containing compositions from returned Apollo samples were considered as the starting compositions for the solubility experiments, including a KREEP basalt (KB; Ryder & Bower, 1976) and granitic lunar rock (LG; Seddio et al., 2013). The target compositions are listed in Table 5. Reagent-grade oxide or carbonate powders were used to synthesize the lunar samples. The carbonates, CaCO_3 and K_2CO_4 , were fired at 800 °C and 600 °C, respectively, to obtain CaO and K_2O prior to mixing with other oxides. Each composition was mixed in a mortar and pestle with ethanol for ~7 hours to ensure homogenization. The basaltic composition, however, was not successful in producing a quenched glass because of rapid crystallization of small microlites even with higher temperatures and the fastest quench method. Hence, the granitic lunar composition was used as the only starting mixture. CaO, K_2O , and the lunar granite powders were stored in a 110 °C oven to prevent hydration.

For each experiment, ~50 mg starting oxide mixtures were loaded in AuPd capsules with distilled water (Fig. 3). The sample capsules were made manually using AuPd tubes (outer diameter: 2- and 3-mm) with one end welded shut. ~4-8 wt.% water was first added to the open capsule to saturate the sample, and the sample powder was loaded after. The material was continuously compacted with a small rod to ensure that the resulting glass would be one consolidated piece. Preliminary experiment runs where this step was not included resulted in sediment-like unconsolidated glass pieces, making for added difficulty in further thin section preparation and analysis processes. Afterwards, the other end of the capsule was crimped and

welded shut. The quality of the welded seals were confirmed via capsule mass after several hours in a 110 °C oven. The experimental conditions were listed in Table 6.

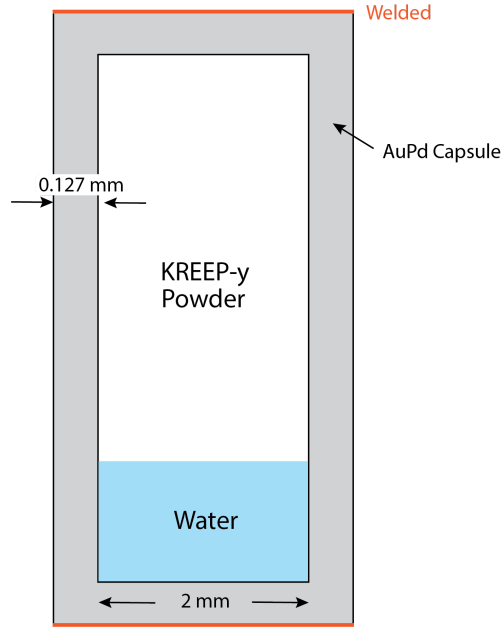


Figure 3: Experimental setup. 2mm AuPd capsule loaded with KREEP-y composition powder and water. One run utilized a 3mm capsule instead with the same setup.

3.2 Experimental Setup

Samples were placed at conditions relevant to the base of the lunar crust using a MHC pressure vessel, pressurized by argon gas. Several bars of methane were added to the pressurizing fluid to reduce the f_{O_2} as well as aid in the generation of an uncrystallized glass. Preliminary experiments without methane added resulted in FeTi-oxides crystallizing along the capsule walls. Rhyolite-MELTS (Ghiorso & Gualda, 2015; Gualda et al., 2012) predicted the

liquidus for the LG composition to be ~ 1100 °C. Experiments were run at 1175 °C to ensure production of uncrystallized glass upon quenching, and at pressures in the range of 50-150 MPa. Once pressurized, LG samples were held at those conditions for ~ 24 hrs. The samples were then quenched by submerging the heated end of the pressure vessel in a bucket of water.

3.3 Analysis

Once quenched into glass the samples were removed from the capsules. If a hissing sound could be heard when first opening the capsule, it is clear that the melt was in equilibrium with the fluid at the melt conditions. All experiments shown in the tables exhibited this sound, making them viable to analyze for solubility. Small pieces of each sample were then mounted in epoxy and singly polished. Thin sections LG-05kb-1.2, LG-1kb-8.1, and LG-15kb-1.4 were carbon coated and analyzed using a JEOL JXA-8200 Electron Microprobe (EPMA) to determine glass composition and confirm it with the target compositions listed in Table 5. To account. Six spots were analyzed on each thin section in regions lacking bubbles or microlite crystals (Fig. A.1-A.3). In order to preserve the alkalis in the hydrated glasses, a defocused 10 μm beam was used with an accelerating voltage of 15 kV and a beam current of 10 nA. Probe for windows was used to account for alkali diffusion during analysis. A rhyolitic glass standard of known composition (KN18; Table A.2) was measured before and after each sample to correct for instrumental uncertainty. Results of EPMA analysis are listed in Table 7. Some variations between samples and variations with the target composition point to a degree of error in the sample synthesis processes.

After being double-polished, thin sections LG-05kb-1.2, LG-1kb-8.1, and LG-15kb-1.4 were analyzed with Thermo Electron Nicolet iN10 Fourier Transform Infrared (FTIR)

Spectrometer. Transmission spectra were collected over 64 scans with a resolution of 4 cm⁻¹ and a collection time of 22 seconds. Using a multi-coated KBr/germanium beam splitter, measurements were made between 7000 and 1000 cm⁻¹. Total water content was measured at the 3570 cm⁻¹ absorption feature, where the peak height is taken as the absorbance. Molecular water (H₂O) content was measured at 1630 cm⁻¹ and 5230 cm⁻¹ absorption features, and hydroxyl (OH⁻) was measured at the 4520 cm⁻¹ feature. Six to seven spots were analyzed on each sample. The thickness of each spot on the examined glasses was measured using a Heidenhain focus drive linear encoder on a petrographic microscope. Thickness measurements were corrected for the diffraction of the light path through the sample with depth.

Only one data point, spot 4 on LG-1kb-8.1, was omitted from analysis because the area of the glass was too dark to obtain an accurate thickness measurement by eye, likely because this region was thicker. See the appendix (Table A.3) for thickness, absorption peak heights, and volatile contents for individual spots of observation. The 1630 cm⁻¹ and 3570 cm⁻¹ absorption features were converted to volatile contents using the Beer Lambert Law.

$$C_{1630; 3570} = \frac{A * MW}{\rho * d * \epsilon} f \quad (13)$$

where C is water concentration (wt.%), A is absorbance, MW is molar weight of H₂O, ρ is the density of rhyolitic glass (2350 g/L), d is thickness of the sample (cm), f is the correction for weight percent (10²), and ϵ is the molar absorptivity coefficient [L/[cm·mol]]. Molar absorptivity for the 3570 cm⁻¹ values range between 56 L/[cm·mol] for H₂O and 100 L/[cm·mol] for the OH⁻ (Newman et al., 1986). Accounting for both species, I chose an ϵ value of 80 L/[cm·mol] using the methods of McIntosh et al. (2017). The ϵ value for the 1630 cm⁻¹ absorption feature is 55 L/[cm·mol] (Newman et al., 1986). The 4520 cm⁻¹ and 5230 cm⁻¹ absorption features were

converted to volatile contents using the methods of Zhang et al. (1997), as described by the following equations.

$$C(1 - C) = a_0 A_{5230} + (b_0 + b_1 A_{5230} + b_2 A_{4520}) A_{4520} \quad (14.1)$$

$$C^w = \frac{1 - \sqrt{1 - 4(a_0 A_{5230} + (b_0 + b_1 A_{5230} + b_2 A_{4520}) A_{4520})}}{2} * f \quad (14.2)$$

$$C_{5230}^w = \frac{a_0 A_{5230}}{1 - C^w} * f \quad (14.3)$$

$$C_{4520}^w = \frac{(b_0 + b_1 A_{5230} + b_2 A_{4520}) A_{4520}}{1 - C^w} * f \quad (14.4)$$

where C^w is the total water in the system, $a_0 = 0.04217 \pm 0.0013$ mm, $b_0 = 0.04024 \pm 0.0023$ mm, $b_1 = -0.02011 \pm 0.0051$ mm², $b_2 = 0.0522 \pm 0.0051$ mm², f is the correction for weight percent (10²), and A_{4520} and A_{5230} are the absorption feature peak heights divided by the thickness of the sample as a correction.

Table 5: Target composition from Seddio et al. (2013), initial measured composition of synthetic sample powder ($\pm$ error), and EPMA measured compositions for each experimental run ($\pm$ error). Phosphorus is not measured with EPMA due to the low concentrations in the desired composition.

Composition/ Sample	SiO ₂ [wt.%]	TiO ₂ [wt.%]	Al ₂ O ₃ [wt.%]	FeO [wt.%]	MgO [wt.%]	CaO [wt.%]	Na ₂ O [wt.%]	K ₂ O [wt.%]	P ₂ O ₅ [wt.%]	Total [wt.%]
Seddio et al. (2013)*	70.17	1.05	13.53	4.97	0.15	3.01	2.51	4.56	0.05	100.00
Initial composition**	69.81 (0.51)	1.15 (0.12)	13.47 (0.11)	5.00 (0.10)	0.18 (0.04)	3.14 (0.18)	2.53 (0.06)	4.66 (0.16)	0.06 (0.02)	100.00
LG-05kb-1.2	71.44 (0.49)	0.95 (0.22)	14.65 (0.16)	3.54 (0.08)	0.21 (0.04)	2.47 (0.11)	2.61 (0.10)	1.97 (0.06)	-	97.84

LG-1kb-8.1	70.22 (0.59)	1.22 (0.32)	14.50 (0.11)	2.89 (0.04)	0.21 (0.03)	2.69 (0.07)	2.69 (0.12)	1.90 (0.07)	-	96.32
LG-15kb-1.4	69.90 (0.35)	1.20 (0.29)	14.26 (0.11)	3.26 (0.16)	0.19 (0.02)	2.32 (0.08)	2.52 (0.15)	1.98 (0.05)	-	95.63

*Normalized for the exclusion of additional oxide phases in the published composition.

**Physical mass of oxide powders measured to synthesis sample

Table 6: Experimental inputs and conditions. One standard deviation of each run's pressure conditions is given in parentheses.

Sample	Powder mass [mg]	H ₂ O [wt.%]	P ($\pm 1\sigma$) [bars]	T [°C]	t [hr]
LG-05kb	50.1	4.02	~509 (1.14)	1175	24
LG-1kb	67.1	5.9	~1023 (8.94)	1175	24
LG-15kb	49.9	7.76	~1520 (13.41)	1175	24

3.4 Thermodynamic Modeling

Previous solubility models do not account for the change in H speciation as a result of variations in f_{O_2} . At reduced redox conditions, H₂ becomes a prominent fluid species. This will effectively reduce the partial pressure of H₂O in the fluid, and therefore also reduce solubility in the melt. I have considered hydroxyl as a direct proxy for molecular water, resulting in observation of speciation effects between H₂ and H₂O. I developed a function to calculate the speciation of H in the fluid phase as a solution. This requires first looking at the thermodynamic behavior of the species in the fluid phase as a function of fugacity.

