



# Lunar volcanism produced a transient atmosphere around the ancient Moon



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## ABSTRACT

Studies of the lunar atmosphere have shown it to be a stable, low-density surface boundary exosphere for the last 3 billion years. However, substantial volcanic activity on the Moon prior to 3 Ga may have released sufficient volatiles to form a transient, more prominent atmosphere. Here, we calculate the volume of mare basalt emplaced as a function of time, then estimate the corresponding production of volatiles released during the mare basalt-forming eruptions. Results indicate that during peak mare emplacement and volatile release  $\sim 3.5$  Ga, the maximum atmospheric pressure at the lunar surface could have reached  $\sim 1$  kPa, or  $\sim 1.5$  times higher than Mars' current atmospheric surface pressure. This lunar atmosphere may have taken  $\sim 70$  million years to fully dissipate. Most of the volatiles released by mare basalts would have been lost to space, but some may have been sequestered in permanently shadowed regions on the lunar surface. If only 0.1% of the mare water vented during these eruptions remains in the polar regions of the Moon, volcanically-derived volatiles could account for all hydrogen deposits – suspected to be water – currently observed in the Moon's permanently shadowed regions. Future missions to such locations may encounter evidence of not only asteroidal, cometary, and solar wind-derived volatiles, but also volatiles vented from the interior of the Moon.

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## 1. Introduction

The lunar atmosphere was first detected by ion and charged particle experiments installed during Apollo (Johnson et al., 1972; Hodges, 1973; Hoffman et al., 1973). The present atmosphere is low density and, thus, is designated a surface boundary exosphere (SBE). Similar exospheres, in which atoms and molecules removed from the surface have only a small probability of suffering a collision before escaping to space, have also been detected around Mercury, Io, Europa, and Callisto. Sources for the lunar atmosphere (e.g., Stern, 1999) include thermal, sputtering, and chemical processes that affect grains at the uppermost surface of the Moon, releasing ions and molecules from the surface into the exosphere. Additionally, meteoritic collisions onto the lunar surface produce impact-generated vapor and melted material that outgasses to the surrounding environment. Furthermore, other processes that release volatiles, including seismically induced seepage of volatiles from the lunar interior and volcanism, could contribute to the development of the exosphere. Although the lunar atmosphere has

likely been a SBE for the past 3 Ga, enhanced volcanic activity early in lunar history may have facilitated development of a more substantial collisional atmosphere around the ancient Moon.

## 2. Methods

### 2.1. Lunar mare basalt volume over time

We investigated the volume of mare basalt and the mass of volatiles released from the Moon as a function of time to determine how the lunar atmosphere may have been affected by more intense volcanic activity early in lunar history. Volumes of mare basalts erupted into each basin (Table 1) vary as a function of basin size and thermal evolution of the lunar interior. Mare basalt thicknesses may also be uncertain, which affect estimated volumes (e.g., from  $\sim 5 \times 10^5$  km<sup>3</sup>, Williams and Zuber, 1998; Hiesinger et al., 2011, to  $10^6$  km<sup>3</sup>, Bratt et al., 1985, in Crisium). In general, initial attempts to estimate mare basalt volumes (Solomon and Head, 1980; Bratt et al., 1985) overestimated those volumes by factors of  $\sim 2$  (Williams and Zuber, 1998; Dobb and Kiefer, 2015). In contrast, estimates of mare basalt thicknesses based on analyses of lunar basin depths (De Hon, 1974, 1976, 1977, 1979) augmented with Clementine altimetry data (Williams and Zuber, 1998) are

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**Table 1**  
Estimated total volume of mare basalt fill in lunar basins.

Basin	Total area (km <sup>2</sup> )	Thickness (m)	Volume (km <sup>3</sup> )
Crisium <sup>a</sup>	156,103	2,940	458,943
Grimaldi <sup>a</sup>	15,359	3,460	53,142
Humorum <sup>a</sup>	101,554	3,610	366,611
Imbrium <sup>a</sup>	1,010,400	5,240	5,294,497
Nectaris <sup>a</sup>	64,277	840	53,993
Oriente <sup>b</sup>	75,975	88	13,294
Procellarum <sup>c</sup>	1,757,799	325	571,285
Serenitatis <sup>a</sup>	342,716	4,300	1,473,679
Smythii <sup>a</sup>	28,075	1,280	35,937
South Pole – Aitken <sup>d</sup>	206,430	varied	153,240
Tranquillitatis <sup>c</sup>	371,257	350	129,940

<sup>a</sup> Williams and Zuber (1998).

