

H₂O AND OTHER VOLATILES IN THE MOON, 50 YEARS AND ON. Youxue Zhang, Department of Earth and Environmental Sciences, the University of Michigan, Ann Arbor, MI 48197, USA <youxue@umich.edu>.

Introduction: H₂O and volatile abundances in the Moon provide key constraints on the origin and evolution of the Moon, and for assessing future human exploration of the Moon. It has been known for a long time that there is no liquid water on the Moon. Apollo missions brought back lunar samples and give humankind the opportunity to investigate the Moon to unprecedented detail. Early (pre-2008) studies did not convincingly reveal any innate lunar H₂O, leading to the notion a completely dry Moon. Saal et al. (2008) first discovered measurable amount of H₂O in lunar volcanic glasses. Numerous subsequent reports (some were planned well before 2008, and some inspired by the study of Saal et al., 2008) showed that the Moon contained significant H₂O, and shifted the paradigm of a bone-dry Moon to a fairly wet Moon, leading to new thinking about the origin of the Moon. New studies also supplied more accurate data on other volatiles. I am fortunate to have witnessed and participated in this exciting paradigm shift. This work will review H₂O and other volatiles in the Moon in the last 50 years of lunar science, with more emphasis on the work of my coworkers and me (bolded citations).

Early (pre-2008) Studies of Apollo Samples on H₂O and Other Volatiles in Lunar Rocks: Epstein et al. (1970) analyzed hydrogen content and D/H ratio in the first batch of Apollo samples and concluded that the hydrogen is of solar wind origin, without detectable innate lunar H₂O. Subsequent work between 1970 and 2007 did not challenge the conclusion. For example, Fogel and Rutherford (1995) used FTIR but found OH and C in lunar volcanic glasses below detection limits (10-50 ppm for H₂O and 50-100 ppm for C). All of these studies led to the widely held view that the Moon was dry, containing no more than 1 ppb H₂O (Taylor et al., 2006). This notion was consistent with earlier thinking of the Giant Impact origin for the Moon.

Data on other volatile elements have also been accumulated (e.g., O'Neill, 1991), although at least for C, Cl, F, Zn, Cu, and S, it is necessary to consider post-eruptive loss to assess the pre-eruptive concentration and hence mantle concentrations (see below).

Post-2008 Studies: Saal et al. (2008) measured H₂O concentration profiles in orange and green volcanic glass beads using SIMS, and the highest H₂O concentration was 46 ppm, which is 46,000 times 1 ppb. The volcanic glasses cooled on the surface of the Moon and hence likely lost much H₂O. Saal et al. (2008) also modeled H₂O concentration profiles and estimated that H₂O in a pre-loss bead is likely 745 ppm, but uncertainties in the assumed thermal history

and diffusivity and other model issues made the estimation questionable. A flurry of papers followed.

H₂O on the lunar surface. Remote spectroscopic studies (Clark, 2009; Pieters et al., 2009; Sunshine et al., 2009) discovered absorbed H₂O and structural OH bands in spectra of lunar surface, with estimated concentrations of 10-1000 ppm (Clark, 2009). LCROSS mission crashed a rocket into a crater near the South Pole of the Moon, detecting both water vapor and ice in the plume (Colaprete et al., 2010). **Liu et al. (2012)** made FTIR and SIMS measurements of lunar soil samples and showed that H₂O in bulk regolith samples is about 70 ppm and such H₂O is largely in glasses. Based on D/H ratio measurements, **Liu et al. (2012)** concluded that lunar surface H₂O originated mostly from solar wind implantation, meaning that other airless bodies such as Mercury and Vesta are also expected to contain such surface H₂O. Liu et al. (2016, 2017) continued the studies.

H₂O in lunar magmatic apatite. Early attempts to obtain OH content in lunar apatite using electron microprobe data were thought to be unreliable. Significant OH in lunar apatite was found using SIMS (Boyce et al., 2010; McCubbin et al., 2010a,b, and Greenwood et al., 2011). Later, the first authors of these four papers co-authored a paper showing that measured OH contents in apatite do not constrain H₂O in the magma because OH is a “major” structural component in apatite rather than a trace component (Boyce et al., 2014), demonstrating the intricacy of such inferences. Pernet-Fisher (2014) also discussed complexities in using apatite to estimate H₂O in the Moon. Nonetheless, numerous studies on lunar apatite have been carried out (Barnes et al., 2013, 2014, 2016a,b; Tartese et al., 2013, 2014a,b; Robinson et al., 2016; Konecke et al., 2017; Potts et al., 2018), constraining H and Cl isotope ratios of lunar igneous materials, origin of lunar volatiles, and possible alteration/metamorphism.

H₂O in lunar volcanic rocks and in the lunar mantle. H₂O content in lunar melts has been determined, and that in the lunar mantle has been inferred by a number of approaches. Using SIMS, Hauri et al. (2011) found up to 1410 ppm H₂O in olivine-hosted melt inclusions (OHMIs) in lunar basalt 74220, and inferred that the some parts of lunar interior contain as much H₂O as the Earth's upper mantle. Saal et al. (2013) reported that hydrogen isotopes in lunar volcanic glasses and OHMIs reveal a carbonaceous chondritic heritage. Using FTIR, **Hui et al. (2013)** measured H₂O in plagioclase crystals in lunar highland anorthosites to be ~6 ppm. Using H₂O partition coefficient of Hamada