The equilibrium constant for the reaction $H_2^{fluid} + \frac{1}{2}O_2 = H_2O^{fluid}$ can be calculated via

Eq (8). Where

$$\Delta G = \Delta_f G(H_2) + \frac{1}{2}\Delta_f G(O_2) - \Delta_f G(H_2O) \quad (15)$$

Because Gibbs free energy (G) is constant for H_2 and O_2 , then $\Delta_f G = 0$ for each species. Eq. (8)

can therefore be solved using the National Institute of Standards and Technology (NIST) JANAF thermodynamic data table for gaseous H_2O (Chase Jr., 1998) to interpolate ΔG for the desired temperature. Eq. (7) can then be rewritten in terms of fugacities:

$$K = \frac{f_{H_2O}}{f_{H_2}\sqrt{f_{O_2}}} \quad (16)$$

Rearranging equations 14 and 16, the following expression for the ratio of H_2O to H_2 in the fluid phase is derived:

$$\frac{X_{H_2O}^g}{X_{H_2}^g} = \exp\left[\frac{-\Delta_f G_{H_2O}}{RT}\right] \sqrt{f_{O_2}} \frac{\phi_{H_2}}{\phi_{H_2O}} \quad (17)$$

where ϕ_{H_2} and ϕ_{H_2O} are fugacity coefficients of H_2 and H_2O , respectively, and calculated using the method of Peng & Robinson (1976), as described by the following series of equations (Eq. 18.1-18.12).

$$T_r = T/T_c \quad (18.1)$$

$$\kappa = 0.37464 + 1.54226\omega + 0.26992\omega^2 \quad (18.2)$$

$$\alpha = [1 + \kappa(1 - T_r^{0.5})]^2 \quad (18.3)$$

where T_c is the critical temperature, 32.98 K for H_2 and 647.14 K for H_2O , and ω is the acentric factor, -0.216 for H_2 and 0.344 for H_2O (Reid et al., 1989).

$$a = \frac{0.45724 R^2 T_c^2}{P_c} \alpha \quad (18.4)$$

$$b = \frac{0.07780 R T_c}{P_c} \quad (18.5)$$

$$A = \frac{aP}{R^2 T^2} \quad (18.6)$$

$$B = \frac{bP}{RT} \quad (18.7)$$

where P_c is the critical pressure, 32.98 °C for H_2 and 647.14 °C for H_2O , a , b , A , and B are constants.

$$c_2 = B - 1 \quad (18.8)$$

$$c_3 = A - 3B^2 - 2B \quad (18.9)$$

$$c_4 = -(AB - B^2 - B^3) \quad (18.10)$$

$$c_1 x^3 + c_2 x^2 + c_3 x + c_4 = 0 \quad (18.11),$$

where $c_1 = 1$ and Z is equal to the maximum value of x from the cubic solution of Eq (18.11).

$$\phi = \exp[Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}} B \ln(\frac{Z + 2.414*B}{Z - 0.414*B})] \quad (18.12)$$

The mole fraction of each species in the system can be inferred from a simple series of equations.

$$X_{H_2}^{fluid} = X_{H\ total}^{fluid} / (1 + \frac{X_{H_2O}^{fluid}}{X_{H_2}^{fluid}}) \quad (19)$$

$$X_{H_2O}^{fluid} = X_{H\ total}^{fluid} - X_{H_2}^{fluid} \quad (20)$$

$X_{H_2O}^{fluid}$ can then be used as an input for previous solubility models, either independently or to

calculate H_2O partial pressure. This allows for f_{O_2} to be considered theoretically in solubility

models and serve as preliminary work for necessary future experimental studies. The full python function can be seen in the appendix.

4. Results

4.1 Solubility measurements

Dissolved water content measurements of samples across a range of pressures were acquired using FTIR. Analysis was run on thin sections LG-05kb-1.2, LG-1kb-8.1, and LG-15kb-1.4. The full data from individual spots across each glass grain can be found in Table A.3. Total water content estimates were derived individually for 3570 cm^{-1} and the $5230\text{ cm}^{-1} + 4520\text{ cm}^{-1}$ features. The $5230\text{ cm}^{-1} + 4520\text{ cm}^{-1}$ features for several FTIR measurements lack necessary sensitivity because many features were nearly indistinguishable from the background. The 3570 cm^{-1} is therefore the feature chosen for derived water contents. All average estimates are listed in Table 7. The lowest pressure sample at 50 MPa, LG-05kb-1.2, was found to have 1.60 wt.% dissolved water. LG-1kb-8.1 at 100 MPa was found to have a dissolved water content of 1.81 wt.%. At the highest pressure of 150 MPa, LG-15kb-1.4, was found to have 2.28 wt.% dissolved water contents. A CO_2 peak is also observed in the spectra, resulting in contents varying between ~90-180 ppm (Table 7).

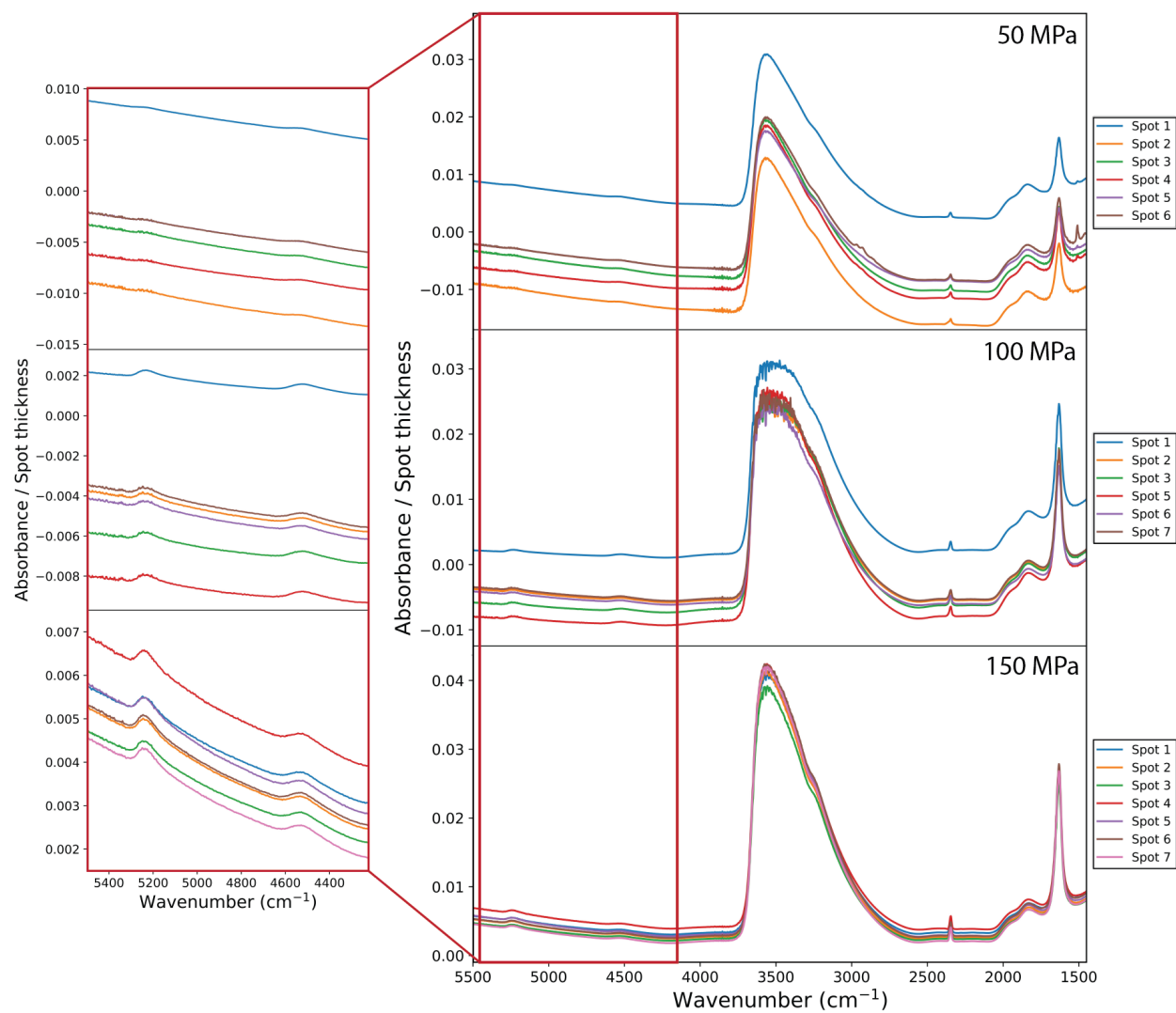


Figure 4: Spectra for each LG-05kb-1.2 (top), LG-1kb-8.1 (middle), LG-15kb-1.4 (bottom) at multiple spots across each glass piece. Absorbance is normalized by the thickness at each individual location. Average thicknesses for each spot are listed in appendix (Table A.3). Cut out to the left shows a magnified view of the 5230 cm⁻¹ and 4520 cm⁻¹ features. A CO₂ peak is present at 2350 cm⁻¹, likely due to incomplete decarbonation of CaCO₃ and K₂CO₄.

Table 7: FTIR measured total water contents from the 1630 cm^{-1} , 3570 cm^{-1} , and the 5230 cm^{-1} + 4520 cm^{-1} features, all expressed in wt.% ($\pm 1\sigma$ error). These values are averages around several analyzed spots on the glass piece. The full table can be seen in the appendix (Table A.3).

Sample	1630 cm^{-1} $\text{H}_2\text{O}_{\text{mol}}$ [wt.%]	3570 cm^{-1} $\text{H}_2\text{O}_{\text{total}}$ [wt.%]	5230 and 4520 cm^{-1} $\text{H}_2\text{O}_{\text{total}}$ [wt.%]	2350 cm^{-1} CO_2 [ppm]
LG-05kb-1.2	0.76 (0.04)	1.60 (0.08)	1.26 (0.09)	90.59 (7.54)
LG-1kb-8.1	1.39 (0.27)	1.81 (0.24)	1.82 (0.42)	128.13 (18.32)
LG-15kb-1.4	1.68 (0.06)	2.28 (0.07)	1.69 (0.07)	181.06 (9.14)

4.2 Model Comparisons

A total of six models were tested against our water content measurements, including MagmaSat (Ghiorso & Gualda, 2015), VolatileCalc-Rhyolite (Newman & Lowenstern, 2002), Iacono-Marziano et al. (2012; IM2012), Liu et al. (2005), Moore et al. (1998), and Shishkina et al. (2014). The measured solubility of water in the LG composition was found to be often lower than the predictions made by a majority of tested solubility models, with the exception of IM2012. The water solubility of the evolved, Fe- and Al-rich lunar composition increases with pressure, as is expected. However, existing solubility models predict up to ~3.3 wt.% at 100 MPa and ~4.2 wt.% at 150 MPa (MagmaSat; VolatileCalc-Rhyolite; Liu et al., 2005; Moore et al., 1998; Shishkina et al., 2014). The difference between the measured values and modeled values increase with pressure for all models except IM2012, for which they decrease with pressure.

Inconsistencies of the models to the observed data could be because the tested melt composition differs from those used for model calibration. However, dissolved CO_2 was also observed in the samples (Table 7; Fig. 4), likely due to incomplete decarbonation of CaCO_3 and

K_2CO_4 . Additional error could therefore result from the use of pure H_2O equations for a melt that equilibrated with an H_2O - CO_2 mixture. Comparison of tested models to the observed data is shown in Fig. 5. Percent errors can be found in Table 8.