<sup>b</sup> Whitten et al. (2011).

<sup>c</sup> Hörz (1978).

<sup>d</sup> Yingst and Head (1997).

generally consistent with more recent estimates using Lunar Orbiter Laser Altimeter (LOLA) topography data (Dibb and Kiefer, 2015) and Gravity Recovery and Interior Laboratory (GRAIL) data (Evans et al., 2016). Specifically, these newer estimates place an upper bound on the thickness of all nearside mare basalts of ~7 km (Evans et al., 2016). Recently reported basin-specific thickness estimates for the nearside mare basalt-filled basins with the greatest fill volumes (Serenitatis and Imbrium) are <15% different (Dibb and Kiefer, 2015) when compared with the work of Williams and Zuber (1998). Because Williams and Zuber (1998) analyzed the majority of lunar mare basalt-filled basins and reported thicknesses that are consistent with new topography and gravity data, we used these thicknesses to calculate the volume of mare basalt in lunar basins, including Crisium, Grimaldi, Humorum, Imbrium, Nectaris, Serenitatis, and Smythii. More recently reported mare basalt thicknesses were included for Oriente (Whitten et al., 2011) and other minor basins (Hiesinger et al., 2011), and mare volumes within Tranquillitatis, Oceanus Procellarum (Hörz, 1978), and South Pole – Aitken (SPA; Yingst and Head, 1997) were also included where more recent volume estimates were not available (Tables S1, S2).

Mare basalt provinces were emplaced from ~3.9 Ga to as recently as ~1.1 Ga (Figs. 1, 2a), as indicated by mare unit boundary mapping and crater size frequency analyses of Lunar Orbiter IV and

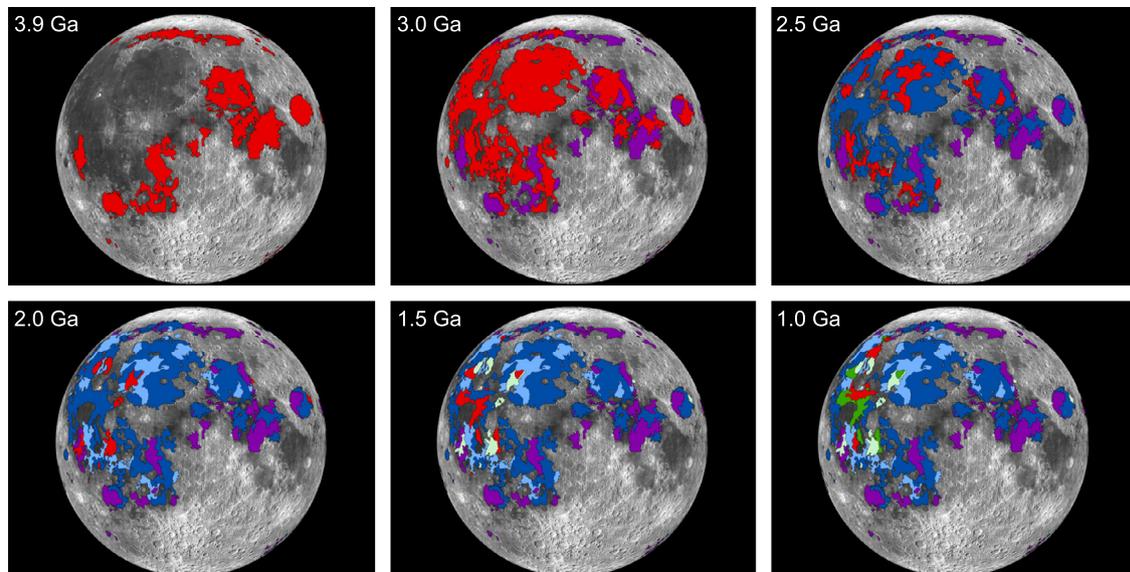
Clementine data for SPA (Yingst and Head, 1997) and for nearly all other basins included in these analyses (Hiesinger et al., 2011; Table S1). Mare basalt unit boundaries and associated model ages for Oriente were determined using data from Lunar Reconnaissance Orbiter Narrow and Wide Angle Camera (LROC NAC, WAC) images and Moon Mineralogy Mapper (M<sup>3</sup>) spectral data (Whitten et al., 2011). Observations of specific mare eruptive units indicate an average mare unit thickness of ~250 m (Weider et al., 2010) within Serenitatis and Oceanus Procellarum. This thickness is expected to incorporate an integrated sequence of thinner flows such as those observed in exposed walls of mare pits (Robinson et al., 2012), and is assumed to be the average thickness for all surface mare units in the absence of other thickness measurements (e.g., in Oriente (Whitten et al., 2011) and in SPA (Yingst and Head, 1997), Table S1).

