



Distribution and habitability of (meta)stable brines on present-day Mars

Edgard G. Rivera-Valentín^{1,5}✉, Vincent F. Chevrier^{2,5}, Alejandro Soto³ and Germán Martínez^{1,4}

Special Regions on Mars are defined as environments able to host liquid water that simultaneously meets certain temperature and water activity requirements that allow known terrestrial organisms to replicate^{1,2} and therefore could be habitable. Such regions would be of concern for planetary protection policies owing to the potential for forward contamination (biological contamination from Earth). Pure liquid water is unstable on the Martian surface^{3,4} but brines may be present^{5,6}. Experimental work has shown that brines persist beyond their predicted stability region, leading to metastable liquids^{6–8}. Here we show that (meta)stable brines can form and persist from the equator to high latitudes on the surface of Mars for a few percent of the year for up to six consecutive hours, a broader range than previously thought^{9,10}. However, only the lowest eutectic solutions can form, leading to brines with temperatures of less than 225 K. Our results indicate that (meta)stable brines on the Martian surface and its shallow subsurface (a few centimetres deep) are not habitable because their water activities and temperatures fall outside the known tolerances for terrestrial life. Furthermore, (meta)stable brines do not meet the Special Region requirements, reducing the risk of forward contamination and easing threats related to the exploration of the Martian surface.

Here, using an experimentally validated thermodynamic framework for the (meta)stability of brines^{8,11–13} paired with results from the Mars Weather Research and Forecasting (MarsWRF) general circulation model (GCM)^{14,15}, we investigated when and where brines may form and persist for at least an hour on the surface of present-day Mars. Specifically, brine formation through deliquescence, the transition from a solid crystalline salt into an aqueous solution, as well as the stability of melt-induced brines against freezing, evaporation and boiling were studied. If these (meta)stable liquids surpassed temperature and water activity limits of $T > 250$ K and $a_w > 0.5$, respectively¹, or stricter limits of $T > 255$ K and $a_w > 0.6$, as set by a later study², their host environments were considered Special Regions. Because these limits are set by the known tolerances of life in extreme environments on Earth, such regions on Mars could be habitable to some terrestrial organisms.

First, we considered the stability of a brine regardless of formation mechanism or composition. To be stable against evaporation, the difference between the atmospheric water vapour pressure e and the water vapour pressure just above the brine e_b must be minimized, such that $e_b \approx e$. Because water activity is defined as $a_w = e_b/p_{\text{sat},l}$ where $p_{\text{sat},l}$ is the saturation vapour pressure above pure liquid water, then when the brine is stable against evaporation $a_w = e/p_{\text{sat},l}$ which is the relative humidity with respect to

liquid. Figure 1 shows the resulting temperatures and water activities of stable solutions over the possible Martian surface T and e . Above about 270 K, brines are not stable against evaporation. At these temperatures, the water activity required to ensure that $e_b \approx e$ is below the lowest water activity observed for even a metastable single-component brine¹². For $T < 230$ K, saturation with respect to water ice occurs (that is, $\text{RH}_{\text{ice}} \geq 100\%$); depending on the eutectic temperature T_E of the brine, ice in a metastable liquid is possible. As an example, the metastable region for calcium perchlorate brines, which have the lowest-known eutectic temperature ($T_E \approx 198$ K)¹⁶ for single-component solutions of Mars-relevant salts, is shown in Fig. 1. At intermediate temperatures (that is, $T_E < T < 270$ K), (meta)stable brines are possible. Indeed, at these temperatures $p_{\text{sat},l}$ is smaller than the low atmospheric pressures typical on Mars (for example, $p_{\text{sat},l}(230 \text{ K}) = 14$ Pa and $p_{\text{sat},l}(270 \text{ K}) = 484$ Pa) and so boiling is not favoured. This regime, in which brines are stable against boiling, evaporation and freezing, constrains the salts that can lead to stable liquids on Mars. From the possible T and e pairings, the highest water activity for a stable brine is 0.66; therefore, brines with a higher eutectic water activity than this value are not stable on present-day Mars (see Extended Data Fig. 2 for further details).

Of the Mars-relevant hygroscopic salts, magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$) and calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$) both have eutectic $a_w \leq 0.66$ (ref. 17). Here we considered brine formation through deliquescence of magnesium perchlorate with a eutectic temperature and water activity of $T_E = 206$ K and $a_w = 0.56$ (ref. 11), respectively, and of calcium perchlorate with eutectic values of $T_E = 198$ K and $a_w = 0.52$ (ref. 16), across the surface of Mars. In order for a salt to deliquesce, the temperature must be above the eutectic and the ambient relative humidity with respect to liquid (RH_{liq}) must be above the temperature-dependent deliquescence relative humidity (DRH). Although thermodynamically solutions should recrystallize once $\text{RH}_{\text{liq}} < \text{DRH}$, owing to a hysteresis effect, efflorescence occurs at a lower relative humidity^{6,12}, allowing for metastable liquids. For example, although calcium perchlorate requires high relative humidity to deliquesce, once in solution it can effloresce, depending on temperature, at $\text{RH}_{\text{liq}} \approx 1\%$ (ref. 12). Furthermore, experiments under Mars-like conditions have shown that solutions persist even after saturation with respect to water ice is reached^{8,12}, up to $\text{RH}_{\text{ice}} \approx 145\%$. In this case, if the local temperature is above the eutectic, a mixture of ice and metastable liquid is present. The phase diagram including both stable and metastable regions of calcium perchlorate is shown in Extended Data Fig. 3.

Using these experimental constraints on brine (meta)stability, in Fig. 2 we mapped the distribution of (meta)stable brines on

¹Lunar and Planetary Institute, Universities Space Research Association, Houston, TX, USA. ²Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, USA. ³Southwest Research Institute, Boulder, CO, USA. ⁴Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA. ⁵These authors contributed equally: Edgard G. Rivera-Valentín, Vincent F. Chevrier