IM2012 is the model that best approximated the dissolved water content at the higher pressure conditions. As pressure decreases to the lowest tested condition, VolatileCalc-rhyolite best reproduces the observed data. I suggest the use of IM2012 for an evolved LMO melt composition, with added caution at low pressures.

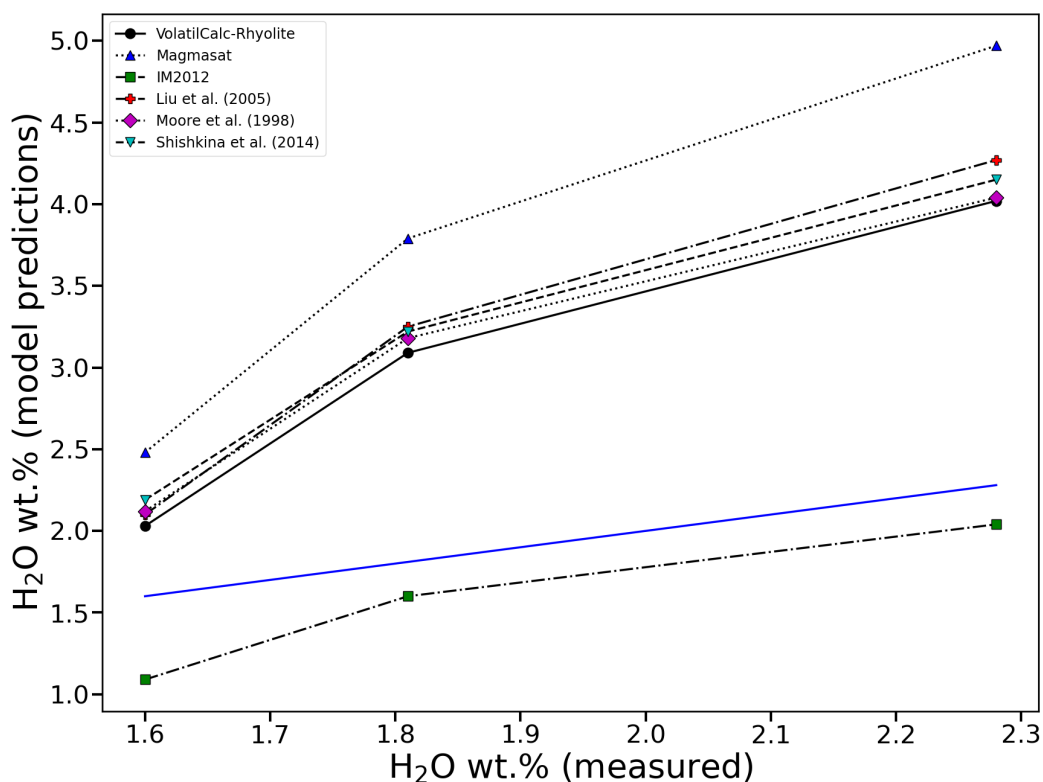


Figure 5: Comparison of tested models to this study's measured data. The blue line is the line of equality for this study's data.

Table 8: Water solubility predictions from existing solubility models for a range of pressures ($\pm$ error). All calculations are assumed to be at terrestrial f_{O_2} conditions ($\sim$ IW+4). Input compositions are those measured by EPMA. Percent error from this study’s measured water solubilities are shown for each pressure.

Model	50 MPa	%err	100 MPa	%err	150 MPa	%err
VolatileCalc-Rhyolite	2.03 (0.20)	21.37	3.09 (0.31)	41.40	4.02 (0.40)	43.27
Magmasat	2.48 (0.25)	35.48	3.79 (0.38)	52.19	4.97 (0.50)	54.13
IM2012	1.09 (0.23)	47.31	1.60 (0.34)	12.89	2.04 (0.43)	11.68
Liu et al. (2005)	2.10 (0.32)	23.82	3.25 (0.49)	44.35	4.27 (0.64)	46.67
Moore et al. (1998)	2.12 (0.05)	24.41	3.18 (0.05)	43.00	4.04 (0.05)	43.56
Shishkina et al. (2014)	2.19 (0.22)	26.99	3.22 (0.32)	43.75	4.15 (0.42)	45.04

4.3 Speciation

H₂ becomes more relevant as a fluid species at reduced conditions (Newcombe et al., 2017), as observed by the identification of H₂ as one of the primary volatile components driving fire-fountain eruptions (McCubbin et al., 2015; Newcombe et al., 2017; Sharp et al., 2013). Though it has been previously observed that speciation of H-bearing volatile species changes with reduction in f_{O_2} to favor H₂ (Fig. 6; Newcombe et al., 2017), current solubility models do not account for this. Ahead of a redox-varying experiment calibrated solubility model, I have produced a thermodynamic framework that circumnavigates the issue by calculating H-volatile speciation as a function of f_{O_2} (see Section 3.4). Application of the IM2012 model using the thermodynamic function is achieved by using the $X_{H_2O}^{fluid}$ output to calculate partial pressure as an input for the model.

The lunar f_{O_2} conditions fall within the range of IW to IW-2 (Wadhwa, 2008), corresponding to H_2O/H_2 ratios of 0.41 to 0.04, meaning that 28.9% down to 3.9% of the fluid phase is H_2O for their respective redox state. This gives effective H_2O partial pressures of $0.29P_{\text{total}}$ to $0.04P_{\text{total}}$. The water capacity of lunar melts is thus reduced by up to 95% compared to terrestrial conditions. Therefore, the saturation limit of lunar melts should also be lower.

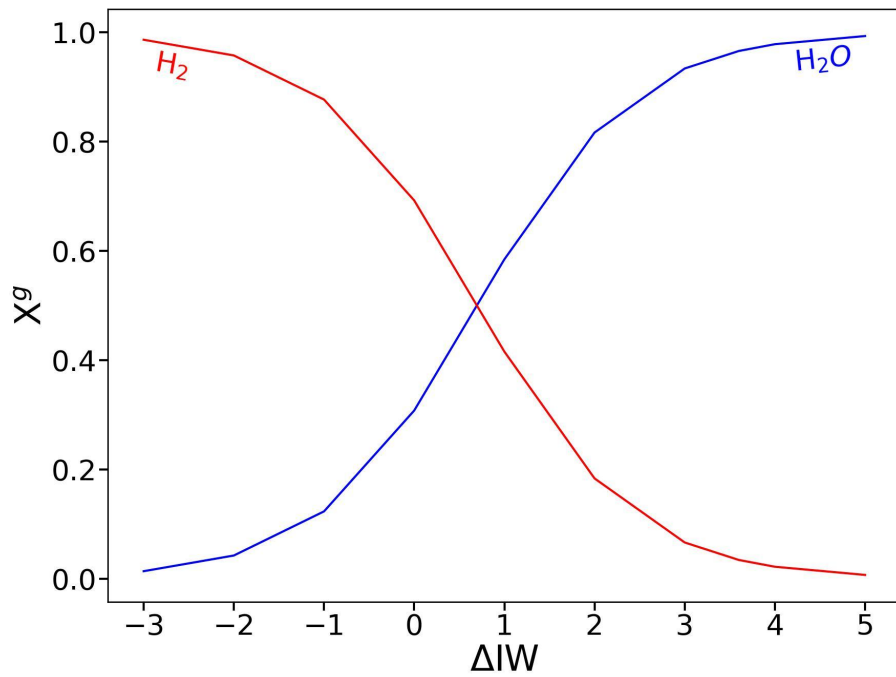


Figure 6: Speciation of H volatiles in the fluid phase with change in f_{O_2} . H_2 is scaled to account for the difference in weight between the two species.

5. Discussion

5.1 Saturation in *urKREEP*

Previous estimates of initial water contents of the LMO vary greatly, with a high end estimate ~500 ppm (Lin et al., 2017) and low end estimate of < 100 ppm (Elkins-Tanton & Grove, 2011), with minimum estimates as low as 27 ppm without significant worry of underestimation (McCubbin et al., 2015). It has been previously hypothesized that *urKREEP* could not reach saturation, due to the lower predicted LMO initial water contents (Elkins-Tanton & Grove, 2011). Using a simple mass balance, the water concentration in *urKREEP* can be calculated from these bulk LMO estimations with the following expression:

$$X_i^{H_2O}[LMO] / F_{liq} = X^{H_2O}[urKREEP], \quad (21)$$

where F_{liq} is the fraction of liquid remaining. This project defines *urKREEP* as the last 1% of the LMO liquid, setting F_{liq} at 0.01. From the range of previously estimated LMO water contents, water available to *urKREEP* would have been between 0.27 to 5 wt.% (Table 9). It is worth noting that some authors consider *urKREEP* as the last 2% of melt (McCubbin et al., 2015), which would increase the initial bulk LMO water contents necessary to reach saturation by 50%.

Table 9: Estimations of water available in the initial bulk *urKREEP* derived from varying $X_i^{H_2O}[LMO]$ and remaining liquid fractions using Eq. (21).

Bulk LMO Initial H_2O	27 ppm (McCubbin et al., 2015)	114 ppm (McCubbin et al., 2015)	320 ppm (Hui et al., 2013)	500 ppm (Lin et al., 2017)
<i>urKREEP</i> initial X_{H_2O} [wt.%]	0.27 wt.%	1.14 wt.%	3.2 wt.%	5 wt.%

Based on current crustal variation of the nearside lunar crust, possible urKREEP overhead pressures range between 140 to 220 MPa corresponding to a range of crustal thicknesses of 25 to 40 km from the current-day nearside (Chenet et al., 2006; Wieczorek et al., 2013). In most tested cases of lunar relevant redox states and pressures from current day near-side crustal thicknesses, the saturation limit is easily achieved with the $X_i^{H2O}[LMO]$ range given by McCubbin et al. (2015; Table 10). Two outlying cases do not reach saturation.

For the lowest $X_i^{H2O}[LMO]$ of 27 ppm (McCubbin et al., 2015), urKREEP would not have been saturated under present day crustal thickness measurements. A thinner crust would be necessary to reach the saturation limit. In this case, the critical pressure for saturation would be 99 MPa, corresponding to a crustal thickness of 17.82 km for IW-2. At the IW buffer, critical thickness for saturation is 2.52 km.

For the highest McCubbin et al. (2015) $X_i^{H2O}[LMO]$ of 114 ppm and a redox state at the IW buffer, urKREEP would not have been saturated under present day crustal thickness measurements. In this case, saturation can be met in two ways: decreasing the crustal thickness or increasing the $X_i^{H2O}[LMO]$ to at least 117 ppm. The critical upper limit pressure for saturation would then be 209 MPa, corresponding to a thickness of 37.62 km.

Table 10: Estimations of water contents necessary to saturate urKREEP.

