Physical adsorption of water vapor plays a much more significant role in eruptive plume energetics on Mars than on Earth. The total surface area in martian plumes is likely comparable to terrestrial ash, while the erupting magma and ambient atmosphere are drier. Plumes cool rapidly during ascent, and a limited population of H$_2$O molecules find adsorption sites to be increasingly stable. Release of latent heat of condensation and the onset of moist convection are diminished, delayed, or even prevented by adsorptive interaction.

We have developed a 5-component numerical model of the behavior of water in eruptive plumes under Mars-like conditions. We have used the model to study the fate of both juvenile and ambient atmospheric water in the eruption column. Here we investigate the adsorptive interaction of water and silicates as they effect plume dynamics and the partitioning and distribution of H$_2$O to the martian environment.

Our focus is on the role of adsorption in scavenging H$_2$O from the ascending eruption column, and the possibility that adsorptive scavenging depresses the vapor pressure in the column below the level considered in most eruptive models.

There has been an increasing recognition of likely airfall and pyroclastic deposits from explosive volcanism, both on ancient highland volcanoes and in the Tharsis complex [1,2,3,4,5,6]. Further, the nature of martian volcanism appears to be increasingly explosive in older terrains [7], where a number of explosive or multi-genetic volcanoes show evidence of channeling on their flanks. For example, Noachian channels in the Thaumasia and Coprates region tend to originate on volcanoes, or close to rifts, both of which could provide a supply of warm H$_2$O [8].

A number of sites have exhibit evidence of airfall deposits, some of them seemingly volatile rich. The Medusae Fossae Formation (MFF) is one example of a potential volcanic airfall deposit. Many hypotheses for the formation of the unit have been proposed. Sakimoto et al., [9] however find that the members of the MFF are not simple, planar strata, but are consistent with eolian or volcanic deposits superposed on top of existing topography.

Grizzaffi and Schultz [10] suggested that the interior plains of the Isidis impact basin reflect the deposition and subsequent removal of a thick layer of material within the basin. They suggested that the deposits contained a significant volatile fraction based on comparison to terrestrial analogs. They argued that ablation of stagnant debris-laden ice cover produces landforms on Earth similar to those observed in Isidis.

In addition to further documentation of unconformable, volatile-rich deposits northwest of Isidis, Grant and Schultz [11] mapped similar deposits in the Electris region of Mars. Electris also displays unconformable deposits with thick, poorly-defined layering on the order of tens to hundreds of meters. The deposits had locally high volatile content, based on the observation that relatively young valley networks that dissect portions of the deposit are entirely confined within it, and hence an intra-deposit source of water is inferred.

Microphysical interactions determine how water behaves in the plume and, through release of latent heat, effect plume energetics and sedimentation [12]. The surface properties of ash are altered by condensation, which increases agglomeration and speeds precipitation. Although other workers have investigated the interaction of H$_2$O and silicates in rising plumes, both on Earth and Mars [12,13,14], they have not considered the possible interaction of H$_2$O and silicates via adsorption; no vapor is removed from the plume until saturation is reached.

Our model is based on Glaze and Baloga [15]. We have expanded their model by allowing H$_2$O to exist as vapor, unfrozen water (adsorbate or bulk liquid), and ice. We use the scheme shown in Fig. 1. H$_2$O partitions between physical adsorption and the vapor phase. If liquid is stable, the vapor pressure is set, and all remaining H$_2$O is in the liquid phase. If ice is present, the vapor and unfrozen phases are set by temperature and the ice vapor pressure. Latent heat is released in the direction indicated by the arrows in the inset.
Figure 1 to determine the distribution of \( H_2O \) among phases. Unfrozen water exists in all fields. If the plume is in the vapor field, the total \( H_2O \) is partitioned between the adsorbed and vapor phases such that the adsorption isotherm is satisfied. Because we do not know the adsorptive response of primary martian ash, we assume here the basalt adsorption isotherm reported by Fanale and Cannon [16].

\[
\rho_a = \frac{\gamma P^{0.51}}{\exp(\delta / T)}
\]

where \( \gamma = 2.09 \times 10^{-12} \) kg \( H_2O \) Pa\(^{-1}\) m\(^2\) and \( \delta = -2679.8 \) K.

