

VOLATILES (H, C, N, F, S, CL) IN THE LUNAR MANTLE, CRUST, AND REGOLITH: WHAT QUESTIONS REMAIN AND WHERE DO WE GO NEXT? F. M. McCubbin¹ and C. K. Shearer¹ ¹Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131. fmccubbi@unm.edu

Introduction: Magmatic volatiles (H₂O, H₂, CO₂, CO, CH₄, HCl, HF, H₂S, SO₃, N₂, NH₃, noble gases, etc.) affect a wide range of important physical properties of geologic materials from the stability of minerals and melts to the structural and rheological characteristics of various rocks and minerals. On the Moon, magmatic volatiles are poorly understood, and the magmatic volatile inventory of the lunar mantle, crust, and surface, aside from being very low, is largely unconstrained. Although the Moon is volatile-depleted [e.g., 1], there is evidence indicating that magmatic volatiles have played a role in a number of geologic processes within and on the Moon.

In recent years, there has been a focused effort to determine the abundances and distributions of magmatic volatiles in lunar materials both through laboratory studies and through orbital spacecraft-based investigations. These modern efforts were largely sparked by substantial advances in detection sensitivity for a number of analytical/remote observation techniques, which led to a renaissance in the study of lunar volatiles that largely started in 2007 when two groups independently began reassessing the hydrogen inventory of lunar samples [2-3]. In addition to all of these recent analyses of volatiles, there were substantial efforts in the 1970's and to a lesser extent the 1980's and 90's to understand the abundances, distribution, and origin of volatiles in lunar materials. Little effort has been made to bridge the initial studies of lunar volatiles to more recent ones. Furthermore, many of the results from sample analysis and remote sensing are highly complementary in nature, and little has been done to merge these data sets into a clear picture of volatiles in and on the Moon. A recent review paper forthcoming in The Lunar Highlands Special Issue in American Mineralogist [4] has compiled information and data on the elements H, C, N, F, S, and Cl in lunar materials and from lunar remote sensing to determine what we know about volatiles and their respective isotopes on the Moon.

Findings and Progress in lunar volatiles: In the review [4], the authors provide the first complete inventory of volatile-bearing minerals that have been reported to occur in lunar samples, along with an estimated likelihood of existence. Analyses of volatiles from lunar glass beads as well as the phase assemblages present in coatings on those beads were used to determine that H₂ is likely the primary gas phase most

responsible for propelling the eruptions that produced the pyroclastic glass beads as opposed to CO with an H₂/H₂O molar ratio in the vapor species of about 10:1 at 1 log unit below the IW buffer at 1300 °C. Mineral-melt partitioning data and analyses of volatiles in lunar soils, glasses, and apatites were used to estimate the relative and absolute abundances of some volatile elements within the bulk Moon, urKREEP, lunar mantle, and crust. Sample studies on lunar soil and remote sensing data are combined to better understand the distribution, origin, and abundances of volatiles on the lunar surface. Isotopic data on volatile elements is used to determine possible sources and reservoirs in and on the Moon. Finally, a compilation of unanswered questions and future avenues of research are presented along with a critical analysis of approaches for answering these questions, which we include in the next section below.

Outstanding questions and future avenues: 1) *What volatile-bearing minerals are indigenous to lunar samples?* Many of the volatile-bearing minerals that have been reported in lunar rocks remain “unverified” and a modern effort to re-examine some of these samples with modern techniques could yield additional important mineral systems through which one can try to understand lunar volatiles. A substantial effort has been put forth to understand the mineral apatite and what secrets it holds regarding volatiles in the lunar environment, but apatite is a complicated mineral to use for determining volatile abundances [i.e., 5-6], and we still have a lot to learn from it. Including additional volatile-bearing mineralogical systems, if present, would greatly enhance the wealth of information about volatile abundances and isotopic compositions of the Moon, which could potentially move the field forward much further than with apatite alone.