✉e-mail: rivera-valentin@lpi.usra.edu

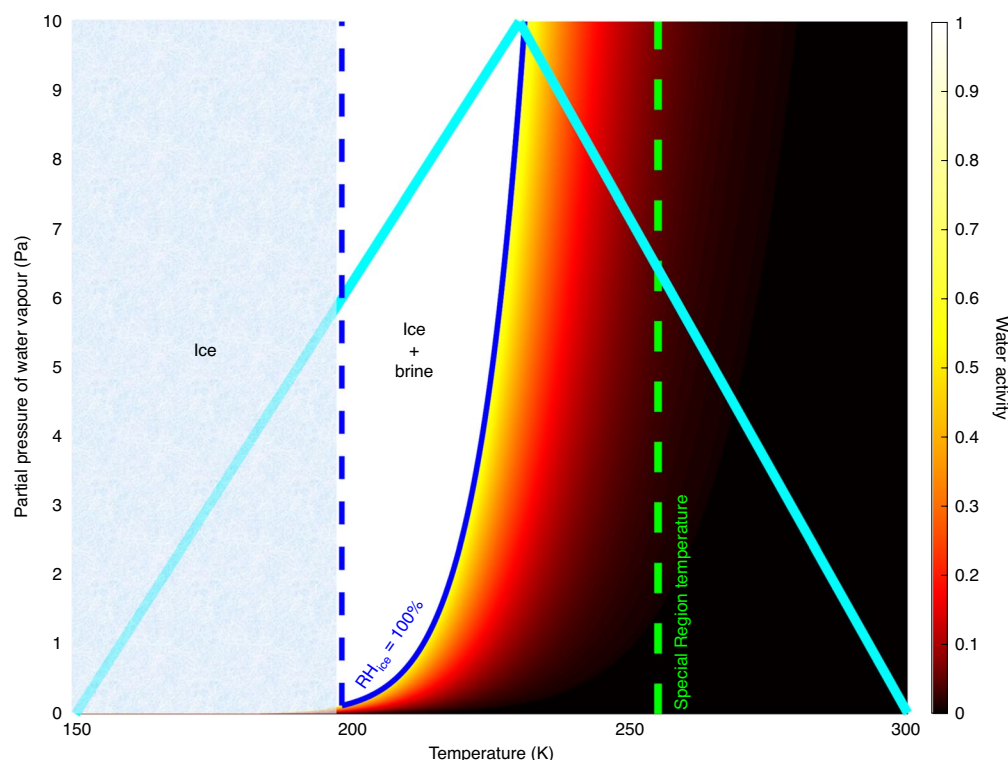


Fig. 1 | Water activity of stable brines over Mars-relevant temperatures and water vapour pressures. Over the range of possible global surface temperatures and water vapour pressures on Mars, the resulting water activity of an arbitrary stable solution is shown here in colour. The Mars-relevant pairings of surface temperature and water vapour are contained between the cyan lines (see Extended Data Fig. 1 for details). The solid blue line is where saturation with respect to ice is achieved (that is, where the relative humidity with respect to ice $RH_{ice} = 100\%$). However, depending on the eutectic temperature of the brine, a metastable liquid and ice solution may be present. Here we show the eutectic temperature of a calcium perchlorate brine (dashed blue line) as an example. Only ice will exist below the eutectic temperature of the brine. Additionally, the Special Region lower limit temperature² ($T = 255$ K) is indicated by the green dashed line.

the surface of Mars. Magnesium perchlorate brines are restricted to the northern hemisphere above 50°N where they may be (meta)stable for up to 0.2% of the year for at most eight hours per sol. Typically, though, these brines only persist for some 2 h per sol for about 0.04% of the year (that is, a total of around 6 h per year). Overall, such brines would be (meta)stable over 5% of the Martian surface around a solar longitude (L_s) of 160° . On the other hand, $\text{Ca}(\text{ClO}_4)_2$ brines can form and persist over some 40% of the Martian surface, including near the equator. These brines are most likely to occur at high northern latitudes, where they are (meta)stable for up to 2% of the year. Although $\text{Ca}(\text{ClO}_4)_2$ brines may persist for at most half a sol per sol, they may be liquid for at most six consecutive hours. Typically, these brines occur transiently (around 3 h per sol) for some 0.4% of the year during the summer. In the northern hemisphere, $\text{Ca}(\text{ClO}_4)_2$ brines form and persist around $L_s \approx 140^\circ$ and in the southern hemisphere around $L_s \approx 225^\circ$.

To constrain the habitability of the most favourable case, in Fig. 3a we mapped the maximum water activity attained by a calcium perchlorate brine formed through deliquescence with the corresponding brine temperature in Fig. 3b. The maximum brine a_w is reached when the solution is metastable with ice. The maximum water activity of such brines is $a_w \approx 0.8$ with a corresponding temperature of around 205 K. On the other hand, the maximum temperature in Fig. 3b of 210 K is associated with a water activity of 0.77. In Extended Data Fig. 4, we show the maximum brine temperature and associated water activity. These conditions are met just prior to efflorescence. Although a brine may reach 225 K, the associated a_w is only 0.24.

Furthermore, using updated and recalibrated in situ measurements by the Phoenix lander¹⁸ paired with a model of the subsurface environment¹⁹, we investigated brine formation in the presence of a shallow ice table 10 cm deep²⁰ and the resulting brine properties in the regolith above the ice. In Extended Data Fig. 5, we plot the conditions during which calcium perchlorate would deliquesce and a resulting brine would persist. Such liquids would have a maximum brine temperature of 217 K with a corresponding $a_w = 0.21$, while the maximum water activity is 0.80 with a corresponding temperature of $T = 206$ K. Such brines would persist longer than at the surface, lasting 5% of the Martian year at depths of 5 cm and up to 10% of the Martian year at 8 cm.

The kinetics of deliquescence may be too slow to form liquids under the low Martian temperatures²¹. Melting through salt–ice interactions, however, has been shown to occur within minutes of reaching the eutectic temperature⁷. Thus, melting may be the preferred liquescence process on present-day Mars, potentially by salts interacting with seasonal surface frost or with subsurface ice tables. The maximum water activity reached by brines formed through melting of surface frost is captured in Fig. 3 because such brines form when $RH_{ice} \geq 100\%$ and thus when surface conditions would be in the ice and liquid metastability region. For brines formed by salt contact with a shallow ice table, the main water vapour source is the ice table, such that $e = p_{\text{sat},i}(T)$, where $p_{\text{sat},i}$ is the saturation vapour pressure above water ice. These brines would then have at most a water activity of $a_w = p_{\text{sat},i}/p_{\text{sat},b}$; thus, for their water activity to surpass the Special Region requirement, $T > 190$ K or $T > 205$ K for a limit of $a_w = 0.5$ and $a_w = 0.55$ respectively^{1,2}. Shallow ice tables a few centimetres deep, however, predominantly exist poleward of

