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D. Möhlmann. Latitudinal distribution of temporary liquid cryobrines on Mars. *Icarus*, 2011, 10.1016/j.icarus.2011.05.006 . hal-00768789

HAL Id: hal-00768789

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Accepted Manuscript

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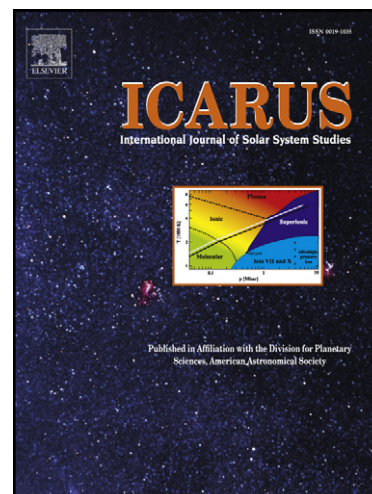
PII: S0019-1035(11)00170-9
DOI: [10.1016/j.icarus.2011.05.006](https://doi.org/10.1016/j.icarus.2011.05.006)
Reference: YICAR 9812

To appear in: *Icarus*

Received Date: 7 October 2010
Revised Date: 27 April 2011
Accepted Date: 2 May 2011

Please cite this article as: Möhlmann, D., Latitudinal distribution of temporary liquid cryobrine on Mars, *Icarus* (2011), doi: [10.1016/j.icarus.2011.05.006](https://doi.org/10.1016/j.icarus.2011.05.006)

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Latitudinal distribution of temporary liquid cryobrines on Mars

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1 **Abstract**

2 Simulations of the surface temperature and atmospheric humidity with a modern Mars climate
3 model (MCD) and with Phoenix data are used to study the conditions for a liquefaction of
4 brines as a function of latitude and season. The results show that, in the presence of
5 appropriate salts, liquid cryobrines can in course of the diurnal cycle temporarily evolve at
6 high latitudes on Mars' current climate. The conditions for the liquefaction of "Mars-
7 relevant" cryobrines and time and duration of their stability during the diurnal cycle are
8 calculated for northern spring and for the Phoenix landing site.

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1 **1. Introduction**

2 Salts found on Mars can, under appropriate conditions, support the formation of liquid brines
3 by deliquescence even on today's climate (Renno et al., 2009; Zorzano et al., 2009;
4 Möhlmann and Thomsen, 2010). "Cryobrines" or "cold liquid water-brines" are water based
5 liquid brines which can remain liquid also when the environmental temperature $T(t)$ is below
6 the freezing temperature of water $T_0 = 0^\circ\text{C}$ (i.e. $T(t) < T_0$).

7 Deliquescence is the liquefaction of salts, which is driven by the sorption of
8 atmospheric water by the salts. This liquefaction process starts when the atmospheric
9 humidity exceeds a critical threshold value, known as the deliquescence relative humidity,
10 DHR. This threshold relative humidity value ($rh = DRH$) is a characteristic parameter for each
11 salt. Therefore, and if $T(t) > T_{\text{eut}}$, cryobrines can remain liquid as long as $rh(t) > DRH$.
12 Frequently, "water activity" a_w is also used to describe relative humidity. Water activity and
13 relative humidity $rh(t)$, what is measured in %, are related via the expression $rh[\%] = 100 a_w$.

14 On Mars, temperature and relative humidity depend on season, areographic longitude
15 and latitude, and the position in the diurnal cycle, measured along the orbit of Mars by the
16 solar longitude L_S . Here, we study the influence of these parameters on presence and
17 distribution of liquid cryobrines on present day Mars.

19 **2. DRH of salts with a low eutectic temperature**

20 Subzero temperatures are typical for present day Mars. Möhlmann and Thomsen (2010) have
21 listed non-organic salts of a remarkable low eutectic temperature, which can be candidates for
22 cryobrines on Mars. These potential candidate salts could deliquesce and remain liquid on
23 Mars, at least temporarily. Table I lists the water activity values of some of these salts with
24 low eutectic temperature.

25 Most of the chemical elements that form the salts or acids listed in Table I are either
26 known to exist or are expected to exist on Mars. However, it is interesting to note that the low
27 eutectic temperatures of Lithium brines may also be relevant to Mars, mainly in view of their
28 very low eutectic temperatures. Lithium has been found on the SNC-meteorites Shergotty,
29 Nakhla, and Zagami (Magna, 2006). Of course, nothing is currently known on distribution,
30 location and concentration of possible Li-salt deposits on Mars, but this is true for almost all
31 of the mentioned non-organic "candidate salts".

32

33

34

Deliquescent material	Eutectic temperature [K]	DRH [%]
H ₃ PO ₄	203	41
LiCl	206	48
KOH	210	50
Mg(ClO ₄) ₂	212	53
AlCl ₃	214	53
H ₂ SO ₄ · 6.5H ₂ O	215	53
ZnCl ₂	221	58
CaCl ₂	226	60
NiCl ₂	230	64

1

2 Table I. Properties of non-organic salts with comparatively low DRH-values at eutectic
3 temperatures below 230K. These properties were calculated with the Extended UNIQUAC
4 model (cf. Thomsen, 2005; Möhlmann and Thomsen, 2010).