Pressure [MPa]	Redox State		
	IW-2	IW-1	IW
140	0.34 wt.%	0.60 wt.%	0.99 wt.%
220	0.43 wt.%	0.78 wt.%	1.29 wt.%

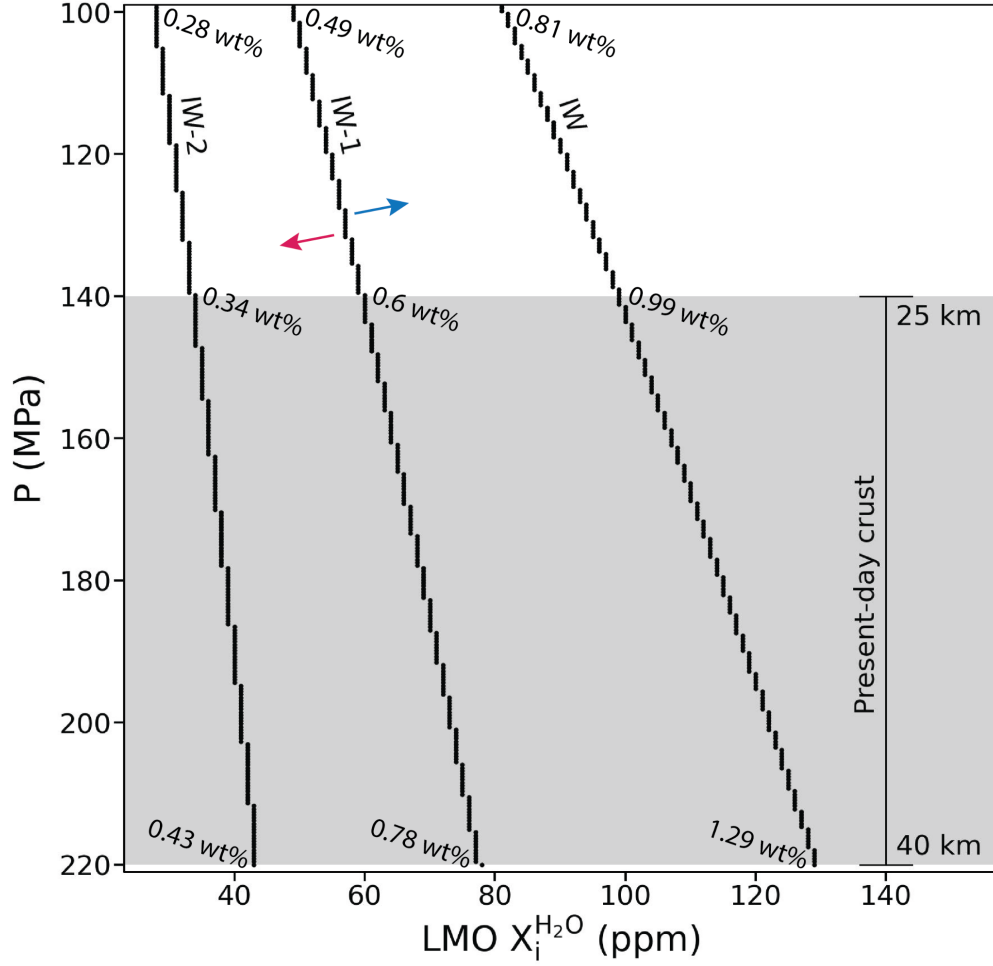


Figure 7: urKREEP saturation lines as a function of initial LMO water content and overhead pressure, corresponding to crustal thickness. Present day crustal thicknesses are indicated by the gray region. Saturation lines for three lunar relevant f_{O_2} conditions are shown, with solubility limits notated along each line. As f_{O_2} decreases, so does the water capacity of urKREEP. Scenarios where urKREEP would be below saturation lay to the left of the saturation line and above saturation to the right, as indicated by the red and blue arrows respectively.

Estimates above 100 ppm for $X_i^{H2O}[LMO]$ have been found to be inconsistent with magma sources and thermodynamic equilibrium necessary with metallic iron in mare basalt (Elkins-Tanton & Grove, 2011), so only contents < 100 ppm are considered. Previous studies found the saturation limit for urKREEP to be up to 5 wt.% at pressures of 200 MPa (Médard &

Grove, 2008), therefore suggesting that water would not be saturated in the layer or degas in any significant quantities (Elkins-Tanton & Grove, 2011). If we assume possible $X_i^{H_2O}[LMO]$ in the range of 27 to 99 ppm and a redox state of IW-2 as was measured for lunar basalts (Nash & Hausel, 1973), green glasses (Steele et al., 1992), and orange glasses (Karner, 2006), urKREEP can hold 0.34-0.43 wt% water. Therefore, there are many scenarios in which urKREEP could have exceeded saturation (Fig. 7). In these cases, degassing of water that exceeds the saturation limit would be likely degassed through cracks in the FAN crust, with a maximum of 0.65 wt.% water that could have been degassed. The capacity limit therefore limits the observable mantle water budget.

5.2 Degassing history of the Moon

The current understanding of the degassing history of the Moon includes three main stages: steam atmosphere building, late-stage LMO melt degassing due to exposure, and volcanic eruptive volatile loss after LMO solidification. Knowing that in many scenarios it is feasible for urKREEP to reach saturation, the second step can be expanded. Elevated $\delta^{37}\text{Cl}$ values in KREEP-y mare basalts have been previously identified as a signature of water attributed to crust breaching impacts exposing the urKREEP liquid (Barnes et al., 2016). If this layer were to exceed its saturation limit, additional degassing would occur as excess H_2O escapes through cracks in the crust. Fig. 8 shows the degassing history of the Moon, where the addition of volatile loss through the crust due to urKREEP saturation is represented in *c*. Though the degassed amount would be very small, likely less than a percent, those fluids could possibly cause minor alteration in regions of the lower crust.

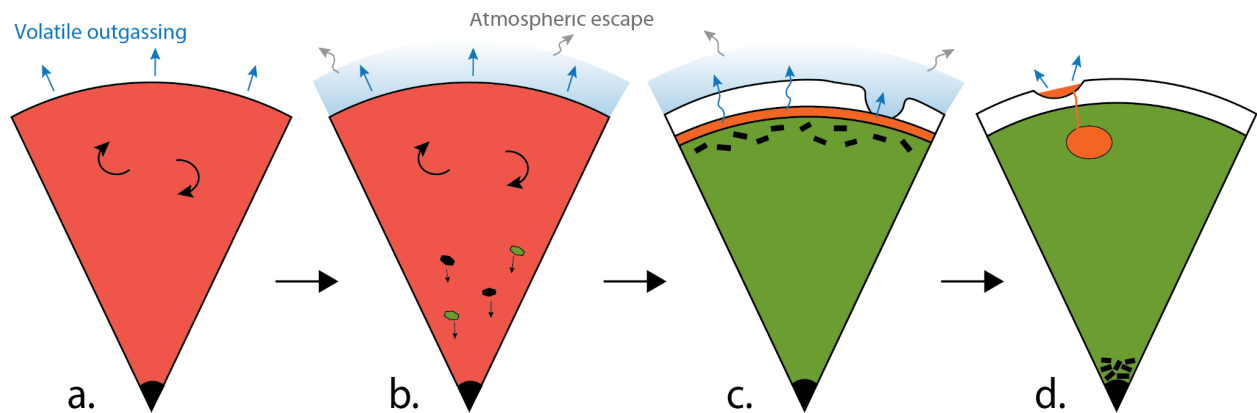


Figure 8: Degassing history of the Moon. (a) Outgassing from initial LMO. (b) LMO with steam atmosphere produced by outgassing. (c) 99% solidified LMO. Degassing from crust breaching impacts exposing that liquid and degassing through the lunar crust due to oversaturation of urKREEP are both shown. (d) Magmatism and volcanic degassing after complete LMO solidification and subsequent remelting due to enrichment of heat-producing elements in the upper mantle.

5.3 Future solubility model calibration

Although the IM2012 model best matches results of this study, our samples still measure more water than is predicted by the model. All other tested models overestimate the water content. In the future, a new solubility model should be calibrated for evolved lunar compositions. An increase in water solubility estimations would increase the saturation limit and reduce the number of urKREEP saturation scenarios shown in Fig. 7. Additionally, experimentally constrained solubility at reduced f_{O_2} would allow for more accurate evaluations of current models and predictions of lunar history.

6. Conclusions

1. The Iacono-Marziano et al. (2012) solubility model is the best fit for an evolved LMO melt composition, though it is worth noting that the predictions are underestimations compared to this study's measured samples. Future works should calibrate a new model for this composition and experimentally constrain the effects of reduced f_{O_2} on solubility.
2. I provide a thermodynamic framework to calculate H₂O-H₂ speciation as a function of f_{O_2} and pressure. Total pressure, temperature, and f_{O_2} serve as inputs to yield outputs of H₂O/H₂ ratio, H₂O mole fraction, and H₂ mole fraction in the fluid phase. The H₂O mole fraction can be utilized as an input for existing solubility models, primarily by calculating partial pressure.
3. H₂O solubility is lower at reduced f_{O_2} due to a reduction in H₂O partial pressure as H₂ becomes the dominant fluid species. The saturation limit of urKREEP is therefore also reduced, effectively making it easier to reach saturation without increasing the initial quantity of water in the LMO.
4. At IW-2, urKREEP has a water capacity of 0.34-0.43 wt% for crust-supplied pressures of 140-220 MPa. Even under conservative estimates of initial LMO water contents (<100 ppm; McCubbin et al., 2015), there are many scenarios in which urKREEP exceeds its saturation limit. Late-stage degassing of the LMO could have occurred due to urKREEP exceeding its saturation limit, allowing water to escape through the crust and reducing the observable lunar mantle water budget.