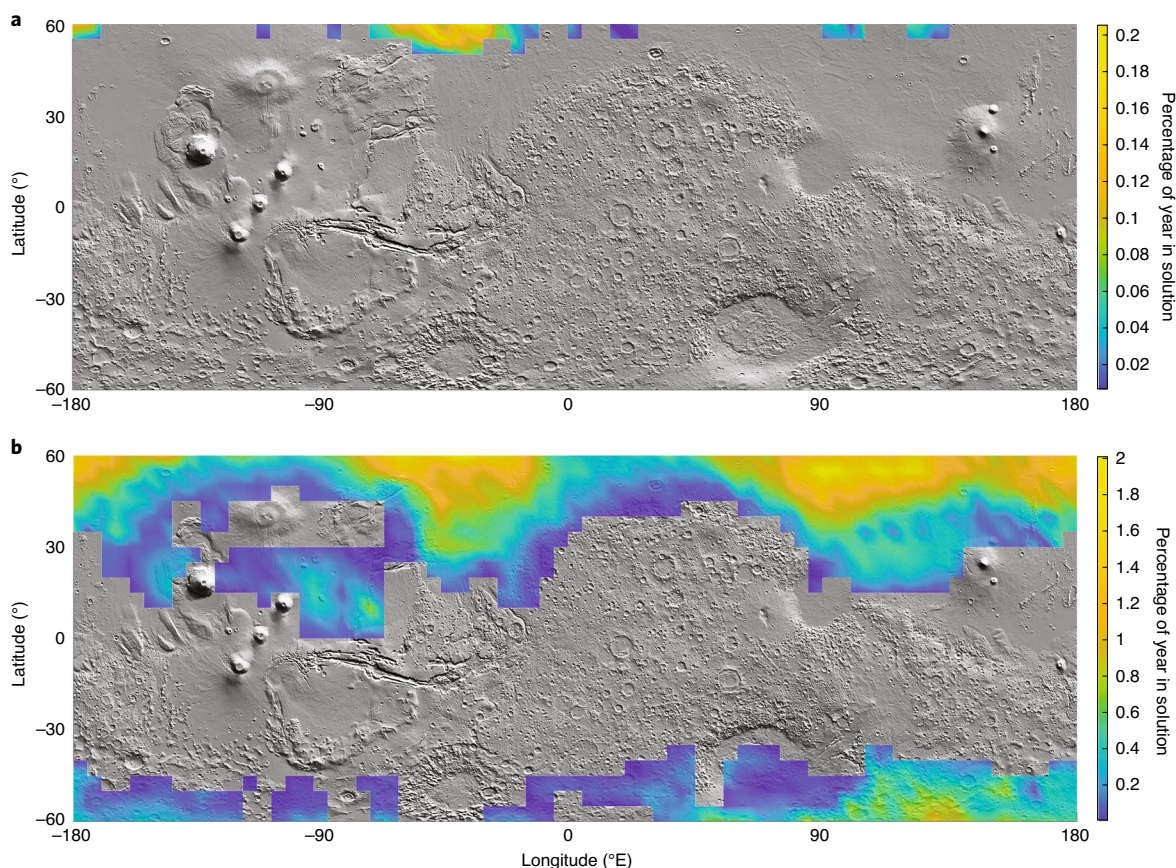


Fig. 2 | Distribution of (meta)stable brines on the Martian surface. a, b, The total number of hours, in terms of percentage of the Martian year (shown in colour), that a magnesium perchlorate (**a**) and calcium perchlorate (**b**) brine formed by deliquescence can exist on the Martian surface, as constrained by the MarsWRF predicted surface environment. Areas where such brines cannot form and persist are shown as the background, grey-scaled shaded relief map based on Mars Orbiter Laser Altimeter (MOLA) data. The latitude range is restricted to non-polar regions.

50° latitude on Mars^{20,22}, where the average annual surface temperatures are around 200 K. Additionally, the maximum diurnal temperature substantially decreases with depth, with typical diurnal skin depths of 5 cm (ref. ²²). Thus, although brines formed in the subsurface through salt-induced melting of the ice table may form and persist diurnally⁷, their habitability would be largely temperature-limited.

Indeed, at the Special Region limit a stable brine would require a local water vapour pressure of $e = 47$ Pa ($T = 250$ K, $a_w = 0.5$)¹ or $e = 88$ Pa ($T = 255$ K, $a_w = 0.6$)². This is much higher than is available at the Martian near-surface^{22,23}, where in situ measurements at contradistinct latitudes have peaked at $e \approx 1$ Pa (ref. ^{18,19}). Nevertheless, were such a brine to form, it would evaporate at some $20 \mu\text{m h}^{-1}$ and $50 \mu\text{m h}^{-1}$, respectively, and thus would persist for much less than an hour, even taking into account the total Martian atmospheric column abundance of water vapour^{22,23}.

Our work here has focused on pure phases, whereas most naturally occurring salt deposits on Mars are salt mixtures. In this case, depending on the composition, the resulting eutectic temperature of the brine will be affected. Indeed, multicomponent brines have systematically lower T_E and DRH values than do pure phases²⁴. Although such brines could amplify both the global distribution and duration of liquids on Mars, they would not increase their habitability because such liquids would be forming at colder temperatures and lower water activities. Another consideration is local-scale effects. The GCM employed here has a resolution of $5^\circ \times 5^\circ$ and so averages over smaller, local-scale effects (such as topography and terrain differences). Again, such effects would primarily affect the spatial and temporal distribution of brines.

Our results show that metastability expands the locations and duration of brines on Mars, beyond what was previously thought^{9,10} by including some equatorial regions. Various observations have indicated that brines may be at present forming on Mars (such as recurring slope lineae^{17,25,26}, and in situ environmental data^{13,19}), although the only direct observation of liquids has been on the Phoenix lander strut as droplets that formed under the spacecraft-induced warmed environment²⁷. Considering the distribution of active mass movement events on Mars, such as recurring slope lineae, calcium perchlorate brines, or brines with similar properties, may act as a trigger mechanism^{25,26} owing to their predicted broader distribution compared to magnesium perchlorate brines. However, should future experiments demonstrate that the timescale for deliquescence under Mars-relevant conditions is much longer than six hours, then another trigger mechanism for these mass movement events would be required.

Considering planetary protection, our results indicate that although high-water-activity solutions ($a_w \geq 0.6$) may be stable on present-day Mars, the corresponding brine temperature is systematically below 210 K, which is well below the Special Region temperature requirement and temperature limits for life²⁸. Although brines with temperatures up to 225 K may form, their $a_w < 0.25$, which is well below the Special Region water activity requirement and known water activity limits for life²⁹. Our work shows that stable or even metastable brines do not simultaneously attain the conditions required for their locations to be considered a Special Region. This is because of the hyperarid conditions of Mars, which require lower temperatures to reach high relative humidities and tolerable