If the plume element is in the unfrozen phase domain, all remaining vapor is assumed to condense to liquid, and the presence of liquid sets the vapor pressure in the plume element. When the plume reaches the freezing point, most of the remaining water is frozen, although a small amount of unfrozen water always remains, in equilibrium with the temperature and vapor pressure over ice.

The plume model itself conserves silicate mass, \( H_2O \) mass, \( CO_2 \) mass, momentum and energy throughout the convective rise height. It assumes that ambient atmosphere is entrained at a rate proportional to the rise velocity \( (u) \) of the plume.

The background atmosphere into which the eruptions occur is a significant control on the evolution of the plume [15]. In the model runs explored here, we will assume that Noachian conditions, and a total atmospheric pressure of 8x10\(^6\) Pa (800 mbar). We assume a plausible thermal profile that is valid up to at least 10 km (-4.78 K/km) based on a radiative-convective model [17] (the thermal gradient near the surface is independent of pressure, although the surface temperature is not).

The size frequency distribution of the plume material is specified by the user. We assume that the size frequency distribution of the particles is log-normal. Therefore, in practice, the user specifies the mean and standard deviation of the population.

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There are no measurements of the size frequency distribution of silicates in ascending Plinian eruption plumes.

The surface area of martian ash, as produced, is unknown. It is certainly variable among volcanoes on Earth, and between eruptions, even eruptive phases of the same volcano. Therefore, no prescription can be made for this key variable. It will be explored numerically.

One effect that is certainly understood is that the relative importance of internal surface area (cracks, irregularities, vesicles, etc.) becomes greater for smaller particles. The largest particles (cm-scale) have surface areas not much greater than would be expected from their geometric dimensions. Smaller particles however have significantly greater surface area, as measured in standard surface area test such as the BET test. We explore the effects of different size-frequency distributions and specific-surface area v. grain size relationships. One example is shown in Figure 2, which will be the nominal case for this study.

The adsorptive calculation partitions the total amount of water in each element, which represents the erupted+entrained water, according to Eq. 1, across the surface area available in the log-normal distribution specified by the user (e.g. Fig. 2).

The sensitivity of adsorptive scavenging in the ascending cloud to particle size frequency distribution can be explored with this adsorptive subroutine. We define a parcel of silicates and \( H_2O \) and allow that parcel to cool, monitoring the total \( H_2O \) remaining in the vapor phase. In this case, we have defined 10\(^7\) kg of silicates in the test volume, with a log-normal size-frequency distribution, a mean grain size of 10\(^{-5}\) m, and a minimum area of 10\(^{-6}\) m\(^2\) per particle. This is based on observations of terrestrial ash particles that reveal enormous internal surface area. We assume 10\(^5\) kg of \( H_2O \) (\( \approx \)1 wt%). The results of this study show significant dependence of the \( H_2O \) sequestered in the adsorbed phase. In Figure 3, we show the effects of varying the standard deviation (\( \sigma \)) of the log-normal size frequency
distribution from 0.2 to 0.4. During cooling of a parcel, a sharply-peaked ($\sigma = 0.2$) distribution will adsorb considerably more water than a broad ($\sigma = 0.4$) distribution. For the surface area distribution and adsorption isotherm assumed here, approximately 80% of the total water is adsorbed by a $\sigma=0.2$ distribution in cooling to the liquid condensation temperature, and only about 1% by a $\sigma = 0.4$ distribution. This indicates that the partitioning of H$_2$O is a sensitive function of the total silicate area in ascending plume. Latent heat of adsorption would be released gradually in the $\sigma = 0.2$ plume, with only 20% of the original H$_2$O available for rapid condensation to liquid, the process that initiates moist convection in ascending plumes. Virtually all H$_2$O remains in the vapor phase in the $\sigma = 0.4$ plume.