We use observed mare basalt properties to calculate the volume of surface mare basalts across the Moon as a function of time (Fig. 2a and Table S2). The surface mare units represent the final stages of mare emplacement and, thus, are interpreted to post-date underlying mare units. We assume that the underlying flows were emplaced as older surface flows that were embayed by younger surface flows, such that the mare units are stacks of superposed lava units emplaced via effusive surface eruptions. Although ages of underlying basalts, with volumes taken as the difference between the total mare basalt for a given basin and the volume of the mapped surface flows, are not identified directly, these deposits are at least as old as the oldest surface unit (noted in italics in Table S1).

Mare volcanism peaked between 3.8 Ga and 3.1 Ga, with the largest volumes erupted ~3.5 Gyrs ago (Figs. 1 and 2a). Most mare basalts were emplaced within Serenitatis at 3.8 Ga, and within Imbrium and Oceanus Procellarum basins at 3.5 Ga. After those voluminous effusions of mare basalt, mare emplacement waned to near zero. Additional volumes of maria or cryptomaria that predate Oriente may not be included in our analyses, but would further contribute to the early release of volatiles.

## 2.2. Production of lunar volatiles over time

Measurable volatile abundances associated with lunar basalt eruptions [H, C, N, F, S, and Cl], began to emerge with direct measurements of Apollo 15 and 17 volcanic glasses (Saal et al., 2008,



**Fig. 1.** A time sequence of lunar mare basalt emplacement in 0.5 Ga time increments, with red areas in each time step denoting the most recently emplaced basalts. Ages of mare basalt units are from Hiesinger et al. (2011).

**Table 2**  
Proportion of volatiles degassed during mare emplacement.

Mare volatiles	Reported mass		% Liberated	Degassed mass	
	(ppm)	(ppm)		(ppm)	(ppm)
CO <sup>a</sup>	80	750	100	80	750
H <sub>2</sub> O <sup>b</sup>	2	10	90	1.8	9
H <sub>2</sub> <sup>c</sup>	0.007	45	100	0.007	45
OH <sup>b</sup>	0	0	99	0	0
S <sup>d</sup>	200	600	90	180	540

<sup>a</sup> Housley (1978).

<sup>b</sup> Robinson and Taylor (2014).

<sup>c</sup> McCubbin et al. (2010).

<sup>d</sup> Shearer et al. (2006).

Rutherford and Papale, 2009; Hauri et al., 2011). Those studies demonstrated that the volatiles released in pyroclastic eruptions include CO (100% liberated from parent magma, 105–1050 ppm), CO<sub>2</sub> (100% liberated, 18–183 ppm), H<sub>2</sub>O (98% liberated, 77–400 ppm), F (45% liberated, 3–12 ppm), S (19% liberated, 37–67 ppm), and Cl (57% liberated, 0–0.6 ppm). Volatiles associated with mare eruptions have lower concentrations (Table 2): CO (100% liberated, 80–750 ppm, Housley, 1978), H<sub>2</sub> (100% liberated, 0.007–45 ppm, McCubbin et al., 2010), H<sub>2</sub>O or OH (85–99% liberated, 1.98–9.9 ppm, Robinson and Taylor, 2014), and S (90% liberated, 170–540 ppm, Shearer et al., 2006), based on analyses of Fe metal (Hauri et al., 2011) and picritic basalts (Shearer et al., 2006) in Apollo 17 high-Ti samples, and of apatite in highly fractionated KREEP basalt samples (McCubbin et al., 2010; Robinson and Taylor, 2014).

