Resolving the Water Cycle on a Salty Mars: Planetary Science and Astrobiology Exploration Strategies for the Next Decade

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<https://tinyurl.com/SaltyMarsSupport>

1 Executive Summary

Characterizing the dynamics of the present-day Martian water cycle is paramount to understanding climatic processes, water ice stability, the potential for in-situ resource utilization, and present-day habitability. The wealth of data now available from orbiters and in situ measurements strongly suggest the regolith is an important component of the water cycle. Indeed, the in situ and orbital detection of hygroscopic salts further increases the regolith's role because salts lead to temperature- and humidity-dependent water vapor sinks and sources in the shallow subsurface that compete for water vapor on diurnal and seasonal timescales. While extensive laboratory studies on these processes have been conducted, significant knowledge gaps remain including (1) fundamental thermodynamic parameters, e.g., enthalpies of hydration and liquefaction, and (2) kinetics of phase transition. In particular, there is ambiguity on whether liquid formation at the near-surface is kinetically inhibited and whether liquescence can compete against other water vapor sinks. Investment in experiments that replicate surface conditions, particularly the relevant combination of temperature and relative humidity, are needed to resolve these knowledge gaps. Such experiments can elucidate the potential to form brines on present-day Mars, which has important implications for astrobiology and planetary protection policies. Furthermore, improved near-surface environmental measurements are needed. The environmental payloads of past, ongoing, and scheduled lander Mars missions were not designed to investigate atmosphere-regolith water vapor exchange processes, and thus important constraints are missing to resolve the near-surface water cycle. Environmental instrumentation on future Mars landers that make high fidelity, simultaneous, in situ measurements (e.g., surface, shallow subsurface, and at height) of the near-surface absolute water vapor content, temperature, and wind speeds are strongly recommended.

2 Introduction

The Martian regolith can exchange water vapor with the atmosphere as a result of adsorption/desorption (e.g., Zent et al., 1993; Chevrier et al., 2008; Rivera-Valentín & Chevrier, 2015; Savijärvi et al., 2020), solid-state salt hydration (Vaniman et al., 2004; Gough et al., 2020), brine formation (e.g., Martínez & Renno, 2013; Rivera-Valentín et al., 2018; 2020a), and frost formation (e.g., Jones et al., 1979; Smith et al., 2009; Martínez et al., 2016). These processes are dependent on temperature and humidity, which on Mars can undergo significant diurnal and seasonal variations. As water vapor diffuses in a porous regolith, low energy collisions with grains lead to water molecules sticking to them (i.e., adsorption). Adsorption is facilitated at low temperatures, while at high temperatures desorption is favored. Solid-state salt hydration occurs when water is incorporated into a salt's crystal structure. This typically requires high relative humidity and low temperatures; dehydration occurs at low humidity and high temperatures. Regardless of liquescence process, brine formation requires the temperature to be above a salt's eutectic temperature. Deliquescence further requires that the relative humidity with respect to liquid be above a temperature-dependent threshold called the deliquescence relative humidity. Recrystallization occurs when the brine freezes or the efflorescence relative humidity is reached. Given their affinities to act as water vapor sinks at low temperatures and high humidity, these salt-facilitated processes will be simultaneously competing for water. Indeed, there remain major unknowns regarding how these processes interact and simultaneously compete for water vapor on Mars, leading to a priority science question, **"What are the thermodynamics of salt-facilitated water vapor sinks and sources on Mars?"**

An important constraint on how atmosphere-regolith water vapor exchange processes interact is their kinetics (i.e., the timescale for phase transitions). For example, while the conditions required for changes in hydration state and brine formation occur on Mars, it is unknown whether the processes are rapid enough to allow for phase transitions (e.g., deliquescence, adsorption) at diurnal time scales. Re-calibrated in situ measurements by the Phoenix mission (Fischer et al., 2019) and ongoing measurements by the Mars Science Laboratory (MSL) (Harri et al., 2014) show that relative humidity > 50% is only achieved at temperatures < 210 K (see Figure 1). Because water vapor exchange processes primarily act as sinks at low temperatures and high humidity, kinetics become increasingly important on Mars as transition timescales are significantly slowed under the expected Martian conditions. Thus, a priority science question in the next decade is, “**What are the kinetics of phase transitions?**”

