THE COMPOSITION OF LUNAR VOLCANIC VOLATILE OUTGASSING FROM MARE ERUPTIONS.

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Introduction: Lunar mare eruptions had individual flow volumes up to the order 10^3 km^3 [1], and so would have exsolved large quantities of volatiles. However, the current literature disagrees on the composition of the released gases. We examine these disagreements to illuminate the range in C-O-H-S-Cl-F lost from the magmas that formed the mare. We investigate the volatility of the traditional volatile elements within the melt, and assess outputs of speciation studies to estimate the gaseous species released during mare volcanism.

Motivation: Extensive mare outgassing could have created a transient lunar atmosphere up to 1 kPa around 3.5 Ga [2]. However, such a view is controversial [3]. The atmosphere could also have been a source for volatiles found in the permanently shadowed regions at the lunar poles. Atmospheric modeling demonstrates that the longevity of this atmosphere depends on its composition [4], which motivates our examination of the quantity and speciation of the lunar volcanic volatiles as input data to general circulation models (GCMs). Future work will use these results for lunar GCM simulations to improve our understanding of lunar atmospheric longevity. The results could also help future modelers of lunar eruption dynamics and geological products.

Volatile composition of samples: A recent review of lunar volcanic literature [5] amalgamates information about the abundance and isotopic composition of volatile elements and isotopes in lunar samples to provide insight into the distribution of these volatiles between different lunar geochemical reservoirs. However, this work did not aim to explicitly review the quantities of volatiles outgassed from mare melts.

Volatility: The tendency of each volatile element within a lunar magma to enter the gas phase has previously been estimated using: (i) comparison of melt inclusions with glass beads [6,7]; (ii) diffusion profile modeling [8]; and (iii) analog degassing experiments [9]. Results are summarized in Table 1.

Table 1: Estimates of each volatile element lost from lunar magma as a percentage of the pre-eruptive composition. For comparison, diffusion coefficients would predict H>>F>Cl>>S.

Ref.	Target	H (%)	S (%)	Cl (%)	F (%)
[6]	High-Ti Bead	99	38	96	69
[7]	High-Ti Bead	–	63	–	–
[8]	Low-Ti Bead	98	19	57	45
[9]	Synthetic	99	93	87	61

The range of absolute percentages for each element is not important, as it simply reflects the overall degassing of the sample. The significance of the data in Table 1 is instead that it captures the relative propensity of each component to degas. Our preferred volatility ordering is H >> Cl > F >> S, as this matches what is observed in samples [6,7,8]. Although it is not included in these studies, carbon is likely to be more volatile than hydrogen.

Gas speciation indicators: Hydrogen, sulfur and chlorine isotopes have been measured in a variety of lunar samples. Hydrogen isotopes are thought to show evidence for H$_2$ degassing because apatites with a lower OH concentration have a greater δD, consistent with the loss of the lighter isotope to the gas (e.g. [10]). Hydrogen loss has also been shown in glass beads [8]. Sulfur isotopes in glass beads [11], show depleted δ^{34}S with decreasing sulfur content, though this is not seen mare basalts [12]. Isotope systematics, however, cannot determine the relative proportions of H$_2$S, COS and S$_2$ that degassed to deplete the residual bead. δ^{37}Cl values for lunar samples are variable and extend to heavy values, which suggests Cl was possibly degassed as HCl or XCl, where X is a volatile metal [12].

Current mare volcanic gas compositions: There are a number of studies that examine the speciation of gases from lunar eruptions. The majority of these are based on lunar glass bead volatile compositions [13,14,15,16], though one is an explicit attempt at mare compositions [2]. The studies have a large range of compositional output, summarized in Table 2.

Table 2: Ranges of estimates for the volatile species emitted by lunar eruptions, as reported in literature, given in µg of volatile per g of basalt [2,13,14,15,16].

Volatiles	H_2O	H_2	CO	CO_2	COS
Volatile content (µg/g)	0 to 923	0.007 to 88	12 to 1395	0 to 328	0 to 142
Volatiles	S_2	H_2S	SO_2	HF	HCl
Volatile content (µg/g)	0 to 2645	0 to 794	0 to 234	3 to 101	0 to 163

Table 3 expands upon Table 2 and presents the ranges of gas compositions from a number of references.

Table 3: Relative proportions of volatiles estimated to have been emitted by lunar eruptions, given both as an overall molar percentage of the gas (top half of table) and relative to hydrogen mole abundance (bottom half of table).

Ref.	H (mol%)	C (mol%)	O (mol%)	S (mol%)	F (mol%)	Cl (mol%)
[16]	35	24	37	3	0.6	0.006
[14]	62	0.3	33	4	1.0	0.02
[14]	39	18	38	4	0.9	1.5
[15]	31.83	15.91	15.45	34.65	1.98	0.17
[15]	29.95	14.98	20.44	32.61	1.86	0.16
[2]	1.8	25	25	48	–	–
[2]	39	23	23	14	–	–
[13]	81	4	15	–	–	–
Ref.		**C/H**	**O/H**	**S/H**	**F/H**	**Cl/H**
[16]		0.69	1.08	0.09	0.016	0.0002
[14]		0.004	0.52	0.06	0.016	0.0003
[14]		0.45	0.97	0.11	0.02	0.0005
[15]		0.50	0.49	1.09	0.06	0.005
[15]		0.50	0.68	1.09	0.06	0.005
[2]		13.81	14.30	27.15	–	–
[2]		0.60	0.59	0.37	–	–
[13]		0.04	0.19	–	–	–

Some of the input gas proportions, like those involving carbon contents, are poorly constrained by lunar sample measurements to date [14]. This explains the large ranges of carbon species (Tables 2 & 3). Similarly, reported oxygen contents have a large range between 15% and 38% of the total moles of volatiles. This implies radically different oxygen fugacities. The difference arises as some models do not impose an oxygen fugacity of between IW and IW-2 when assembling their summaries [2,14,15,16]. The mole percentage of sulfur also varies dramatically between the summaries, with a range from 3% to 48% of the total moles [15,16]. Usage of sulfur to hydrogen ratios might be expected to reduce anomalies arising from uncertainties in carbon and oxygen content. The references, however, still show a large range from 0.06 to 27, even though lunar sample measurements suggest tighter bounds could be imposed [5].

Summary: Current literature on the composition of gases produced by lunar mare and pyroclastic bead forming eruptions show a large range of values. While some of this range is due to real uncertainty in the samples, such as carbon content, other parts have scope for refinement. Without a process to narrow uncertainties and converge on improved bounds for lunar gas compositions future research relying on these results will be handicapped by the uncertainties.

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