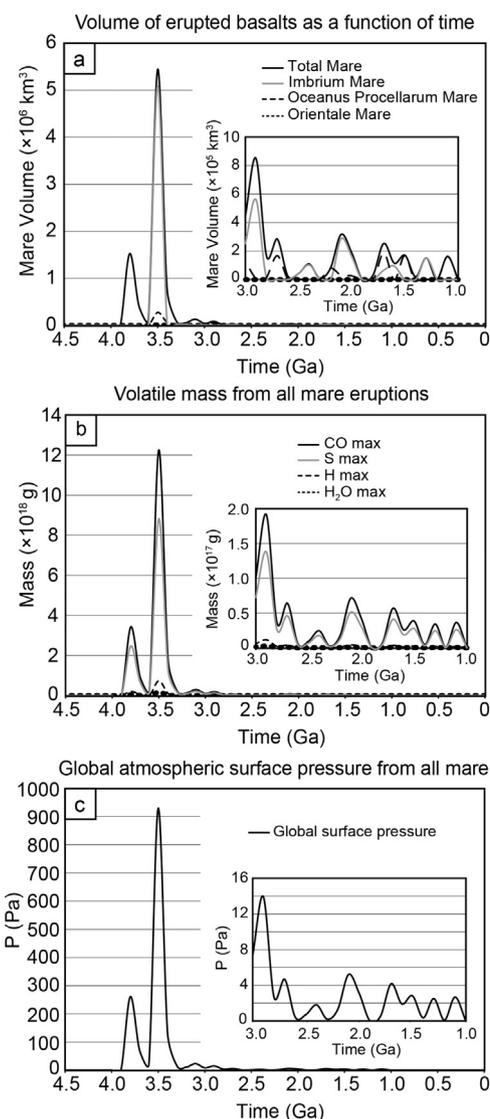
These values were used to calculate a production function of volatiles released over lunar history. Following a recent approach for lunar pyroclastic eruptions (Kring, 2014), the mass of erupted lava was calculated by multiplying the estimated volume by the bulk density of typical mare basalt (~3.00 g/cm<sup>3</sup>; Macke et al., 2014). This mass was then multiplied by the minimum and maximum contents of each volatile species for maria indicated in Table 2 to determine the mass range of each volatile released during an eruption. Incremental production was calculated for mare volumes erupted every 0.1 Ga. The resulting production functions for the Moon are plotted in Fig. 2b and summarized in Table S3, with peak volatile releases at 3.8 Ga and 3.5 Ga.

Generally, the most prevalent volatile species released are CO (0.2–2.0 × 10<sup>19</sup> g total over all mare eruptions) and S (0.5–1.4 × 10<sup>19</sup> g), while H<sub>2</sub>O is the third-most prevalent volatile released at peak eruption volumes (0.5–2.6 × 10<sup>17</sup> g). It has recently been suggested that 10–20% of the total H released in mare eruptions would be in the form of molecular hydrogen (Robinson and Taylor, 2014), which would proportionately decrease the volume of vented H<sub>2</sub>O. Contents of F and Cl in mare basalt parent magmas have not yet been reported and are, therefore, assumed to have been released in amounts smaller than anticipated for pyroclastic deposits (2–9 × 10<sup>14</sup> g of F and 0–4 × 10<sup>13</sup> g of Cl).

### 3. Discussion and conclusions

These gas volumes are sufficiently large (Fig. 2b) to produce a significant atmospheric surface pressure (Fig. 2c). Calculations (Table S3) utilizing those atmospheric masses and the Moon's gravity indicate a maximum surface pressure of a globally homogeneous atmosphere of ~1 kPa, or 0.01 atm (Fig. 2c) during the peak eruption epoch of 3.5 Ga. That value is ~1% of Earth's current surface pressure (101,325 Pa, or 1 atm) and ~1.5 times higher than Mars' current surface pressure (600 Pa, or 0.006 atm). The corresponding scale height of a CO–S–H<sub>2</sub>O lunar atmosphere is 60–100 km during lunar day and 15–30 km during lunar night.