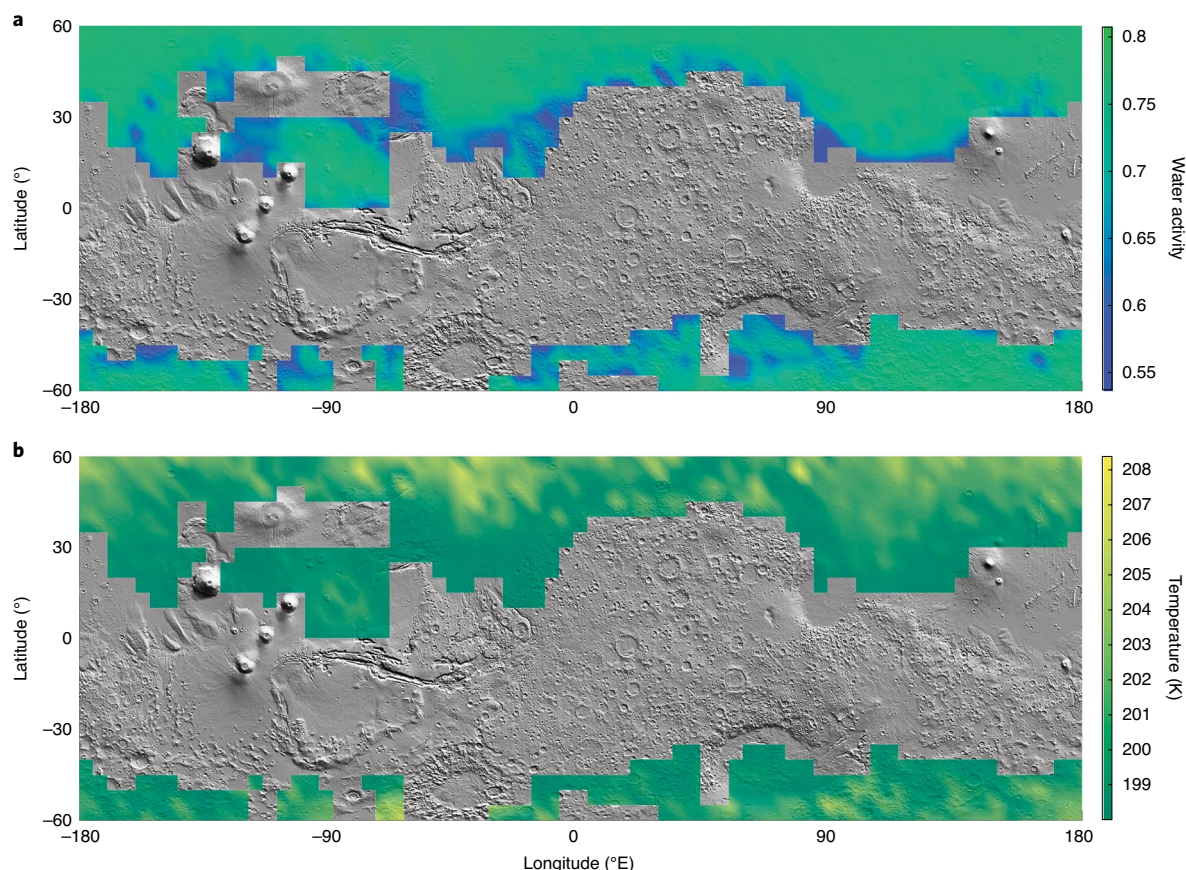


Fig. 3 | Maximum achievable water activity and corresponding temperature of calcium perchlorate brines. a, b. To better resolve the habitability of the most favourable liquid case, here the maximum water activity achievable by brines formed through deliquescence of calcium perchlorate (**a**) is shown along with the corresponding brine temperature (**b**). The latitude range is restricted to non-polar regions. The background is the grey-scaled, shaded relief map of Mars based on MOLA data.

water activities. Indeed, the expected maximum brine temperature (225 K) is at the boundary of the theoretical low temperature limit of life²⁸; thus, present-day conditions on Mars mean that brine habitability is temperature-limited. Consequently, the expected properties of (meta)stable brines on the surface and shallow subsurface of Mars are not habitable to known terrestrial life, which reduces the potential for forward contamination of the Martian surface.

Methods

General circulation model. For this study, we used the Mars Weather Research and Forecasting (MarsWRF) GCM, a Mars version of the National Center for Atmospheric Research's Weather Research and Forecasting model^{14,30,31}, which has been vetted against measurements by Viking and the Thermal Emission Spectrometer on the Mars Global Surveyor¹⁵. MarsWRF solves the primitive equations on a finite difference mesh using an Arakawa C-grid. For surface temperature calculations, a multilayer subsurface thermal diffusion and surface energy balance model uses surface albedo and thermal inertia maps derived from orbital observations of the Martian surface by the Thermal Emission Spectrometer, with water ice albedo and emissivity set to 0.33 and 1.0, respectively. For radiation calculations, we use a two-stream radiation code that implements a k -distribution radiative transfer scheme (see ref. ³²). The total present-day atmospheric CO₂ budget has been tuned such that the modelled pressure curves match the observed pressure curves at the Viking 1 and Viking 2 landing sites. MarsWRF simulates the sublimation, condensation, sedimentation and transport of water ice particles in the atmosphere. This version uses the water cycle and radiatively active microphysics scheme implemented by Lee et al.¹⁵.

For this work, simulations were run at $5^\circ \times 5^\circ$ horizontal resolution with 52 vertical levels. The vertical grid stretches from about 75–100 m above the ground, depending on location and season, up to 120 km; this grid uses a modified-sigma, terrain-following vertical coordinate. We ran the simulations for a total of six Martian years. For the final year, we output hourly surface conditions.

Brine modelling. The hourly surface conditions, specifically surface temperature T_s , surface pressure P , and the water vapour specific mixing ratio γ_{wv} from MarsWRF were used in the thermodynamic analysis. For every simulated location on the surface of Mars and for every modelled hour, the surface water vapour specific mixing ratio was converted to water vapour pressure by

$$e = \frac{\gamma_{\text{wv}} P}{\mu + \gamma_{\text{wv}}}, \quad (1)$$

where μ is the ratio of the gas constants for dry and moist air. Surface relative humidity with respect to liquid (RH_{liq}) is then found by $\text{RH}_{\text{liq}} = 100 \left[e/p_{\text{sat,l}}(T_s) \right]$, where $p_{\text{sat,l}}$ is the temperature-dependent saturation vapour pressure above pure liquid water, here following the formulation from ref. ³³. Ice formation at the surface can occur when saturation with respect to ice is reached (that is, $\text{RH}_{\text{ice}} = 100\%$). Relative humidity with respect to liquid is related to relative humidity with respect to ice as $\text{RH}_{\text{ice}} = \text{RH}_{\text{liq}} \left[p_{\text{sat,l}}(T_s)/p_{\text{sat,i}}(T_s) \right]$, where $p_{\text{sat,i}}$ is the saturation vapour pressure above ice, here following the formulation of ref. ³⁴. For every hour, the DRH was calculated for calcium perchlorate¹⁹ and magnesium perchlorate¹³. If $\text{RH}_{\text{liq}} \geq \text{DRH}$ and the surface temperature surpassed the brine's eutectic temperature, a brine was considered to have formed. The properties of the brine (temperature and water activity) along with the time in solution were tracked until either $\text{RH}_{\text{ice}} > 145\%$ (ref. ⁹), at which point the solution would entirely freeze out, or the efflorescence relative humidity was reached, at which point the salt recrystallizes and water is lost to the ambient atmosphere, thus accounting for metastable brines.