Appendix

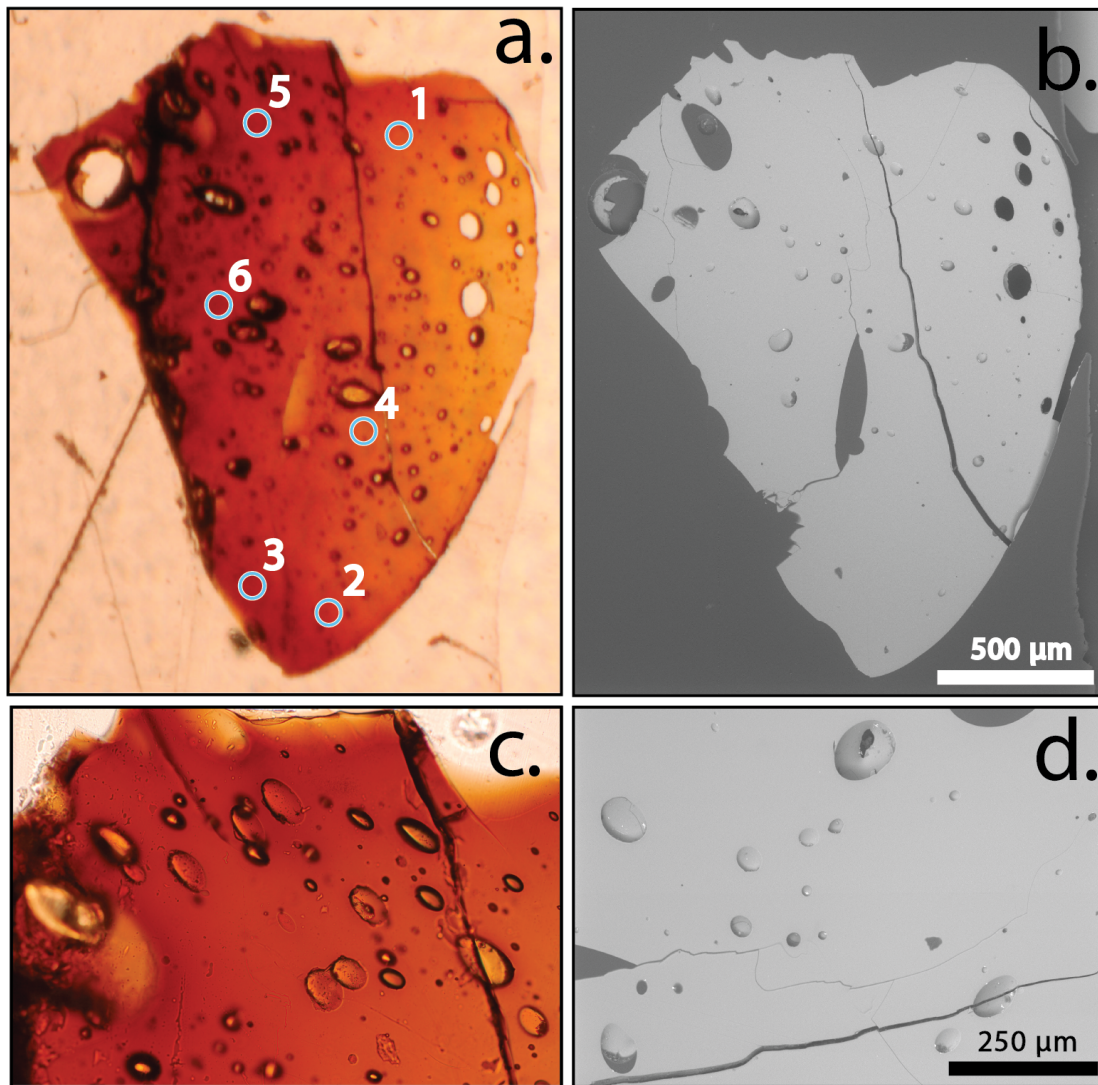


Figure A.1: Sample LG-05kb-1.2 under cross-polarized light (a and c) and imaged via Scanning Electron Microprobe (SEM; b and d).

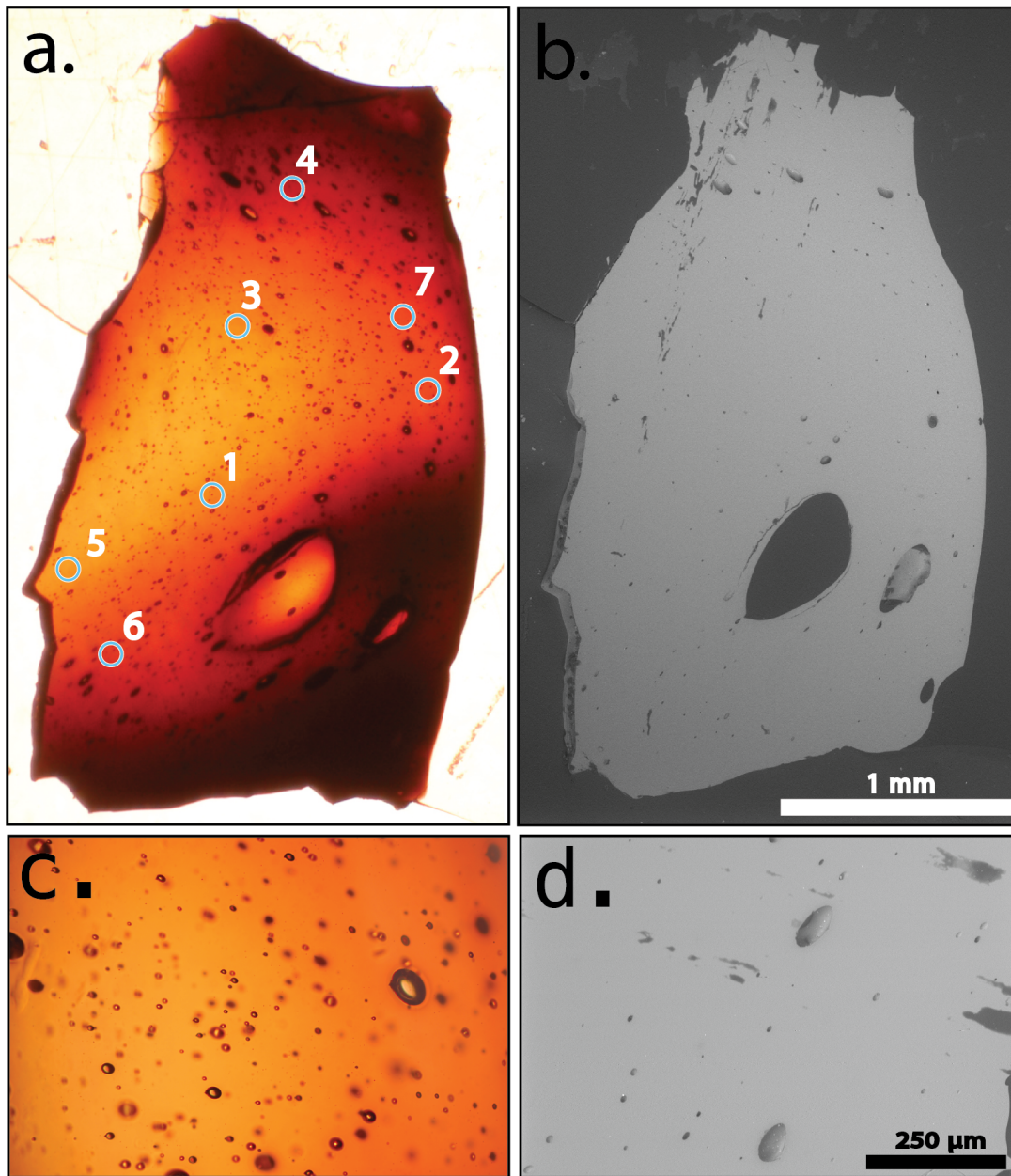


Figure A.2: Sample LG-1kb-8.1 under cross-polarized light (a and c) and imaged via SEM (b and d).

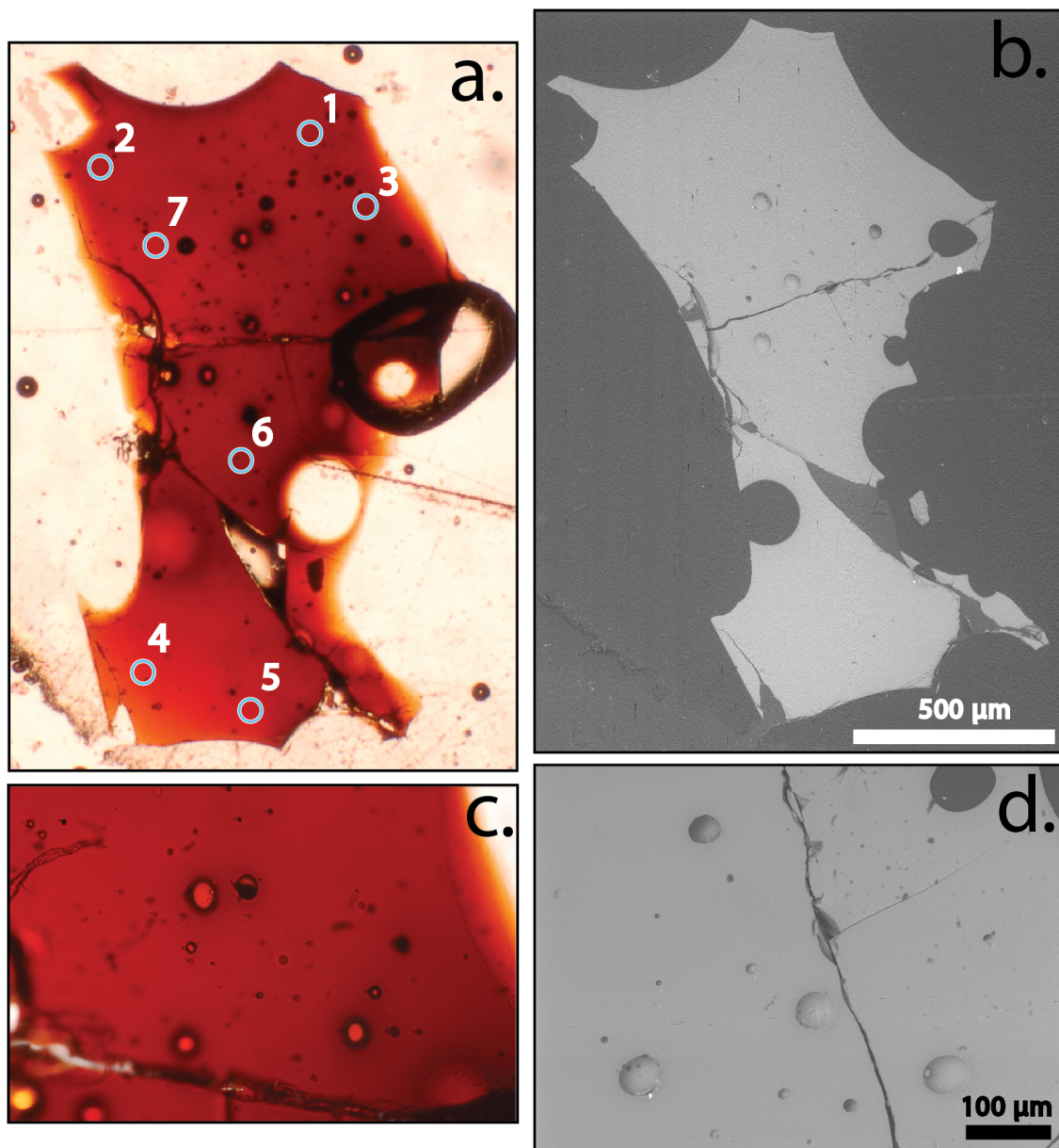


Figure A.3: Sample LG-15kb-1.4 under cross-polarized light (a and c) and imaged via SEM (b and d).

Table A.1: An Apollo KREEP basalt composition (KB; Ryder & Bower, 1976) was also tested. Rhyolite-MELTS (Ghiorso & Gualda, 2015; Gualda et al., 2012) predicted the liquidus for the KB composition to be 1125 °C. A KB sample was run at 1200 °C and held at a pressure of ~100 MPa for ~5 hrs. It was with a different method than the LG samples. The pressure vessel was flipped so that the sample dropped from the heated end to the water cooled end. The difference in quenching methods was in anticipation of the known higher rate of crystallization characteristic of basalts. Unfortunately, even with the rapid quench, crystallization of small microlites made it unusable for FTIR. The composition was not explored further. Below are the compositions of published KREEP basalt, composition of synthesized KB sample ($\pm$ error), measured EPMA KB composition.