Because the environmental payloads of past, ongoing, and scheduled lander Mars missions were not designed to investigate atmosphere-regolith exchange processes, constraints are lacking to better resolve the near-surface water cycle. Understanding exchange processes requires high fidelity measurement of very small fluxes of water vapor out of the surface and through the atmosphere, requiring simultaneous and very high frequency (10s of Hz) measurement of absolute water vapor and three-dimensional wind speeds. This cannot be achieved using current flight hardware. Thus, the present-day role of a salty Martian regolith on the diurnal and seasonal water cycle remains critically unknown. Fundamentally, a priority science question for the next decade is, “**How does water vapor vary at the Martian near-surface on diurnal and seasonal timescales?**”

Resolving these priority questions and identifying the regolith processes interacting with atmospheric water vapor addresses Mars Exploration Program Analysis Group Goal I “Determine if Mars ever supported, or still supports life” and Goal II “Understand the processes and history of climate on Mars”¹. Atmosphere-regolith interactions control part of the water cycle, and so are an important aspect of the present-day Martian climate (i.e., Goal II). Furthermore, a potential component of the water cycle is brine formation. Because brines on Mars may provide suitable conditions for life as we know it, or even extant Martian life (Carrier et al., 2020), understanding when it is occurring, its duration, and resultant physicochemical properties is needed to constrain the dynamic habitability of the Martian subsurface (i.e., Goal I). Thus, the studies encouraged in this white paper also further an identified goal in the National Academies Study² on astrobiology science strategy. The work here also supports the white paper by Diniega et al. (2020) on emphasizing studying atmosphere-regolith interactions in the next decade. Here, we particularly advocate for investment in experimental research, mission science, and numerical modeling that addresses in the next decade the identified knowledge gaps.

3 Strategies for Future Experiments

Although there have been several laboratory studies investigating atmosphere-regolith exchange processes (e.g., Zent & Quinn, 1997; Chevrier et al., 2008; Gough et al., 2011), the majority have not fully replicated current surface conditions on Mars (see Figure 1), specifically the combination of both temperature and relative humidity. This is due to the experimental obstacles to achieving such Mars-like conditions. Thus, a complete understanding of these

¹ https://mepag.jpl.nasa.gov/reports/MEPAGGoals_2020_MainText_Final.pdf

² <https://www.nap.edu/resource/25252/RH-astrobio.pdf>

processes under Mars-relevant conditions is lacking. In order to resolve the top priority science questions posed here, we recommend investment in facility improvements, as well as technology development that enables appropriate replication of Martian conditions in the lab. Furthermore, in the next decade it is recommended that research programs be supported that answer:

- How do the various water vapor sinks interact with each other and compete for water under realistic conditions (e.g., appropriate temperature, humidity, regolith analogs, diurnal cycles, and in the presence of ice tables)?
- What are the kinetics of phase transitions over a broad range of Mars-relevant conditions (e.g., temperature, humidity, pressure, and regolith physical properties)?
- Which phase transitions occur under Mars-like diurnal conditions?

Uncertainties remain with respect to simple systems (i.e., pure soils, pure and binary salt systems), as well as fundamental thermodynamic parameters. For example, the Gibbs free energies for each relevant salt, as well as enthalpies of hydration and liquefaction, at temperatures relevant to Mars are not known. Further, studies show perchlorate salt deliquescence may (Primm et al., 2017) or may not (Fischer et al., 2014) occur under given Martian conditions depending on the sample size. Thus, we recommend investigating simple systems on small scales before building up to complex, realistic, multi-component systems.