The water activity a_w of a brine is by definition $a_w = e_b/p_{\text{sat,l}}$, where e_b is the water vapour pressure directly above the brine. If $e_b > e$, the brine will lose water via evaporation, which on Mars would follow the Ingersoll formulation³, until e_b approaches e . When the brine is at equilibrium with the ambient air, $a_w = e/p_{\text{sat,l}}$ and thus $a_w = \text{RH}/100$. Such a relation has been extensively verified by Mars-relevant evaporation experiments (see, for example, refs. ^{11,35,36}), and is usually used for food storage and preservation regulations (see ref. ²⁹ and references therein). Stability against boiling was checked, ensuring $e_b \leq P$.

Subsurface modelling. Newly recalibrated environmental data from the Thermal and Electrical Conductivity Probe on the Phoenix lander¹⁸ were used to validate our subsurface environmental modelling, following the methods described in refs. ^{17,19,37}. The subsurface temperature and humidity environment were simulated by solving the one-dimensional thermal and mass diffusion equations via finite element analysis with element size of 1 cm and time step of 26 s. We modelled to a depth of 4 m, which is several times the annual skin depth, and simulated three Martian years, saving the results of the last year. Running over multiple years ensures that the code converges to a stable solution. We assumed regolith properties of $\Gamma = 150 \text{ J m}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$, $A = 0.18$, $\phi = 0.16$ and $\tau = 2$ for thermal inertia, albedo, porosity and tortuosity, respectively^{38–40}. Environmental conditions per element were saved at hourly increments. Simulated surface conditions were validated against Phoenix Thermal and Electrical Conductivity Probe temperature and relative humidity measurements.

Data availability

The data that support the figures within this paper are available at <https://doi.org/10.6084/m9.figshare.11907984> or from the corresponding author upon reasonable request. The newly recalibrated environmental data from the Thermal and Electrical Conductivity Probe on the Phoenix lander are available on the NASA Planetary Data System Geosciences Node (<https://pds-geosciences.wustl.edu/missions/phoenix/martinez.htm>).

Code availability

The MarsWRF (Mars Weather Research and Forecasting) GCM is available from A.S. upon reasonable request. Other software used in this work is available from E.G.R.-V. upon reasonable request.

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Author contributions

E.G.R.-V. wrote software to automate the pairing of the salt stability fields with the GCM outputs, analysed the data, created the figures, and drafted and revised the manuscript. V.F.C. conceived the original concept for this article and developed the stability fields for calcium and magnesium perchlorate. A.S. set up and ran the MarsWRF model, acquired and reduced the GCM results, and drafted the relevant methods section. G.M. provided the recalibrated environmental data from the Phoenix lander, reduced the data and aided in interpretation. All authors contributed to the interpretation of the results and revision of this manuscript.

Competing interests

The authors declare that they have no competing financial interests.

Additional information

Extended data is available for this paper at <https://doi.org/10.1038/s41550-020-1080-9>.

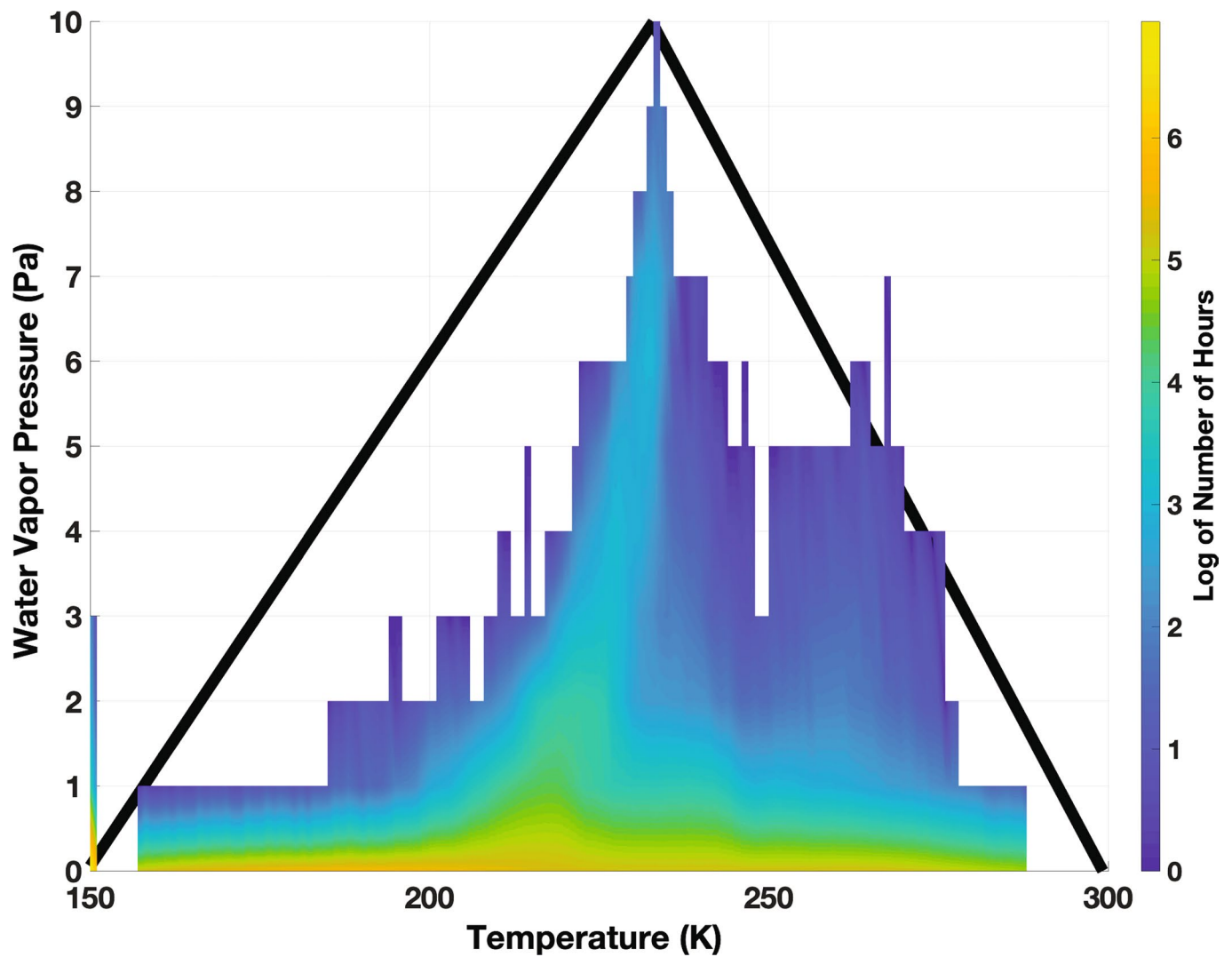
Correspondence and requests for materials should be addressed to E.G.R.-V.