Composition/ Sample	SiO ₂ [wt.%]	TiO ₂ [wt.%]	Al ₂ O ₃ [wt.%]	FeO [wt.%]	MgO [wt.%]	CaO [wt.%]	Na ₂ O [wt.%]	K ₂ O [wt.%]	P ₂ O ₅ [wt.%]	Total [wt.%]
Ryder & Bower (1976)*	51.16	0.55	24.79	3.88	4.48	12.44	0.95	1.73	0.02	100.00
Initial composition**	50.59 (0.51)	0.60 (0.08)	24.34 (0.07)	3.85 (0.05)	4.52 (0.14)	12.82 (0.67)	1.04 (0.13)	1.79 (0.09)	0.0	100.00
KB-1-1.1	62.22	0.82	22.24	3.15	5.51	1.62	0.87	0.74	-	99.55

*Normalized for the exclusion of additional oxide phases in the published composition.

**Physical mass of oxide powders measured to synthesis sample

Table A.2: EPMA glass standard compositions.

	KN18 Rhyolite Glass	VG-2 Basalt Glass
SiO ₂	74.60	50.81
TiO ₂	0.18	1.85
Al ₂ O ₃	10.53	14.06
FeO	3.45	11.84
MgO	0.01	6.71
CaO	0.15	11.12
Na ₂ O	5.68	2.62
K ₂ O	4.39	0.19
MnO	0.06	0.22
Total	99.05	99.62

Table A.3: Full FTIR measurements. Abs. is the uncorrected absorbance peak height.

Sample	Spot	Thickness (1 σ) [μm]	1630 cm^{-1}		3570 cm^{-1}		5230 cm^{-1}		4520 cm^{-1}		5230 & 4520 cm^{-1}	2350 cm^{-1}	
			Abs.	H ₂ O _{mol} [wt.%]	Abs.	H ₂ O _{total} [wt.%]	Abs.	H ₂ O _{mol} [wt.%]	Abs.	OH [wt.%]	H ₂ O _{total} [wt.%]	Abs.	CO ₂ [ppm]
LG-05kb-1.2	1	54.09 (0.58)	0.28	1.56	0.86	1.56	0.005	0.39	0.008	0.69	1.08	0.027	77.82
	2	60.19 (0.86)	0.33	1.59	0.98	1.59	0.008	0.57	0.009	0.69	1.25	0.035	91.93
	3	69.33 (0.48)	0.39	1.65	1.17	1.65	0.009	0.55	0.011	0.74	1.29	0.040	91.41
	4	63.46 (0.80)	0.37	1.71	1.11	1.71	0.009	0.61	0.01	0.73	1.33	0.040	98.63
	5	80.90 (0.77)	0.39	1.47	1.21	1.47	0.011	0.58	0.012	0.68	1.26	0.045	88.09
	6	81.08 (1.06)	0.43	1.60	1.32	1.60	0.011	0.58	0.013	0.75	1.33	0.049	95.67
LG-1kb-8.1	1	137.06 (1.40)	1.41	1.47	2.51	1.80	0.031	0.97	0.027	0.92	1.90	0.11	128.83
	2	143.11 (0.79)	1.51	1.50	2.87	1.96	0.036	1.08	0.028	0.91	1.99	0.121	133.30
	3	132.64 (0.59)	1.47	1.58	2.67	1.97	0.035	1.14	0.028	0.99	2.13	0.124	147.39
	5	113.66 (0.77)	0.69	0.86	1.55	1.34	0.014	0.53	0.012	0.46	0.99	0.068	93.76
	6	137.34 (0.46)	1.36	1.41	2.61	1.86	0.032	1.00	0.025	0.84	1.84	0.111	127.42
	7	143.89 (0.99)	1.55	1.53	2.87	1.96	0.038	0.04	0.029	0.94	2.07	0.126	138.05
LG-15kb-1.4	1	71.23 (0.69)	0.82	1.64	1.62	2.22	0.017	1.02	0.01	0.61	1.63	0.079	175.52
	2	65.08 (0.66)	0.76	1.65	1.52	2.28	0.016	1.05	0.009	0.60	1.65	0.073	176.83
	3	82.55 (0.91)	0.94	1.62	1.86	2.21	0.019	0.99	0.012	0.64	1.63	0.090	172.08
	4	47.47 (0.86)	0.54	1.62	1.08	2.22	0.011	1.02	0.007	0.64	1.66	0.052	172.68

5	58.86 (0.85)	0.70	1.70	1.39	2.30	0.015	1.09	0.008	0.58	1.68	0.069	184.00
6	78.90 (1.33)	0.97	1.76	1.90	2.36	0.02	1.09	0.012	0.67	1.76	0.098	193.83
7	70.94 (0.77)	0.87	1.74	1.72	2.37	0.019	1.15	0.011	0.68	1.83	0.087	192.47

Table A.4: H-volatile speciation derived from the function shown below.

P [MPa]	ΔIW	H₂O/H₂	X^g H₂ Scaled	X^g H₂O	IM2012 H₂O^{melt} [wt.%]
50	-3	0.01	0.99	0.01	1.10
	-2	0.04	0.96	0.04	1.18
	-1	0.13	0.89	0.11	1.35
	0	0.41	0.71	0.29	1.63
	+1	1.28	0.44	0.56	2.01
	+2	4.06	0.20	0.80	2.32
	+3	12.83	0.07	0.93	2.48
	+4	40.58	0.02	0.98	2.54
	+5	128.32	0.01	0.99	2.56
100	-3	0.01	0.99	0.01	1.15
	-2	0.04	0.96	0.04	1.28
	-1	0.13	0.88	0.12	1.54
	0	0.43	0.70	0.30	2.03
	+1	1.35	0.43	0.57	2.72
	+2	4.26	0.19	0.81	3.33
	+3	13.48	0.07	0.93	3.65
	+4	42.64	0.02	0.98	3.78
	+5	134.84	0.01	0.99	3.82
150	-3	0.01	0.99	0.01	1.19
	-2	0.04	0.96	0.04	1.37
	-1	0.14	0.88	0.12	1.73
	0	0.44	0.69	0.31	2.43
	+1	1.41	0.42	0.58	3.48
	+2	4.45	0.18	0.82	4.43

+3	14.06	0.07	0.93	4.95
+4	44.47	0.02	0.98	5.15
+5	140.64	0.01	0.99	5.22

Below is the complete H-volatile speciation calculation python function. Inputs are the pressure, temperature, and $\log f_{O_2}$ of your system. Also required is the NIST Janaf gaseous H₂O table, found here: <https://janaf.nist.gov/tables/H-064.html>. The function outputs the H₂O/H₂ ratio as well as the mole fractions of H₂ and H₂O in the fluid phase. Fugacity coefficient calculations follow the methods of Peng & Robinson (1976; see section 3.4).

```
def H_fluid_speciation(P, T, logfO2):
    import numpy as np

    H2O_g_NISTdata = pd.read_excel('NIST_H2O_g.xlsx', skiprows=1)

    R = 8.3145 #J mol-1 K-1

    delta_G = np.interp(T, H2O_g_NISTdata['T(K)'], H2O_g_NISTdata['delta-f G']) * 1000 # J mol-1

    K = np.exp(-delta_G / (R*T))

    fO2 = 10**(logfO2)

    #H2O fugacity coefficient calculation using methods of Peng & Robinson (1976)

    T_r_H2O = T / 647.14

    kappa_H2O = 0.37464 + 1.54226 * 0.344 + 0.26992 * 0.344**2

    alpha_H2O = (1 + kappa_H2O*(1 - T_r_H2O**0.5))**2

    a_H2O = ((0.45724 * R**2 * 647.14**2) / 220.6) * alpha_H2O

    b_H2O = (0.07780 * R * 647.14) / 220.6

    A_H2O = (a_H2O * P) / (R**2 * T**2)

    B_H2O = (b_H2O * P) / (R * T)
```

```

c1 = 1
c2_H2O = -(1-B_H2O)
c3_H2O = A_H2O - 3*(B_H2O**2) - 2*B_H2O
c4_H2O = -(A_H2O*B_H2O - B_H2O**2 - B_H2O**3)
c_H2O = [c1, c2_H2O, c3_H2O, c4_H2O]
rt_H2O = np.roots(c_H2O)
Z_H2O = max(rt_H2O)

ln_fH2Ocoeff = Z_H2O - 1 - np.log(Z_H2O - B_H2O) - (A_H2O/(2*np.sqrt(2)*B_H2O))*np.log((Z_H2O +
    2.414*B_H2O)/(Z_H2O - 0.414*B_H2O))
fH2O_coeff = np.exp(ln_fH2Ocoeff)

#H2 fugacity coefficient calculation using methods of Peng & Robinson (1976)
T_r_H2 = T / 32.98
kappa_H2 = 0.37464 + 1.54226 * -0.216 + 0.26992 * -0.216**2
alpha_H2 = (1 + kappa_H2*(1 - T_r_H2**0.5))**2
a_H2 = ((0.45724 * R**2 * 32.98**2) / 12.93) * alpha_H2
b_H2 = (0.07780 * R * 32.98) / 12.93
A_H2 = (a_H2 * P) / (R**2 * T**2)
B_H2 = (b_H2 * P) / (R * T)

c2_H2 = -(1-B_H2)
c3_H2 = A_H2 - 3*(B_H2**2) - 2*B_H2
c4_H2 = -(A_H2*B_H2 - B_H2**2 - B_H2**3)
c_H2 = [c1, c2_H2, c3_H2, c4_H2]
rt_H2 = np.roots(c_H2)

```

```

Z_H2 = max(rt_H2)

ln_fH2coeff = Z_H2 - 1 - np.log(Z_H2 - B_H2) - (A_H2/(2*np.sqrt(2)*B_H2))*np.log((Z_H2 +
    2.414*B_H2)/(Z_H2 - 0.414*B_H2))
fH2_coeff = np.exp(ln_fH2coeff)

#Calculating fluid speciation
xgH2O_xgH2 = K * np.sqrt(fO2) * (fH2_coeff / fH2O_coeff) #H2O/H2 ratio
xg_Htot = 1
xg_H2 = xg_Htot / (1 + xgH2O_xgH2) # mole fraction
xg_H2O = xg_Htot - xg_H2 # mole fraction

return xgH2O_xgH2, xg_H2, xg_H2O

```

References

- Abe, Y., & Matsui, T. (1985). The formation of an impact-generated H₂O atmosphere and its implications for the early thermal history of the Earth. *Journal of Geophysical Research: Solid Earth*, 90(S02). <https://doi.org/10.1029/JB090iS02p0C545>
- Aiuppa, A., Baker, D. R., & Webster, J. D. (2009). Halogens in volcanic systems. *Chemical Geology*, 263(1–4), 1–18. <https://doi.org/10.1016/j.chemgeo.2008.10.005>
- Barnes, J. J., Franchi, I. A., Anand, M., Tartèse, R., Starkey, N. A., Koike, M., Sano, Y., & Russell, S. S. (2013). Accurate and precise measurements of the D/H ratio and hydroxyl content in lunar apatites using NanoSIMS. *Chemical Geology*, 337–338, 48–55. <https://doi.org/10.1016/j.chemgeo.2012.11.015>
- Barnes, J. J., Tartèse, R., Anand, M., McCubbin, F. M., Franchi, I. A., Starkey, N. A., & Russell, S. S. (2014). The origin of water in the primitive Moon as revealed by the lunar highlands samples. *Earth and Planetary Science Letters*, 390, 244–252. <https://doi.org/10.1016/j.epsl.2014.01.015>
- Barnes, J. J., Tartèse, R., Anand, M., McCubbin, F. M., Neal, C. R., & Franchi, I. A. (2016). Early degassing of lunar urKREEP by crust-breaching impact(s). *Earth and Planetary Science Letters*, 447, 84–94. <https://doi.org/10.1016/j.epsl.2016.04.036>
- Boyce, J. W., Liu, Y., Rossman, G. R., Guan, Y., Eiler, J. M., Stolper, E. M., & Taylor, L. A. (2010). Lunar apatite with terrestrial volatile abundances. *Nature*, 466(7305), 466–469. <https://doi.org/10.1038/nature09274>
- Boyce, J. W., Treiman, A. H., Guan, Y., Ma, C., Eiler, J. M., Gross, J., Greenwood, J. P., & Stolper, E. M. (2015). The chlorine isotope fingerprint of the lunar magma ocean. *Science*