et al. (2013) and data in **Hui et al. (2013)**, H₂O in the primordial lunar magma ocean and hence in the primitive lunar mantle is about 130 ppm (**Chen et al., 2015**). **Hui et al. (2017)** followed the study of **Hui et al. (2013)** with the very difficult SIMS measurement of D/H ratio in lunar highland plagioclase and used the data to infer that the Moon lost a significant amount of H₂O during its magma ocean stage. **Chen et al. (2015)** measured by SIMS concentrations of volatiles and other elements in OHMIs and used the elemental ratios approach to assess primitive mantle compositions. Using H₂O/Ce, F/Nd and S/Dy ratios with some assumptions, they estimate H₂O, F and S concentrations in the primitive lunar mantle to be about 110, 5.3 and 70 ppm. Albarede et al. (2015) determined Zn concentration and Zn/Fe ratio in lunar samples and used the degree of Zn depletion to extrapolate H₂O concentration in the primitive lunar mantle to be sub-ppm level. They also discounted high H₂O data in 74220 as a local anomaly. **Ni et al. (2017)** investigated diffusive degassing from OHMIs and found H₂O can be lost easily (depending on the size of an MI), whereas F, Cl and S can be better retained by MIs. Mills et al. (2017) found alkali feldspar in a lunar granitoid contains about 20 ppm H₂O, from which they estimated that the lunar mantle had < 100 ppm H₂O for most of its history.

New debate on H₂O content in the lunar mantle. The reported H₂O/Ce ratio in large OHMIs is variable from 0.3 to 55 (Hauri et al., 2011; **Chen et al., 2015**; **Ni et al., 2017, 2019**). Highest ratios (40-60) are in naturally glassy OHMIs in 74220. Lower ratios (3-10) are in partially glassy OHMIs, and even lower ratios (down to 0.3) are in crystalline OHMIs that were homogenized in the lab. My coauthors and I argue that the glassy MIs best represent true pre-eruptive H₂O/Ce ratio of lunar basalts with ~100 ppm H₂O in the lunar mantle (**Chen et al., 2015**; **Ni et al., 2017, 2019**). However, Albarede et al. (2015) argue that the high ratios are local anomalies and lower ratios are more representative of lunar basalts and mantle. In addition, Albarede et al. (2015) used new Zn data (not in MIs) and constructed a lunar depletion trend as a function of the condensation temperature, from which they argued that H₂O in the lunar mantle is 1 ppm or less.

Other volatiles in lunar rocks. Wetzel et al. (2015) made the first detection of C in lunar samples: OHMIs may contain up to 4 ppm C, but glass beads contain only 0.25-0.75 ppm C. By comparing concentration data in OHMIs and in glass beads in 74220 (Hauri et al., 2011; Saal et al., 2013; **Chen et al., 2015**; Wetzel et al., 2015; **Ni et al., 2017, 2019**), it can be seen that H, C, Cl, F, Zn, Cu, and S are prone to post-eruptive loss by degassing or diffusion even for rapidly quenched samples. The loss trend from magmas on the

lunar surface is not controlled by the condensation temperature alone. The results indicate that literature data on these elements may not reflect pre-eruptive concentrations and hence cannot be used to model the composition or the depletion trend of the lunar mantle. Unlike H₂O and C, melt inclusions, even crystalline ones that are homogenized, provide reasonably good protection against the loss of Cl, F, Zn, Cu and S. Hence, it is necessary to use OHMIs to determine the pre-eruptive volatile contents. On the other hand, for Li, K, Na, Rb, Cs, Pb and Ga, post-eruptive loss is insignificant, and literature data can be used to model the lunar mantle composition. (Due to measurement limitations, other highly volatile elements, including noble gases, N, Hg, Tl, I, In, Br, Cd, Se, Sn, Te, Bi and Cs have not been examined yet.)

Significance on the Origin of the Moon: The paradigm shift from a dry to a wet Moon is having a significant impact on the Giant Impact Hypothesis for the origin of the Moon. Before 2013, only relatively young (≤ 3.9 Ga) mare basalts were found to contain high H₂O concentrations, which permits a bone dry Moon at the time of formation from the Giant Impact because there was sufficient time for H₂O to be gradually added after the Giant Impact (Hauri, 2013; Tartese and Anand, 2013). At the time **Hui et al. (2013)** published results that the lunar magma ocean contained >100 ppm H₂O, it was thought then that the Giant Impact Hypothesis for Moon formation would be in trouble (Hauri, 2013). However, it turned out that the Giant Impact Hypothesis is resilient and flexible enough to accommodate the new discoveries. For example, one suggested solution is that right after the Giant Impact, a gas disk enveloped the newly formed proto-Moon, and dissolution of H species (mostly OH) from the gas disk into the lunar magma ocean is enough to establish lunar H₂O abundance (Pahlevan et al., 2016; Sharp, 2017). Another suggested solution is that the upper parts of the Moon-forming disk are dominated by an atmosphere of heavy atoms or molecules, leading to diffusion-limited H loss, which is inefficient, meaning that the Moon was able to retain H₂O (Nakajima and Stevenson, 2018). These developments do highlight the importance of establishing the abundances of not only H₂O but also other volatiles in the Moon in setting stringent constraints on the origin of the Moon.

Selected References: [1] Albarede et al., 2015, *MPS*, 50, 568. [2] **Chen et al.**, 2015, *EPSL*, 427, 37. [3] Hauri et al., 2011, *Science*, 333, 213. [4] **Hui et al.**, 2013, *Nature Geosci.*, 6, 177. [5] **Hui et al.**, 2017, *EPSL*, 473, 14. [6] **Liu et al.**, 2012, *Nature Geosci.*, 5, 779. [7] **Ni et al.**, 2017, *EPSL*, 478, 214. [8] Saal et al., 2008, *Nature*, 454, 192. [9] Wetzel et al., 2015, *Nature Geosci.*, 8, 755.