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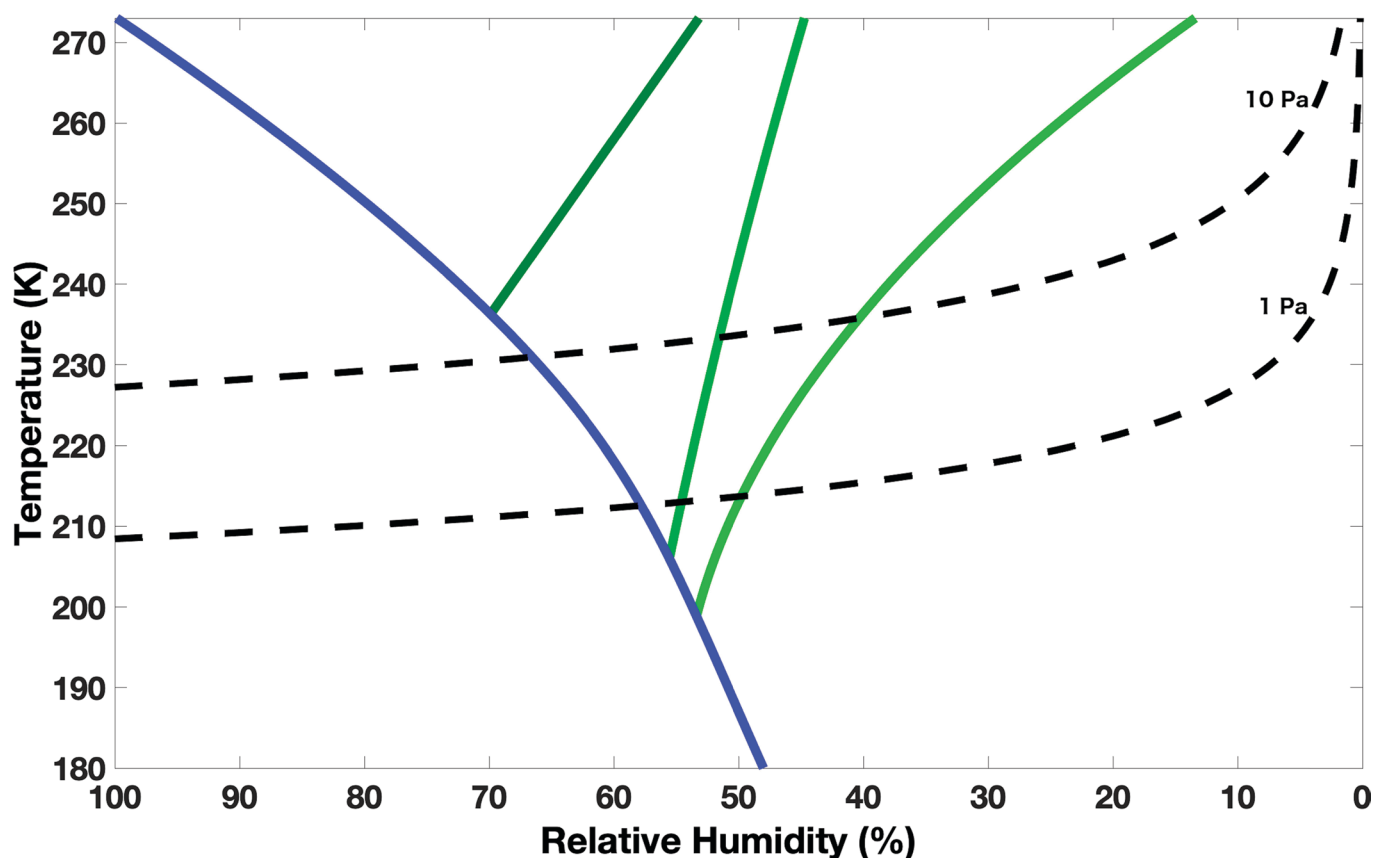
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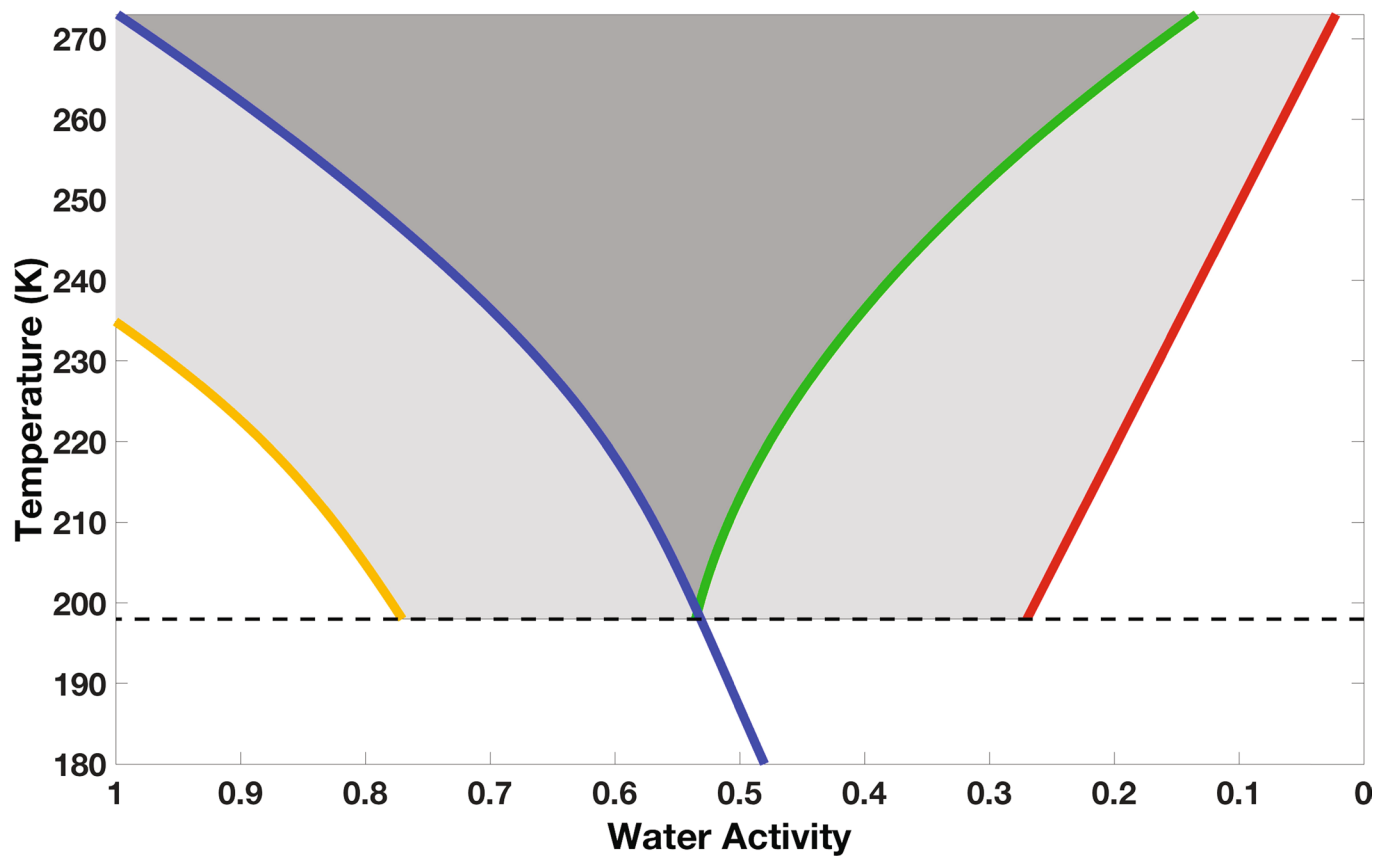
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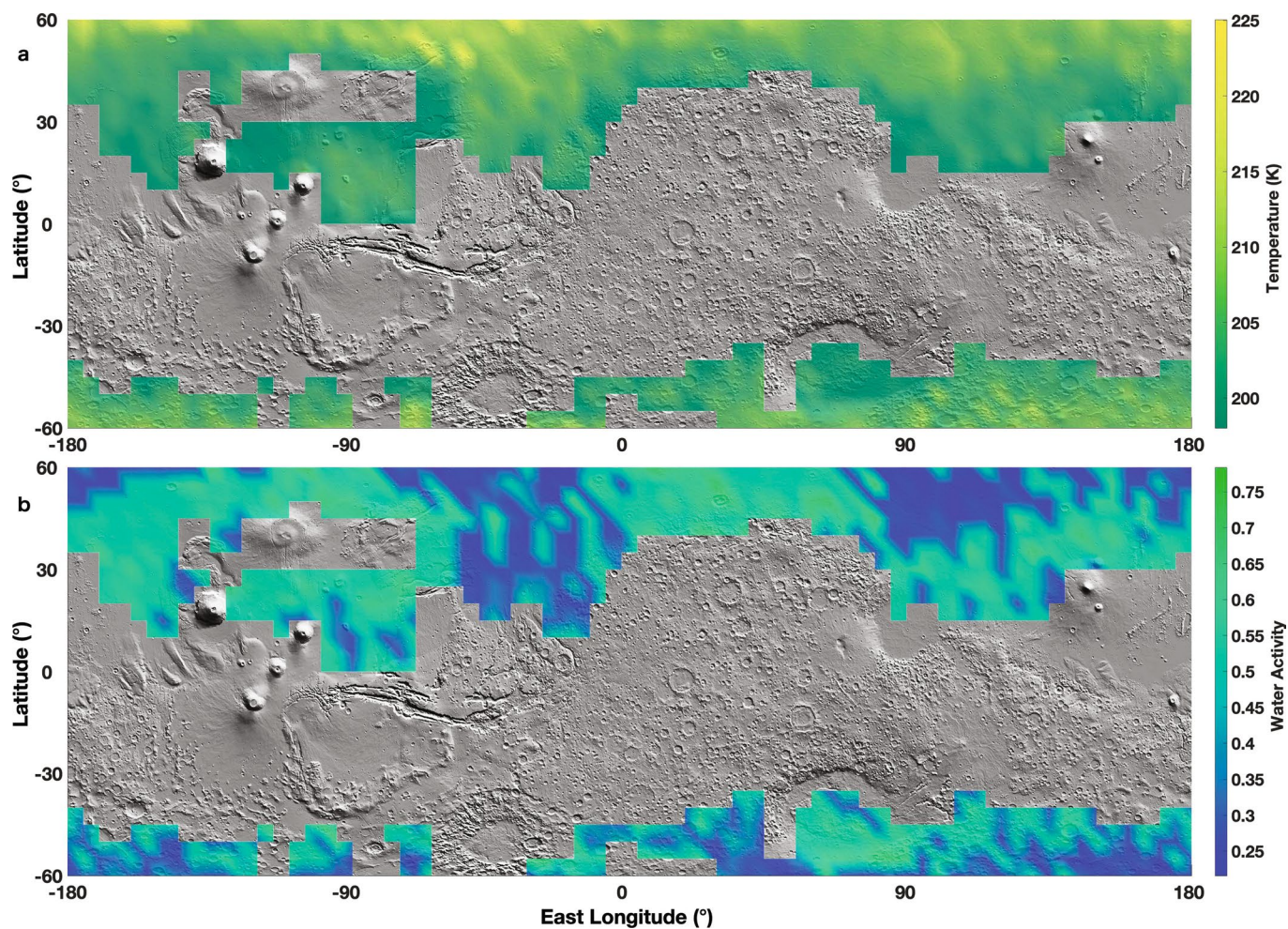
Extended Data Fig. 1 | Frequency of temperature and water vapour pressure pairings. In Fig. 1, the Mars-relevant pairings of surface temperature and atmospheric water vapour pressure are contained between the cyan lines. Here we show the frequency (in colour) of each combination of surface temperature and water vapour pressure predicted by MarsWRF in support of the presented analysis in Figure 1. Frequency here is the log base 10 of the number of hours across the surface of Mars at a $5^\circ \times 5^\circ$ latitude/longitude grid and one-hour temporal resolution. For the purposes of counting, temperature and water vapour pressure were binned in increments of 1 K and 1 Pa. Here the cyan lines from Fig. 1 are in black.