Moreover, in-situ measurements have now shown that conditions at the Martian near-surface can change rapidly (Harri et al., 2014; Fischer et al., 2019). Thus, it is necessary to study the kinetics of water uptake and loss by salts and soils. For example, the efflorescence of a brine is often kinetically hindered; thermodynamic calculations cannot predict this metastability. Experiments should probe the rates of deliquescence/efflorescence and hydration/dehydration as a function of humidity (absolute and relative) and temperature. Furthermore, experiments should also be performed on the timescale of a Martian sol and under realistic diurnal cycles. Indeed, it may be important to perform consecutive cycles to ensure continuity in the reactant-product cycle. The objective is to determine if the diurnal cycle can lead to accumulation of metastable phases, which would otherwise be unstable.

Once pure salts are well understood, studies are needed on salt/regolith, as well as salt/regolith/ice systems that have realistic salt content (~0.5% by mass). Experiments should be performed that compare the water uptake by pure regolith (0% salt) vs slightly salty regolith (0.5% salt), to elucidate the relative importance of intermixed hygroscopic salts. Additionally,

salts known to either only hydrate or only deliquesce should be introduced; this would probe the relative roles of hydration, adsorption, and deliquescence in the Martian regolith. Reverse pathways (e.g., dehydration) should also be investigated to detect any hysteresis in transitions.

Although surface frost was observed at the Viking 2 (Jones et al., 1979) and Phoenix landing sites (Smith et al., 2009), it has not been observed at MSL where the measured environmental conditions favor its formation (Martínez et al., 2016). Thus, experiments are needed to investigate the properties (e.g., porosity and thermal inertia) of regolith analogs on which frost preferentially forms, the environmental conditions needed, and the effect of frost on surface salts, in order to improve understanding of this aspect of surface-atmosphere exchange.

Rover/lander observations of near-surface conditions on Mars should be used as parameters for laboratory experiments. Given the limited in-situ environmental data currently available, though, experiments can also be informed by general circulation models (e.g., MarsWRF) and subsurface models (e.g., Rivera-Valentín et al., 2018). Such numerical models are critical to performing realistic, large scale experiments that probe the water uptake/release of a macro-scale regolith column with a temperature gradient. Therefore, relying on both the data available and model results would allow experiments to be more broadly applicable across Mars.

4 Strategies for Mission Science

To date, environmental payloads to Mars have not been designed to directly investigate atmosphere-regolith exchange processes, nor to measure the vertical distribution of water vapor

Figure 2: Inferred water vapor pressure on sol 773 (black dots), with the 1- σ error margin (blue lines). The cyan space then indicates the potential values within error.

(Martínez et al., 2016, Spiga et al., 2018; Rodríguez-Manfredi et al., 2020). MSL's Rover Environmental Monitoring Station measured relative humidity with respect to ice at a height of 1.6 m (Harri et al., 2014). The Phoenix lander's Thermal and Electrical Conductivity Probe (TECP) measured the same at varying heights, including in the regolith a few centimeters deep (Fischer et al., 2019). As can be seen from the isobars in Figure 1, though, under Martian conditions a small change in temperature can result in a large change in relative humidity while water vapor remains unchanged. Additionally, translating such measurements to absolute water vapor to study the near-surface water cycle results in significant

uncertainty. This is due to propagating two sources of error (uncertainty in temperature and relative humidity). For example, in Figure 2 we plot the inferred water vapor pressure from MSL measurements on what may have been the most humid sol. As can be seen, daytime water vapor pressure is ill-constrained. Thus, critical information is missing to understand the role of a salty Martian regolith on the diurnal water cycle, as well as its impact on the vertical distribution of water vapor from the surface into the first few kilometers (Tamppari & Lemmon, 2020). Understanding water exchange processes requires high fidelity measurements of small fluxes of water vapor out of the surface and through the atmosphere, requiring simultaneous and very high frequency (10s of Hz) measurement of absolute water vapor content and three-dimensional wind speeds, as well as simultaneous ground and air temperature measurements.