Whether the atmosphere produced by the release of magmatic volatiles would have lingered around the Moon depends on its loss



**Fig. 2.** Volumes of erupted basalts and volatiles, and lunar atmospheric pressure as a function of time. (a) Volume of erupted basalts as a function of time, indicating peak volcanic activity primarily in Imbrium basin ca. 3.5 Ga; the inset in each graph shows results for the time period from 3.0 Ga to 1.0 Ga at an expanded scale. (b) Mass of volatiles, primarily CO and S, degassed during mare emplacement. (c) Atmospheric surface pressure resulting from the volatiles released during mare emplacement, with a peak pressure ~1% of Earth's current atmospheric pressure corresponding to peak volcanic activity 3.5 Ga. Quantified results for panel (a) are included in Table S2, and for panels (b) and (c) in Table S3.

rate. A combination of Suprathermal Ion Detector Experiment measurements (Vondrak et al., 1974), photoionization atmospheric loss rates (Killen and Ip, 1999), and He gravitational escape rate estimates (Stern, 1999) suggest a current lunar atmospheric loss rate of ~1 g s<sup>-1</sup> (Killen and Ip, 1999) to ~10 g s<sup>-1</sup> (Stern, 1999). This rate is controlled by particle interactions in a thin atmosphere (e.g., collisional ionization) and with the solar wind (e.g., photoionization) — ions in a thin atmosphere are expected to be lost equally to space and to the surface (Vondrak et al., 1974). However, such interactions and the consequent loss rate change significantly when gas is added to the atmosphere (e.g., through an eruption) at rates greater than 100 kg s<sup>-1</sup>, and when the atmospheric mass exceeds 10<sup>8</sup> kg (Vondrak et al., 1974). Under those conditions, the atmosphere transitions to a conventional collisional atmosphere, with a higher loss rate on the order of 10<sup>4</sup> g s<sup>-1</sup> (Stern, 1999). This higher loss rate is dominated by thermal escape and is independent of atmospheric mass. At peak lunar volcanic activity ~3.5 Ga, the to-

tal mass of particles released into the atmosphere was  $\sim 10^{16}$  kg at eruption rates of  $10,000 \text{ kg s}^{-1}$  (Wilson and Head, 1981), suggesting the lunar atmosphere at this time was a conventional collisional atmosphere. At a loss rate of  $10^4 \text{ g s}^{-1}$ , this thicker lunar atmosphere would have dissipated in  $\sim 70$  million years. The actual duration of the atmosphere may exceed this estimate, because the loss rate is expected to decrease as the atmosphere thinned. The higher atmospheric pressures during that interval may have been significant enough to influence local chemical reactions in basalts and highlands materials in the vicinity of eruption vents, producing, perhaps, the magnetite seen in Apollo sample 60016 (Joy et al., 2015).

Erupted volatiles would have been susceptible to migration towards the poles (Watson et al., 1961; Arnold, 1979), where they would have been trapped in permanently shadowed regions (PSRs). Recent analyses suggest a large portion of the measured polar hydrogen in the lunar PSRs may be ancient (Siegler et al., 2016). If 0.1% of the vented mare water (calculated above to be  $\sim 10^{17}$  g) is trapped in current PSRs, volcanically-derived volatiles could account for all of the water currently observed in these regions ( $10^{14}$  g; Eke et al., 2009). If the polar wander theory is correct, then the lunar poles would have been in their original north/south orientation 3.5 Ga as volcanic activity peaked. The poles would then have been repositioned to their current orientation after the volatiles were sequestered in the polar regions. The relative contributions of indigenous and exogenous sources are still uncertain, but these results suggest transport models need to consider higher indigenous fluxes of volatiles to properly evaluate their contribution to PSR volatile-rich deposits. As indigenous volatiles will have a distinct isotopic signature (Barnes et al., 2016), those model calculations can be tested with future lunar surface missions, such as the upcoming Resource Prospector mission.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2017.09.002>.

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