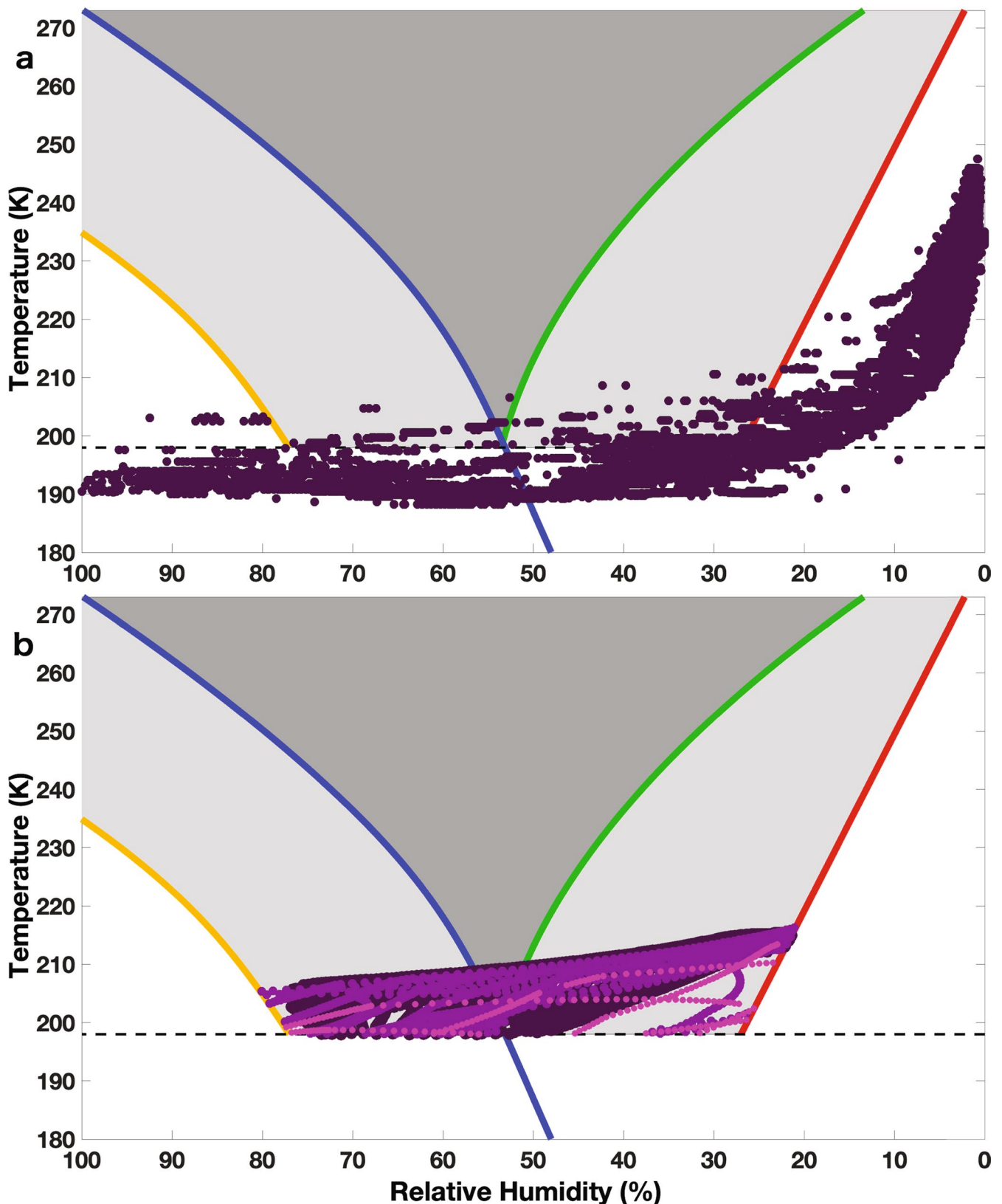
Extended Data Fig. 2 | Limits for Martian brine chemistries. As per Fig. 1, the maximum water activity of a brine that is thermodynamically stable on Mars is 0.66. This would imply that a brine with a eutectic water activity higher than this value would not readily form on present-day Mars. Another way of seeing this is in the phase diagram. Following the typical phase diagram (relative humidity vs temperature), here we show the ice line in blue (that is, $RH_{ice} = 100\%$), the temperature-dependent deliquescence relative humidity (DRH) for calcium and magnesium perchlorate, as well as the sodium chlorate hydrate line in shades of green, from light to dark respectively. In dashed black lines, we plot two isobars for water vapour pressure, showing the typical maximum water vapour pressure measured on Mars by the Mars Science Laboratory rover and Phoenix lander, as well as the maximum surface water vapour pressure predicted by the MarsWRF model. The hyperarid conditions on Mars would not permit a salt with a eutectic water activity higher than 0.66 to form (that is, eutectic temperature > 230 K). For example, at a eutectic temperature of 236 K, sodium chlorate would not form a brine because there is insufficient water vapour in the Martian atmosphere.