Furthermore, subsurface measurements are required to more accurately understand how the regolith “breathes”. Geophysical tools have the ability to remotely monitor the water vapor as the regolith exchanges it with the atmosphere. For example, brine formation results in a dramatic increase in the dielectric permittivity and electrical conductivity of the regolith (Stillman et al., 2011; Heinz et al., 2016; Primm et al., 2020). Such a measurement has been made by the Phoenix TECP. This instrument was able to measure the conductivity at 1 kHz and permittivity at ~6 MHz between two of its four needles that were 15 mm long and separated by 7 mm. TECP registered increases in permittivity that corresponded with increasing relative humidity at night, likely due to the adsorption of water (Stillman et al., 2011).

A more advanced method called dielectric spectroscopy (DS; a.k.a. impedance spectroscopy) could be used to make even more precise measurements and at shallow depth. DS is a diffusive surficial electromagnetic method where an alternating current is injected into the subsurface by capacitively-coupled electrodes. Two other electrodes then measure the resultant voltage and phase difference between the current of the other two electrodes. The frequency of the current is then swept over a large bandwidth (10 Hz – 100 kHz) to build up a spectrum of the subsurface resistivity. DS can generally sense into the subsurface 20% of the array’s longest length. This system could monitor for changes in the conductivity and permittivity associated with phase changes of a brine system. This monitoring, combined with near-surface water vapor and temperature measurements, can allow for in situ studies of water vapor interaction with shallow subsurface salts at the required high-temporal resolution.

Therefore, environmental instrumentation for in-situ measurements on future Mars landers are strongly recommended that make the following measurements:

- High fidelity measurements of the near-surface and atmospheric *absolute water vapor content*, temperature, and wind speeds in order to constrain the diurnal water vapor exchange between the atmosphere and regolith.
- High frequency measurements of the regolith’s water content in order to constrain the time periods when the regolith is acting as a water vapor sink, particularly when brine formation is occurring. This could be facilitated by dielectric permittivity and electrical conductivity measurements of the regolith.

Near-surface environmental measurements along with those in the regolith can be correlated to improve our understanding of the Martian water cycle. Results from such modeling and experimental work can be used to inform observation strategies for future missions.

5 Strategies for Salt Identification

Measurements of the regolith’s salt content and composition are required to constrain water exchange processes. On Mars, salts have been identified both in situ and from orbit; however, uncertainty remains on the hydration state and composition (e.g., Gough et al., 2019). VNIR (visible to near-infrared) reflectance spectroscopy is one of the primary detection methods for minerals on Mars, and is optimum for detecting hydrated minerals from orbit because of the strong features in the spectrum due to structurally bound water in minerals. However, one drawback is that many hydrated salts have similar spectral features that make them difficult to distinguish, particularly at high hydration states (e.g., Hanley et al., 2015; Lynch et al., 2015). Increasing both spatial and spectral resolution will enable improved characterization of regions of interest, e.g., recurring slope lineae (RSL). CRISM’s spectral resolution is ~18 m, where a typical RSL is less than 1 m wide (Ojha et al., 2015). However, the higher the spatial resolution, the less

surface the camera can cover. Another possibility is extending orbital spectroscopic measurements into the mid-infrared (MIR), which would permit distinguishing between sulfates and oxychlorine salts (e.g., Hanley et al., 2015). Therefore, *in order to fully characterize various salts on the surface of Mars, both higher spatial and spectral resolution spectrometers are needed, as are instruments that can measure in the MIR wavelengths.*

For landed missions, there are a variety of in situ methods that can be used to detect salts. Raman spectroscopy, which is complementary to IR spectroscopy, can aid in understanding the mineralogy of the surface, and can distinguish salts that may not have unique NIR spectral features, or even have no/very small features in the NIR (e.g., anhydrous salts). Another technique, XRD, is considered definitive identification, but it still requires updated spectral databases, particularly the high hydrate phases existing at temperatures below 0°C, which requires special chambers for measurements. Indeed, there is still some fundamental laboratory characterization required. For example, though pure oxychlorine salts have been well characterized by VNIR (Hanley et al., 2014; 2015), there has been little-to-no experimental work conducted to understand the fundamental spectral characteristics of oxychlorine salts when mixed with other spectrally active minerals. This lack of knowledge makes it difficult to fully deconvolve oxychlorine spectra from other aqueous minerals (especially sulfates) and confirm unambiguous detections, let alone characterizations (Lynch et al, 2015).