- Advances*, 1(8), e1500380. <https://doi.org/10.1126/sciadv.1500380>
- Canup, R. M., & Asphaug, E. (2001). Origin of the Moon in a giant impact near the end of the Earth's formation. *Nature*, 412(6848), 708–712. <https://doi.org/10.1038/35089010>
- Chen, Y., Zhang, Y., Liu, Y., Guan, Y., Eiler, J., & Stolper, E. M. (2015). Water, fluorine, and sulfur concentrations in the lunar mantle. *Earth and Planetary Science Letters*, 427, 37–46. <https://doi.org/10.1016/j.epsl.2015.06.046>
- Chenet, H., Lognonne, P., Wieczorek, M., & Mizutani, H. (2006). Lateral variations of lunar crustal thickness from the Apollo seismic data set. *Earth and Planetary Science Letters*, 243(1–2), 1–14. <https://doi.org/10.1016/j.epsl.2005.12.017>
- Elkins-Tanton, L. T. (2008). Linked magma ocean solidification and atmospheric growth for Earth and Mars. *Earth and Planetary Science Letters*, 271(1–4), 181–191. <https://doi.org/10.1016/j.epsl.2008.03.062>
- Elkins-Tanton, L. T., Burgess, S., & Yin, Q.-Z. (2011). The lunar magma ocean: Reconciling the solidification process with lunar petrology and geochronology. *Earth and Planetary Science Letters*, 304(3–4), 326–336. <https://doi.org/10.1016/j.epsl.2011.02.004>
- Elkins-Tanton, L. T., & Grove, T. L. (2011). Water (hydrogen) in the lunar mantle: Results from petrology and magma ocean modeling. *Earth and Planetary Science Letters*, 307(1–2), 173–179. <https://doi.org/10.1016/j.epsl.2011.04.027>
- Ghiorso, M. S., Carmichael, I. S. E., Rivers, M. L., & Sack, R. O. (1983). The Gibbs free energy of mixing of natural silicate liquids; an expanded regular solution approximation for the calculation of magmatic intensive variables. *Contributions to Mineralogy and Petrology*, 84(2–3), 107–145. <https://doi.org/10.1007/BF00371280>
- Ghiorso, M. S., & Gualda, G. A. R. (2015). An H₂O–CO₂ mixed fluid saturation model

- compatible with rhyolite-MELTS. *Contributions to Mineralogy and Petrology*, 169(6), 53. <https://doi.org/10.1007/s00410-015-1141-8>
- Greenwood, J. P., Itoh, S., Sakamoto, N., Warren, P., Taylor, L., & Yurimoto, H. (2011). Hydrogen isotope ratios in lunar rocks indicate delivery of cometary water to the Moon. *Nature Geoscience*, 4(2), 79–82. <https://doi.org/10.1038/ngeo1050>
- Gualda, G. A. R., Ghiorso, M. S., Lemons, R. V., & Carley, T. L. (2012). Rhyolite-MELTS: A Modified Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal of Petrology*, 53(5), 875–890. <https://doi.org/10.1093/petrology/egr080>
- Hauri, E. H., Saal, A. E., Rutherford, M. J., & Van Orman, J. A. (2015). Water in the Moon's interior: Truth and consequences. *Earth and Planetary Science Letters*, 409, 252–264. <https://doi.org/10.1016/j.epsl.2014.10.053>
- Hauri, E. H., Weinreich, T., Saal, A. E., Rutherford, M. C., & Van Orman, J. A. (2011). High Pre-Eruptive Water Contents Preserved in Lunar Melt Inclusions. *Science*, 333(6039), 213–215. <https://doi.org/10.1126/science.1204626>
- Hess, P. C., Rutherford, M. J., & Campbell, H. W. (1978). Ilmenite crystallization in nonmare basalts: Genesis of KREEP and high-Ti mare basalt. *Lunar and Planetary Science Conference Proceedings*, 1, 705–724.
- Hirschmann, M. M. (2006). WATER, MELTING, AND THE DEEP EARTH H₂O CYCLE. *Annual Review of Earth and Planetary Sciences*, 34(1), 629–653. <https://doi.org/10.1146/annurev.earth.34.031405.125211>
- Hirschmann, M. M., Withers, A. C., Ardia, P., & Foley, N. T. (2012). Solubility of molecular hydrogen in silicate melts and consequences for volatile evolution of terrestrial planets. *Earth and Planetary Science Letters*, 345–348, 38–48.

<https://doi.org/10.1016/j.epsl.2012.06.031>

- Hirth, G., Escartín, J., & Lin, J. (1998). The Rheology of the Lower Oceanic Crust: Implications for Lithospheric Deformation at Mid-Ocean Ridges. In W. Roger Buck, P. T. Delaney, J. A. Karson, & Y. Lagabriele (Eds.), *Geophysical Monograph Series* (pp. 291–303). American Geophysical Union. <https://doi.org/10.1029/GM106p0291>
- Hu, S., He, H., Ji, J., Lin, Y., Hui, H., Anand, M., Tartèse, R., Yan, Y., Hao, J., Li, R., Gu, L., Guo, Q., He, H., & Ouyang, Z. (2021). A dry lunar mantle reservoir for young mare basalts of Chang’e-5. *Nature*, 600(7887), 49–53. <https://doi.org/10.1038/s41586-021-04107-9>
- Hui, H., Guan, Y., Chen, Y., Peslier, A. H., Zhang, Y., Liu, Y., Flemming, R. L., Rossman, G. R., Eiler, J. M., Neal, C. R., & Osinski, G. R. (2017). A heterogeneous lunar interior for hydrogen isotopes as revealed by the lunar highlands samples. *Earth and Planetary Science Letters*, 473, 14–23. <https://doi.org/10.1016/j.epsl.2017.05.029>
- Hui, H., Peslier, A. H., Zhang, Y., & Neal, C. R. (2013). Water in lunar anorthosites and evidence for a wet early Moon. *Nature Geoscience*, 6(3), 177–180. <https://doi.org/10.1038/ngeo1735>
- Hurwitz, S., & Navon, O. (1994). Bubble nucleation in rhyolitic melts: Experiments at high pressure, temperature, and water content. *Earth and Planetary Science Letters*, 122(3–4), 267–280. [https://doi.org/10.1016/0012-821X\(94\)90001-9](https://doi.org/10.1016/0012-821X(94)90001-9)
- Iacono-Marziano, G., Morizet, Y., Le Trong, E., & Gaillard, F. (2012). New experimental data and semi-empirical parameterization of H₂O–CO₂ solubility in mafic melts. *Geochimica et Cosmochimica Acta*, 97, 1–23. <https://doi.org/10.1016/j.gca.2012.08.035>
- Iacovino, K., Matthews, S., Wieser, P. E., Moore, G. M., & Bégué, F. (2021). VESIcal Part I: An

- Open-Source Thermodynamic Model Engine for Mixed Volatile (H_2O - CO_2) Solubility in Silicate Melts. *Earth and Space Science*, 8(11), e2020EA001584.
<https://doi.org/10.1029/2020EA001584>
- Ikoma, M., Elkins-Tanton, L., Hamano, K., & Suckale, J. (2018). Water Partitioning in Planetary Embryos and Protoplanets with Magma Oceans. *Space Science Reviews*, 214(4), 76.
<https://doi.org/10.1007/s11214-018-0508-3>
- Karner, J. M. (2006). Application of a new vanadium valence oxybarometer to basaltic glasses from the Earth, Moon, and Mars. *American Mineralogist*, 91(2–3), 270–277.
<https://doi.org/10.2138/am.2006.1830>
- Killen, R. M., & Ip, W. (1999). The surface-bounded atmospheres of Mercury and the Moon. *Reviews of Geophysics*, 37(3), 361–406. <https://doi.org/10.1029/1999RG900001>
- Lin, Y., Tronche, E. J., Steenstra, E. S., & Van Westrenen, W. (2017). Evidence for an early wet Moon from experimental crystallization of the lunar magma ocean. *Nature Geoscience*, 10(1), 14–18. <https://doi.org/10.1038/ngeo2845>
- Liu, Y., Guan, Y., Zhang, Y., Rossman, G. R., Eiler, J. M., & Taylor, L. A. (2012). Direct measurement of hydroxyl in the lunar regolith and the origin of lunar surface water. *Nature Geoscience*, 5(11), 779–782. <https://doi.org/10.1038/ngeo1601>
- Liu, Y., Zhang, Y., & Behrens, H. (2005). Solubility of H_2O in rhyolitic melts at low pressures and a new empirical model for mixed H_2O – CO_2 solubility in rhyolitic melts. *Journal of Volcanology and Geothermal Research*, 143(1–3), 219–235.
<https://doi.org/10.1016/j.jvolgeores.2004.09.019>

- Malcolm W. Chase, Jr. (1998). NIST-JANAF thermochemical tables. Washington, DC: New York: American Chemical Society; American Institute of Physics for the National Institute of Standards and Technology.
- McCubbin, F.M., Nekvasil, H., Lindsley, D.H. (2007). Is There Evidence for Water in Lunar Magmatic Minerals? A Crystal Chemical Investigation. 38th Lunar and Planetary Science Conference, Abs# 1354.
- McCubbin, F.M., Nekvasil, H., Jolliff, B.L., Carpenter, P.K., Zeigler, R.A. (2008). A Survey of Lunar Apatite Volatile Contents for Determining Mining Bulk Lunar Water: How Dry is “Bone Dry”? 39th Lunar and Planetary Science Conference, Abs# 1788.
- McCubbin, F.M., Nekvasil, H., Jolliff, B.L., Carpenter, P.K., Zeigler, R.A., (2009). Inhomogeneous Distribution of Magmatic Volatiles in the Lunar Interior: Clues from the Mineral Apatite. 40th Lunar and Planetary Science Conference, Abs# 2246.
- McCubbin, F. M., Steele, A., Hauri, E. H., Nekvasil, H., Yamashita, S., & Hemley, R. J. (2010). Nominally hydrous magmatism on the Moon. *Proceedings of the National Academy of Sciences*, 107(25), 11223–11228. <https://doi.org/10.1073/pnas.1006677107>
- McCubbin, F. M., Vander Kaaden, K. E., Tartèse, R., Klima, R. L., Liu, Y., Mortimer, J., Barnes, J. J., Shearer, C. K., Treiman, A. H., Lawrence, D. J., Elardo, S. M., Hurley, D. M., Boyce, J. W., & Anand, M. (2015). Magmatic volatiles (H, C, N, F, S, Cl) in the lunar mantle, crust, and regolith: Abundances, distributions, processes, and reservoirs. *American Mineralogist*, 100(8–9), 1668–1707. <https://doi.org/10.2138/am-2015-4934CCBYNCND>
- McIntosh, I. M., Nichols, A. R. L., Tani, K., & Llewellyn, E. W. (2017). Accounting for the species-dependence of the $3500\text{ cm}^{-1}\text{ H}_2\text{O}$ infrared molar absorptivity coefficient:

- Implications for hydrated volcanic glasses. *American Mineralogist*, 102(8), 1677–1689.
<https://doi.org/10.2138/am-2017-5952CCBY>
- McMillian, P. F. (1994). Water solubility and speciation models. In M. R. Carroll & J. R. Holloway (Eds.), *Volatiles in Magmas*. De Gruyter.
<https://doi.org/10.1515/9781501509674>
- Médard, E., & Grove, T. L. (2008). The effect of H₂O on the olivine liquidus of basaltic melts: Experiments and thermodynamic models. *Contributions to Mineralogy and Petrology*, 155(4), 417–432. <https://doi.org/10.1007/s00410-007-0250-4>
- Mills, R.D., Simon, J.I., Alexander, C.M.O., Wang, J., Christoffersen, R., and Rahman, Z. (2014) Chemical zoning of feldspars in lunar granitoids: Implications for the origins of lunar silicic magmas. 45th Lunar and Planetary Science Conference, Abs# 1547.
- Moore, G., Vennemann, T., & Carmichael, I. S. E. (1998). An empirical model for the solubility of H₂O in magmas to 3 kilobars. *American Mineralogist*, 83(1–2), 36–42.
<https://doi.org/10.2138/am-1998-1-203>
- Morgan, C., Wilson, L., & Head, J. W. (2021). Formation and dispersal of pyroclasts on the Moon: Indicators of lunar magma volatile contents. *Journal of Volcanology and Geothermal Research*, 413, 107217. <https://doi.org/10.1016/j.jvolgeores.2021.107217>
- Nash, W. P., & Hausel, W. D. (1973). Partial pressures of oxygen, phosphorus and fluorine in some lunar lavas. *Earth and Planetary Science Letters*, 20(1), 13–27.
[https://doi.org/10.1016/0012-821X\(73\)90135-0](https://doi.org/10.1016/0012-821X(73)90135-0)
- Needham, D. H., & Kring, D. A. (2017). Lunar volcanism produced a transient atmosphere around the ancient Moon. *Earth and Planetary Science Letters*, 478, 175–178.
<https://doi.org/10.1016/j.epsl.2017.09.002>

- Newcombe, M. E., Brett, A., Beckett, J. R., Baker, M. B., Newman, S., Guan, Y., Eiler, J. M., & Stolper, E. M. (2017). Solubility of water in lunar basalt at low pH₂O. *Geochimica et Cosmochimica Acta*, 200, 330–352. <https://doi.org/10.1016/j.gca.2016.12.026>
- Newman, S., & Lowenstern, J. B. (2002). VolatileCalc: A silicate melt–H₂O–CO₂ solution model written in Visual Basic for excel. *Computers & Geosciences*, 28(5), 597–604. [https://doi.org/10.1016/S0098-3004\(01\)00081-4](https://doi.org/10.1016/S0098-3004(01)00081-4)
- Newman, S., Stolper, E. M., & Epstein, S. (1986). Measurement of water in rhyolitic glasses; calibration of an infrared spectroscopic technique. *Mineralogical Society of America*, 71(11–12), 1527–1541.
- Ni, P., Zhang, Y., Chen, S., & Gagnon, J. (2019). A melt inclusion study on volatile abundances in the lunar mantle. *Geochimica et Cosmochimica Acta*, 249, 17–41. <https://doi.org/10.1016/j.gca.2018.12.034>
- Peng, D.-Y., & Robinson, D. B. (1976). A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals*, 15(1), 59–64. <https://doi.org/10.1021/i160057a011>
- Reid, R. C., Prausnitz, J. M., & Poling, B. E. (1989). *The properties of gases and liquids* (4. ed., international ed., 2. printing). McGraw-Hill.
- Renggli, C. J., King, P. L., Henley, R. W., & Norman, M. D. (2017). Volcanic gas composition, metal dispersion and deposition during explosive volcanic eruptions on the Moon. *Geochimica et Cosmochimica Acta*, 206, 296–311. <https://doi.org/10.1016/j.gca.2017.03.012>
- Rutherford, M. J., Head, J. W., Saal, A. E., Hauri, E., & Wilson, L. (2017). Model for the Origin, Ascent, and Eruption of Lunar Picritic Magmas. *American Mineralogist*.

<https://doi.org/10.2138/am-2017-5994CCBYNCND>

Ryder, G., & Bower, J. F. (1976). Poikilitic KREEP impact melts in the Apollo 14 white rocks.

Lunar and Planetary Science Conference Proceedings, 2, 1925–1948.

Saal, A. E., Hauri, E. H., Cascio, M. L., Van Orman, J. A., Rutherford, M. C., & Cooper, R. F.

(2008). Volatile content of lunar volcanic glasses and the presence of water in the Moon's interior. *Nature*, 454(7201), 192–195. <https://doi.org/10.1038/nature07047>

Seddio, S. M., Jolliff, B. L., Korotev, R. L., & Zeigler, R. A. (2013). Petrology and geochemistry of lunar granite 12032,366-19 and implications for lunar granite petrogenesis. *American Mineralogist*, 98(10), 1697–1713. <https://doi.org/10.2138/am.2013.4330>

Sharp, Z. D., McCubbin, F. M., & Shearer, C. K. (2013). A hydrogen-based oxidation mechanism relevant to planetary formation. *Earth and Planetary Science Letters*, 380, 88–97. <https://doi.org/10.1016/j.epsl.2013.08.015>

Shishkina, T. A., Botcharnikov, R. E., Holtz, F., Almeev, R. R., Jazwa, A. M., & Jakubiak, A. A. (2014). Compositional and pressure effects on the solubility of H₂O and CO₂ in mafic melts. *Chemical Geology*, 388, 112–129. <https://doi.org/10.1016/j.chemgeo.2014.09.001>

Silver, A. L. (1988). Water in Silicate Glasses. *Dissertation (Ph.D.)*.
<https://doi.org/10.7907/z336-zw46>

Silver, L. A., Ihinger, P. D., & Stolper, E. (1990). The influence of bulk composition on the speciation of water in silicate glasses. *Contributions to Mineralogy and Petrology*, 104(2), 142–162. <https://doi.org/10.1007/BF00306439>

Silver, L., & Stolper, E. (1989). Water in Albitic Glasses. *Journal of Petrology*, 30(3), 667–709.
<https://doi.org/10.1093/petrology/30.3.667>

Snyder, G. A., Taylor, L. A., & Neal, C. R. (1992). A chemical model for generating the sources

- of mare basalts: Combined equilibrium and fractional crystallization of the lunar magmasphere. *Geochimica et Cosmochimica Acta*, 56(10), 3809–3823.
[https://doi.org/10.1016/0016-7037\(92\)90172-F](https://doi.org/10.1016/0016-7037(92)90172-F)
- Steele, A. M., Colson, R. O., Korotev, R. L., & Haskin, L. A. (1992). Apollo 15 green glass: Compositional distribution and petrogenesis. *Geochimica et Cosmochimica Acta*, 56(11), 4075–4090. [https://doi.org/10.1016/0016-7037\(92\)90017-D](https://doi.org/10.1016/0016-7037(92)90017-D)
- Stephant, A., Anand, M., Tartèse, R., Zhao, X., Degli-Alessandrini, G., & Franchi, I. A. (2020). The hydrogen isotopic composition of lunar melt inclusions: An interplay of complex magmatic and secondary processes. *Geochimica et Cosmochimica Acta*, 284, 196–221.
<https://doi.org/10.1016/j.gca.2020.06.017>
- Stern, S. A. (1999). The lunar atmosphere: History, status, current problems, and context. *Reviews of Geophysics*, 37(4), 453–491. <https://doi.org/10.1029/1999RG900005>
- Stolper, E. (1982a). The speciation of water in silicate melts. *Geochimica et Cosmochimica Acta*, 46(12), 2609–2620. [https://doi.org/10.1016/0016-7037\(82\)90381-7](https://doi.org/10.1016/0016-7037(82)90381-7)
- Stolper, E. (1982b). Water in silicate glasses: An infrared spectroscopic study. *Contributions to Mineralogy and Petrology*, 81(1), 1–17. <https://doi.org/10.1007/BF00371154>
- Tartèse, R., Anand, M., Barnes, J. J., Starkey, N. A., Franchi, I. A., & Sano, Y. (2013). The abundance, distribution, and isotopic composition of Hydrogen in the Moon as revealed by basaltic lunar samples: Implications for the volatile inventory of the Moon. *Geochimica et Cosmochimica Acta*, 122, 58–74.
<https://doi.org/10.1016/j.gca.2013.08.014>
- Tartèse, R., Anand, M., McCubbin, F. M., Elardo, S. M., Shearer, C. K., & Franchi, I. A. (2014). Apatites in lunar KREEP basalts: The missing link to understanding the H isotope

- systematics of the Moon. *Geology*, 42(4), 363–366. <https://doi.org/10.1130/G35288.1>
- Wadhwa, M. (2008). Redox Conditions on Small Bodies, the Moon and Mars. *Reviews in Mineralogy and Geochemistry*, 68(1), 493–510. <https://doi.org/10.2138/rmg.2008.68.17>
- Warren, P. H., & Wasson, J. T. (1979). The origin of KREEP. *Reviews of Geophysics*, 17(1), 73. <https://doi.org/10.1029/RG017i001p00073>
- Wieczorek, M. A., Neumann, G. A., Nimmo, F., Kiefer, W. S., Taylor, G. J., Melosh, H. J., Phillips, R. J., Solomon, S. C., Andrews-Hanna, J. C., Asmar, S. W., Konopliv, A. S., Lemoine, F. G., Smith, D. E., Watkins, M. M., Williams, J. G., & Zuber, M. T. (2013). The Crust of the Moon as Seen by GRAIL. *Science*, 339(6120), 671–675. <https://doi.org/10.1126/science.1231530>
- Wieser, P. E., Iacovino, K., Matthews, S., Moore, G., & Allison, C. M. (2022). VESIcal: 2. A Critical Approach to Volatile Solubility Modeling Using an Open-Source Python3 Engine. *Earth and Space Science*, 9(2), e2021EA001932. <https://doi.org/10.1029/2021EA001932>
- Zhang, Y., Belcher, R., Ihinger, P. D., Wang, L., Xu, Z., & Newman, S. (1997). New calibration of infrared measurement of dissolved water in rhyolitic glasses. *Geochimica et Cosmochimica Acta*, 61(15), 3089–3100. [https://doi.org/10.1016/S0016-7037\(97\)00151-8](https://doi.org/10.1016/S0016-7037(97)00151-8)