Extended Data Fig. 3 | Phase diagram of calcium perchlorate. In Figures 2 and 3 we showed results for the (meta)stability of brines formed by the deliquescence of calcium and magnesium perchlorate. Here we show the thermodynamically stable (area shaded in dark grey) and metastable (area shaded in light grey) regions of a calcium perchlorate brine in the typical phase diagram. A brine can form between the ice line (that is, $RH_{ice} = 100\%$), here the blue solid line, and the temperature-dependent deliquescence relative humidity (DRH), here shown as the green solid line. However, experiments have shown that metastable solutions exist beyond $RH_{ice} = 100\%$, up to $RH_{ice} = 145\%$, here shown as the orange solid line. Furthermore, although thermodynamically a solution should effloresce once conditions fall below the DRH, experimental work has shown that solutions persist until much lower relative humidities are reached (that is, the efflorescence relative humidity, here the red solid line). Non-shaded regions on this plot are conditions that would not permit for stable or metastable solutions of calcium perchlorate. The eutectic temperature (~ 198 K) is the black dashed line.



Extended Data Fig. 4 | Maximum achievable brine temperature and corresponding water activity of calcium perchlorate brines formed through deliquescence. To better resolve the habitability of (meta)stable calcium perchlorate brines, here we plot **(a)** the maximum temperature and **(b)** corresponding water activity of resulting brines. The latitude range is restricted to non-polar regions. The background is the grey-scaled shaded relief map of Mars based on MOLA data.



Extended Data Fig. 5 | Measured surface and modeled subsurface conditions at the Phoenix landing site. Using newly recalibrated environmental data from the Thermal and Electrical Conductivity Probe on the Phoenix lander along with a model of the subsurface, we studied the potential to form liquids at the Phoenix landing site. In **a**, we plot the Phoenix measured temperature and relative humidity with respect to liquid (purple points) on the phase diagram of calcium perchlorate (following the colour code in Supplementary Fig. 3). As can be seen, several measured conditions are within the liquid stability region of calcium perchlorate brines. Furthermore, in **b** we plot the simulated subsurface conditions during which a brine is (meta)stable, assuming an ice table depth of 10 cm. The model's surface predictions for both temperature and relative humidity were validated against the Thermal and Electrical Conductivity Probe measurements. In purple scale, from light to dark, we show results for 2, 5 and 8 cm.