Finally, electrochemical methods are also highly desirable to characterize the chemical composition of the soluble (and thus deliquescent) phases in the regolith. These methods can determine with high precision the ions present in the regolith. The caveat with these methods is that the salt composition has to be determined from thermodynamic modelling and the hydration state of the salts is unknown.

Thus, in the next decade investment in the following is needed:

- Continued and expanded laboratory development of spectral libraries for improved salt identification, particularly mixed salt samples.
- Improved spatial and spectral resolution of spectrometers, including MIR wavelengths, on orbital assets.

Improved salt identification can then be used to inform experimental set ups in replicating Mars-relevant regolith analogs, and to understand the water uptake of appropriate salts.

6 Strategies for Astrobiology

Resolving the Martian near-surface water cycle provides the necessary constraints to understand the potential to form brines on present-day Mars. Recent work showed that (meta)stable brines on present-day Mars may only form at temperatures below 225 K (Rivera-Valentín et al., 2020a). Although such liquids would not be considered suitable to known terrestrial organisms, which have not been observed to undergo cell division or metabolic activity below 255 K and 240 K, respectively (Rummel et al., 2014 and refs therein), extant Martian life cannot be ruled out (Carrier et al., 2020). In fact, these temperature limits may be instrumentation limits as they are based on measurements of metabolic activity and cell division, which could be slowed beyond currently measurable levels at extreme cold temperatures (Rummel et al., 2014 and refs therein). Furthermore, small-scale, local niches may exist in the Martian subsurface that facilitate out-of-equilibrium processes, which may allow for viable liquids. On Mars, though, deliquescence may not be favored as it is competing for water vapor against adsorption, solid-state salt hydration, and frost formation in a resource-

limited environment. Additionally, at low temperatures deliquescence may not be rapid enough to allow for brine formation at diurnal time-scales. Thus, answering the priority questions posed here would provide the insights needed to understand the potential to form brines on present-day Mars, an astrobiology goal for the exploration of the Martian surface and near-subsurface and a concern for planetary protection.

Experiments into bacterial growth have shown survival under brine eutectic conditions for some Mars-relevant salts (e.g., Al Soudi et al., 2017; Wilks et al., 2019). Given the current state of knowledge of the Martian near-surface environment, though, expanded work into bacterial growth under Mars-relevant conditions is needed. Thus, in the next decade investment in astrobiological studies is needed, particularly for studies that

- investigate the physicochemical properties (e.g., temperature, water activity, chaotropicity, ionic strength) of stable brines under Mars-relevant conditions, and
- explore the potential for terrestrial organisms to grow and survive in brines under Mars-relevant conditions (e.g., Figure 1).

Results from such astrobiology experiments, along with the laboratory studies posed in this white paper, direct measurements from landed and orbital assets, and constraints from numerical modeling can elucidate the present-day habitability of Mars and provide important information for planetary protection policies (e.g., Rummel et al., 2014).

7 Statement on Diversity, Equity, and Inclusion

Understanding the water cycle on a salty Mars and its implications requires drawing on different perspectives. Thus, it is critical that the community fosters an interdisciplinary, diverse, equitable, inclusive, and accessible environment. We strongly encourage the decadal survey to closely consider the state of the profession and issues of equity, diversity, inclusion, and accessibility. Background information on the demographics of the field and specific, actionable, and practical recommendations can be found in e.g., white papers Milazzo et al. (2020), Piatek et al. (2020), Rivera-Valentín et al. (2020b), and Rathbun et al. (2020).

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