ENDEGEOUS LUNAR VOLATILES: THE VIEW FROM 50 YEARS AFTER APOLLO 11. F. M. McCubbin1, J. J. Barnes 1, and Y. Liu. 1ARES NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058. 2Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA

Introduction: Neil Armstrong first stepped onto the surface of the Moon on July 20, 1969, marking a definitive milestone in our progress as a species. With the return of approximately 382 kilograms of lunar samples across all the Apollo missions, this event also marked the beginning of space exploration as a means to study other worlds in laboratories on the Earth. When the Apollo 11 astronauts stepped onto the surface of the Moon, they entered a desiccated and dusty world. Furthermore, the returned samples seemed to reflect the dry nature of the lunar surface, as the samples lacked many of the hydrated or aqueously altered features that are common in rocks from the Earth. In fact, the lunar samples indicated strong depletions in all volatile elements relative to the Earth, which was a key observation that has helped to understand the origin of the Earth-Moon system as well as the distribution and origin of volatiles elsewhere in our solar system.

Nearly all differentiated terrestrial bodies in our solar system are depleted in volatile elements relative to Carbonaceous Ivuna-type (CI) chondrites (volatile elements are defined here as elements with 50% condensation temperatures less than 1300 K). These depletions in volatiles are thought to be linked, at least in part, to the high-temperature formation processes of planetary accretion. Consequently, the inventory of volatile elements in a planetary body records important clues as to the formation history and subsequent thermal evolution of that body. The Moon is highly depleted in volatile elements compared with CI chondrites and further, it is volatile-depleted relative to the terrestrial planets. This volatile depletion is thought to be due to a combination of the cataclysmic circumstances under which the Moon formed [1], a geochemical signature of the protoplanet Theia [thought to be the impactor that collided with the proto-Earth; 2], and the process of planetary differentiation. The abundances, distributions, and isotopic compositions of volatile elements in and on the Moon have been intensely scrutinized over the last 50 years. However, tremendous insights have been gained into the roles that volatiles have played in the origin, formation, and subsequent thermochemical evolution of the Moon in the last decade.

Although the study of lunar volatiles began as soon as the Apollo samples were returned, the primary motivation behind the lunar volatile studies of the last decade stems from the discovery of indigenous hydrogen in lunar samples [3-6], the remote detection of H, OH, or H2O on the lunar surface [7-10], and the discovery that stable isotopic compositions of moderately volatile and volatile elements are fractionated in lunar samples relative to terrestrial values [11-15]. Prior to these studies, the Moon was commonly referred to as “bone dry”, and was thought to host less than 1 part per billion (ppb) H2O in its interior [e.g., 16]. These studies initiated a reassessment of the abundances of volatiles within the Moon as well as of the isotopic compositions of volatile and moderately volatile elements in lunar samples. This work represents a summary on the status of endogenous lunar volatiles.

Insights into lunar volatiles in the last decade:

The recent progress in our understanding of endogenous lunar volatiles also comes largely through the study of lunar samples. In particular, the abundances of the volatile elements F, Cl, S, and H have been studied extensively in lunar apatites [4-6, 13, 14, 17-33], glass beads and mesostasis glasses [3, 34, 35], olivine-hosted melt inclusions [34, 36-40], and within nominally anhydrous mineral (NAM) phases [41-43]. Although there has been less progress in determining the abundance of C compared to F, Cl, S, and H in lunar samples, several recent reports exist for lunar basalts and volcanic glasses [44-47]. In addition to elemental abundances, the H- and CI-isotopic compositions of apatites, glasses, and NAMs have been reported [13, 14, 18-24, 28-34, 38, 43, 48]. Bulk rock N-, Cl-, and S-isotopic data have also been reported [13, 46, 49-52]. Finally, there has been substantial progress in determining and evaluating the abundances and isotopic compositions of a number of other volatile to moderately volatile elements in lunar samples, including Li, Cu, K, Ga, B, Ge, Rb, Cs, Pb, and Zn [11, 12, 15, 36, 37, 39, 40, 53-63]. All of these data were used to compute an updated abundance of volatile elements in the bulk Moon, specifically the elements Li, K, Ga, Na, Cl, B, Rb, Cs, F, Pb, Zn, S, C, and H.

Discussion: The silicate portion of the Moon is depleted in volatile elements relative to the Earth, and the Earth and Moon are both depleted in volatile elements relative to CI chondrites (Figure 1). Lithium is not depleted in the Moon relative to the Earth, so lithium does not behave as a volatile element in the Earth-Moon system, consistent with the results of previous studies [61, 64]. In general, volatile elements with condensation temperatures between 650 K and 1050 K are depleted in the Moon relative to the Earth by a factor of 2 to 10, and there is not a strong correlation between the degree of...
depletion relative to Earth and 50% condensation temperature (Figure 1b). These depletion factors for the moderately volatile and volatile elements match well with those reported by Hauri et al. [62] and Ni et al. [40], indicating that volatile depletion in the Moon relative to Earth is less extreme than previously reported [e.g., 63, 65]. However, Cl and possibly Zn are notable exceptions to this trend. Although more Zn data are needed to constrain the Zn content of the Moon, the low abundance of Cl in the Moon is well established.

Of the highly volatile elements, we aimed to constrain abundances of H and C in the bulk silicate portion of the Moon. Our calculations suggest that the Moon is more depleted in H and C relative to the Earth compared to estimates from previous studies [44, 62], indicating that there is additional work needed to further constrain the abundances of H and C in BSM. Importantly, even the lower end of our estimated range of H2O abundances in the lunar interior (i.e., 480 ppb H2O) is enriched by more than a factor of 500 relative to estimates of bulk lunar H2O abundances prior to 2008 [e.g., 16, 66]. The lunar H and C abundances estimated in this work both match the general trend of volatile depletion relative to CI chondrites that would be predicted based on 50% condensation temperatures, although the range in H abundances would match a large range of depletion trend slopes (Figure 1). The large range in H highlights the need for additional work to constrain H abundances in the bulk Moon.

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Figure 1. Abundances of select volatile elements in BSM, BSE, and CI chondrite as a function of 50% condensation temperature at 10^{-4} bars [67]. Volatile depletion trends for the Earth (blue) and Moon (gray) are estimated with an envelope that has a slope defined by Li and C abundances (a) Abundances of select volatile elements in BSE (blue symbols) and BSM (orange symbols), normalized to Mg and Cl chondrite [after 68]. Data for H2O and C in BSE are from Marty [69], data for H2O in CI are from Alexander et al. [70], and all other data for BSE and CI are from McDonough and Sun, [68]. Volatile abundances for BSM are from the estimates reported in this study. (b) Abundances of select volatile elements in BSM normalized to BSE.