The plume model is initialized by specifying the initial velocity of the plume at the volcano throat, the radius of the plume, the initial volatile content (assumed to be H$_2$O) and the temperature. We assume that the volcanic gases are not overpressured at the base (i.e. the plume internal pressure is identical to atmospheric ambient), and assume that the silicate particles have a density of 2600 kg m$^{-3}$. This assumption may be inaccurate if the silicate material traps significant gas.

These assumptions are adequate to calculate the mass eruption rate of the individual plume components, silicate and H$_2$O, as well as the bulk plume density. The initial phase distribution of the H$_2$O is calculated via the phase partitioning calculation described above.

For comparison, we refer to a standard plume, which we specify as $R_0 = 10$m; $V_0 = 200$ m s$^{-1}$; $T_0 = 525$ K. The rise of a 1 wt % H$_2$O ash plume is integrated from the ground upwards via a Runge-Kutta technique.

The behavior of the nominal plume under Noachian conditions is similar to that predicted by other workers (Fig. 4). The plume ascends to approximately 14.5 km. The plume is carried past its neutral buoyancy height (NBH) by momentum. The model assumptions begins to break down near the top of the plume, as the vertical velocity of the plume becomes small. Therefore, precise prediction of the umbrella region of the column is not included in this model.

We next examine the role of varying grain size. The ambient atmosphere is assumed to be dry in this calculation. The standard deviation of the size frequency distribution of the silicate materials is varied to establish the limits of qualitatively similar behavior.

An interesting result is shown in Figure 5. We plot, in blue, the path followed by the vapor pressure curve for two different size-frequency distributions, as they move from high temperature and pressure (upper right), to lower T and P (lower left). For both distributions, the mean grain size is 10 $\mu$m. We vary the standard deviation of the log-normal size frequency distribution from $\sigma = 0.3$ (sharply-peaked distribution) to $\sigma = 0.4$ (somewhat more broadly-peaked distribution).

When the standard deviation of the size frequency distribution is 0.4, the initial conditions ($T_0 = 525$ K, $r_0 = 10$m) force the plume into the superheated liquid phase, even at temperatures well above 373K. The vapor-pressure history follows exactly...
the vapor pressure curve (dashed blue line). However, if $\sigma = 0.3$, then adsorptive equilibration depresses the vapor pressure in the plume, preventing condensation to liquid in the ascending plume, and inhibiting the latent heat release that initiates moist convection. The vapor pressure remains below the saturation pressure throughout plume ascent.

Selection of plausible values for the variables of choice indicates that Martian volcanoes may be near the boundary between two qualitatively different behaviors. The degree of water in the magma probably won't vary by more than a factor of 2, but doubling the magma H$_2$O content to 2 wt % saturates available silicate surface area, and a $\sigma$=0.3 plume condenses liquid just as a $\sigma$ = 0.4 plume.

Entrainment of ambient atmosphere with H$_2$O will also tend to increase adsorptive coverage, and lead to condensation of liquid-phase H$_2$O. However, even in the terrestrial tropics, plume ascent can do no more than triple the initial H$_2$O content [14]. Therefore, a cold-dry Martian atmosphere may not hold enough H$_2$O to saturate in an ascending plume with high surface area. Under warmer, wetter conditions, adsorptive scavenging is less likely to prevent condensation, perhaps leading to enhanced agglomeration and sedimentation of volatile-rich deposits near the source.

References:

There are additional uncertainties in the model result presented here. For example, simple physical adsorption is unlikely to be the only interaction between H$_2$O vapor and the ascending ash. Direct chemical interaction will irreversibly remove some H$_2$O from the plume, producing alteration of the ash. The adsorptive behavior of hot ash particles is unknown, and the adsorption isotherm used here is extrapolated outside the domain in which it is experimentally verified.

The actual size frequency distribution of the silicate material as it is erupted is unknown, as is the specific surface area of the ash particles. The behavior of the plume is extraordinarily sensitive to these variables, since the distribution of available H$_2$O on the available surface area controls latent heat release and plume energetics.

Fig. 5 More surface area per unit mass in the silicate component of the plume adsorbs more water. In this simulation, adsorption prevents the plume from ever entering the liquid H$_2$O field when $\sigma$ is reduced from 0.4 (dashed blue line following phase boundary) to 0.3 (solid blue line).