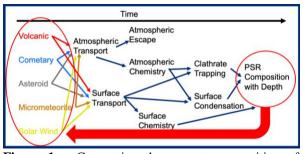
THE ROLE OF CLATHRATE FORMATION IN THE COMPOSITION OF VOLATILES IN LUNAR **PERMANENTLY SHADED REGIONS.** K.E. Mandti, O. Mousis2, D. Hurley1, and A. Luspay-Kuti. 1Johns Hopkins Applied Physics Laboratory, Laurel, MD (Kathleen.Mandt@jhuapl.edu), 2Aix Marseille Univ, CNRS, CNES, LAM, Marseille, France.

**Introduction:** The Moon is recognized as a cornerstone for understanding the history of the solar system. Just as the impact history of the Moon helps us to understand the impact history of the Earth and other solar system bodies, the history of volatiles on the Moon can help us to constrain how volatiles were delivered to the Earth-Moon system as well as the development and loss of secondary atmospheres through internal outgassing.

The Permanently Shaded Regions (PSRs) of the Lunar poles are known to provide an environment well suited for long-term preservation of volatiles [1,2]. However, the exact abundance and composition of the volatiles present in the PSRs is poorly understood. The greatest insight into the composition of volatiles beyond water ice was provided by the Lunar Crater Observation and Sensing Satellite (LCROSS) mission [3,4]. This observation, and future measurements by landed missions [e.g. 5] can provide important insights into the origin and history of volatiles on the Moon and in the Earth-Moon system.



**Figure 1** – Connecting the current composition of volatiles in the Lunar PSRs requires an understanding of the processes that took place between delivery of the volatiles and their sequestering.

We illustrate in Fig. 1 the processes that need to be considered in trying to connect the current composition of volatiles at the poles to the variety of possible sources. These potential sources include volcanic activity that may have been intense enough to form an atmosphere [6], impacts of comets, asteroids, and micrometeoroids occurring over the history of the Moon, and water produced by the interaction of the solar wind with the Lunar surface.

The purpose of this study is to look at the role of clathrate formation in determining the composition of

volatiles originating from volcanic outgassing and major impacts in PSRs, and to compare the predicted composition with measurements currently available.

The LCROSS mission detected Composition: water vapor and OH in the plume resulting from an impact into the Cabeus crater PSR, and determined based on near ultraviolet, visible, and near infrared measurements that the water ice abundance in the soil at the impact site was 5.6±2.9% by mass [3]. Far ultraviolet measurements of CO estimated the soil abundance of this molecule to be 5.7% by mass [4], appearing to suggest that CO is as abundant as water ice in the Cabeus crater PSR. However, we must note that the volume of regolith from which any constituent was volatilized depends on the volatility of the constituent, so the CO amounts in the plume may be inflated because it was volatilized from a larger volume than the water. Other molecules detected include CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, NH<sub>3</sub>, H<sub>2</sub>S, and SO<sub>2</sub>.

Molecular composition is useful in trying to understand the origin of volatiles on the Moon. For example, H<sub>2</sub>O is the most abundant molecule in the comae of comets, with large abundances CO and CO<sub>2</sub> and trace amounts of C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CH<sub>3</sub>OH, NH<sub>3</sub>, H<sub>2</sub>S, and SO<sub>2</sub> [7]. Volcanic gases tend to have large amounts of CO with some CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S, and SO<sub>2</sub> [6,8,9,10]. However, as noted in Fig. 1, the molecular composition of volatiles can change between delivery and long-term storage in the PSRs through atmospheric and surface chemistry. Therefore, the bulk elemental composition could ultimately be a more useful constraint for tracing the origin of volatiles detected in Lunar PSRs.

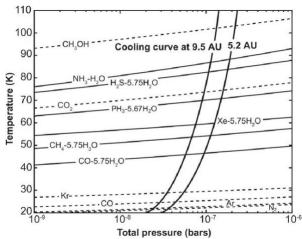
**Table 1** – Bulk elemental composition of volatiles observed by LCROSS [3,4] compared to bulk composition of analogs for volatile sources: Comets based on 67P/Churyumov-Gerasimenko [7], Chondrites [12], and Volcanoes [6,9]. All values are scaled to the solar value representing the gas in the PSN as compiled by [12].

	LCROSS	Comets	Chondrites	Volcanoes
N/C	0.18	0.35	0.25	0
O/C	0.88	5.52	0.46	0.5-1.7
S/C	3.07	3.19	9.84	12-43

In recent efforts to better characterize the composition of solid material in the solar system during

the protosolar nebula (PSN) phase, and to understand their role in planet formation, we have begun comparing the bulk elemental composition of comets and chondrites to solar system bodies [11]. We found that the best approach is to compare the ratio of nitrogen, oxygen, and sulfur to carbon and scaling that ratio to the value of the PSN based on the review of [12]. These results are compared to the LCROSS composition and what is known of volcanic gases in Table 1. As we see in this table, the abundance of nitrogen relative to carbon (N/C) in the LCROSS plume is a poor constraint for separating the three potential sources. However, the oxygen and sulfur ratio relative to carbon (O/C and S/C)can vary significantly based on the potential volatile source. We note that S/C in the LCROSS plume is in reasonable agreement with the cometary value, while the O/C in the plume is depleted compared to comets and is more like a volcanic source.

**Clathrates:** The formation of clathrates would allow trapping of molecules based on the pressure and temperature of the gas produced by volcanic activity and impacts as illustrated in Fig. 2. We model the composition of the clathrates formed based on several input composition profiles for impacts and volcanoes to determine the most likely source or combination of sources of volatiles for the composition of the PSR volatiles observed in the LCROSS plume.



**Figure 2** – Stability curve for the formation of clathrates indicating the temperature and pressure at which clathrates would form in the PSN at 5.2 and 9.5 AU. These same curves determine how clathrates would form in a transient atmosphere on the Moon formed by intense volcanic activity or large impacts (Source: [13]).

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**References:** [1] Watson, K. et al. (1961) *JGR*, 66, 1698-1600. [2] Paige, D. A. et al. (2010) *Science*, 330, 479. [3] Colaprete, A. et al. (2010) *Science*, 330, 463-468. [4] Gladstone, G. R. et al. (2010) *Science*, 330, 472-476. [5] Colaprete, A. et al. (2019) *LPI Contributions*, 2152. [6] Needham, D. H. et al. (2017), *EPSL*, 478, 175-178. [7] Rubin, M. et al. (2019), *MNRAS*, 489, 594-607. [8] Fegley, B. (1991) *GRL*, 18, 2073-2076. [9] Kerber, L. et al. (2017) *GCA*, 206, 296-311. [11] Mandt, K. E. et al. (2019) *MNRAS*, 491, 488-494. [12] Lodders, K. et al. (2009) *Solar System*, Springer, Berlin. [13] Mousis, O. et al. (2009) *ApJ*, 696, 1348.