2) *Concentrations and distribution of volatiles in the lunar interior.* Estimates of the relative abundances of H₂O, F, and Cl in the lunar mantle differ substantially from the estimated relative abundances of H₂O, F, and Cl in urKREEP (i.e., mantle has H₂O > F > Cl, urKREEP has Cl > H₂O ≈ F). Either the estimates for volatile abundances in urKREEP and lunar mantle are inaccurate, or a process that forces the lunar mantle to preferentially store H₂O and F and exclude Cl during LMO crystallization must be at work. The partitioning behavior of H₂O, F, and Cl between pyroxene and silicate melt could operate to include F, and OH in the

mantle while excluding Cl, or there is another phase in the LMO cumulate pile in which F and H₂O are compatible and Cl is incompatible (Fe-Ti oxides?). Experimental work on mineral-melt partitioning of H₂O, F, and Cl between LMO minerals (olivine, pyroxene, Fe-Ti oxides, and anorthitic plagioclase) and silicate melt under reducing conditions relevant to lunar magmatism could help shed light on this issue. Furthermore, the continued analysis of volcanic glasses, including the A-14 KREEP-rich glasses [7] will help constrain the volatile abundances in the lunar mantle and in urKREEP. Lastly, the continued analysis of apatite in mare basalts (including the KREEP basalts), with a specific focus on variations among petrologic types, will help one to understand the range in volatile compositions of the various lunar mare source regions.

3) *What are the sources and/or reservoirs of volatiles on the Moon?* It is still very unclear whether or not the isotopic variations in H and Cl in volcanic lunar samples are being primarily driven by fractionation processes or mixing of various reservoirs. Given that almost the entire spread of $\delta^{37}\text{Cl}$ values observed in lunar samples is thus far observed only on the Moon, it is highly likely that Cl has been fractionated by some process on the Moon, but the process responsible has yet to be proven. Sharp et al. [8] provided evidence for Cl-isotope fractionation occurring as a result of degassing or vaporization of metal chlorides, but this process has yet to be demonstrated experimentally. In fact, experimental work on Cl-degassing from H-poor silicate melts under reducing conditions relevant to lunar magmatism is highlighted here as an important avenue of future research. Determining the fractionation process is a prerequisite to solving the question of the origin of the seemingly heavy Cl isotopic signature in urKREEP. Importantly, this process does not seem to have pervasively affected the lunar mantle in the same way it has affected the lunar crust.

H isotopes were likely affected by secondary processes and mixing of multiple reservoirs, which preclude straightforward interpretations of the existing data. From the plethora of data on lunar soils, it is clear that there is a very light (\sim -1000 ‰) reservoir of solar wind and a fairly heavy reservoir of spallogenic D at the lunar surface available for assimilation into erupted lava flows and impact melts. Furthermore, there has been substantial meteoritic and cometary infall to the Moon over the last \sim 4.35 Ga that could have produced distinct pockets of unique hydrogen isotopic reservoirs in and on the Moon. On account of low oxygen fugacity prevalent in the Moon, H₂ would dominate over H₂O in any degassing vapor, which would cause substantially higher isotopic fractionation of H compared to H₂O-dominated systems. Additional challenges in-

volve identification of any terrestrial contamination in lunar samples and thin sections (e.g., thin section epoxy or terrestrial water in cracks). All of these possible sources could affect our ability to determine the indigenous H isotopic composition of the Moon, which many have recently argued is essentially the same as Earth and chondrites [9-12]. This tantalizing possibility of a common source for water in the Earth-Moon system is gaining traction, but further support for this idea will require placing the isotopic data in the context of Petrographic textures and timing of crystallization. For example, Tartèse et al. [12] report SIMS data for apatites in KREEP basalt 15386, for which apatite H₂O contents increase with decreasing δD values. Petrographic observations show that while most of the apatite grains in 15386 occur closely associated with late stage mesostasis areas, one apatite analyzed is included within a pyroxene, suggesting it crystallized relatively early. Interestingly, this apatite grain is characterized by the lowest δD ($\sim 90 \pm 100$ ‰) and highest OH content (~ 780 ppm H₂O), which is precisely what one would expect if the observed OH/ δD relationship in apatites in 15386 resulted from crystallization during progressive magmatic degassing of H₂.

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