5

6 3. Diurnal martian temperature and water activity

7 Forget et al. (2008) have derived a numerical model to calculate the diurnal variation of
8 atmospheric parameters of Mars and their dependence on season and location. This model
9 was used to generate a Mars Climate Dataset (MCD) as proposed by (Lewis, 1999), which is
10 based on modelling the global atmospheric circulation on Mars, including that of water. Here
11 we use the diurnal and seasonal variation of surface temperature $T(t)$, total surface pressure
12 $p_{\text{tot}}(t)$ and water vapour mixing ratio $Mr(t)$ to calculate via $rh(t) = p_{\text{tot}}(t) Mr(t)/p_{\text{sat}}$ the
13 atmospheric humidity as a function of time $rh(t)$. The water vapour saturation pressure $p_{\text{sat}}(t)$
14 according to the expression described by Marti and Mauersberger (1993) is for the relevant
15 temperatures given in a good approximation by

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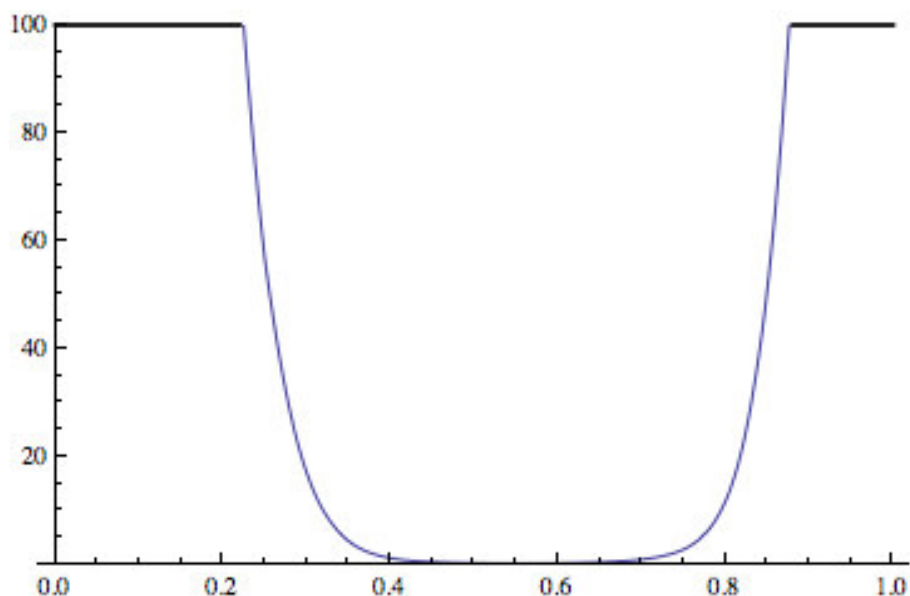
$$17 \quad p_{\text{sat}} [\text{Pa}] = a e^{-b/T[\text{K}]}, \quad (1)$$

18

19 where $a = 3.4435 \cdot 10^{12}$ Pa, and $b = 6132.9354$ K. Water activity a_w is described by $a_w(t) =$
20 $p_P(t)/p_{\text{sat}}(t)$. The partial pressure of water vapour $p_P(t)$ can be found by using MCD-data for
21 mixing ratio and total atmospheric pressure by $p_P(t) = p_{\text{tot}}(t) Mr(t)$. Fig. 1 gives an example of
22 the diurnal variation of the relative humidity $rh[t]$, i.e. the water activity measured in %
23 ($rh[\%] = 100 a_w$), at martian latitude 60° N and 0° E longitude in the interval $L_S = 60^\circ - 90^\circ$.

1 This Figure indicates that the atmospheric relative humidity can, in this exemplary case, in
 2 course of the day temporarily get saturated (over about 8 hours in total) and that it can exceed
 3 the DRH of “Mars-relevant” salts with a low eutectic temperature (cf. Table I). Note that the
 4 diurnal average of the related water activity is in this case $\bar{a}_w = 0.5$.

5



6

7 Fig. 1 Diurnal variation of the near surface relative humidity in the northern pre-spring
 8 interval $L_S = 60^\circ - 90^\circ$ at 60° N latitude and 0° E longitude. The horizontal bars indicate
 9 saturation ($rh = 100\%$). The $rh(t)$ -values have been evaluated by using MCD-data (advised
 10 model, version 4.3) (Forget et al., 2008) for total atmospheric pressure $p(t)$, H_2O -vapour
 11 mixing ratio $Mr(t)$, and temperature $T(t)$.

12

13 As has been described above, the necessary condition for the onset of deliquescence, which is
 14 driven by the uptake of atmospheric water vapour by salts, can be described by the relative
 15 atmospheric humidity in equilibrium with the salt:

16

$$17 \quad rh > DRH. \quad (2)$$

18

19 Another necessary condition for the formation of a liquid brines is that their temperature $T(t)$
 20 exceeds the eutectic temperature T_{eut} of the salts, that is

21

$$22 \quad T(t) > T_{eut}. \quad (3)$$

23

1 Eqs. (2) and (3) are used in modelling the presence of the liquid phase of the cryobrines on
2 listed in Table I on Mars. The results of these calculations are described next.

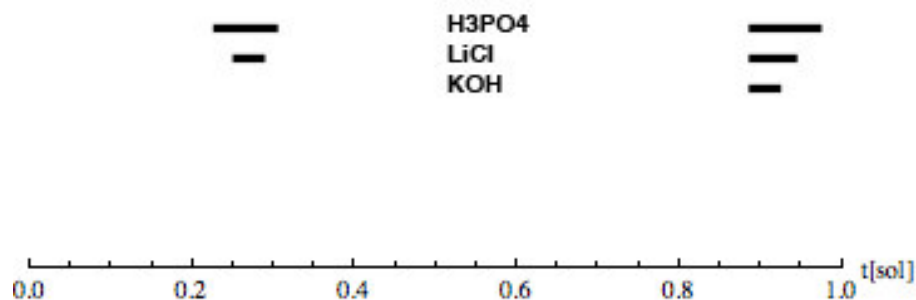
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4 **4. The stability of liquid cryobrines as a function of time of the day**

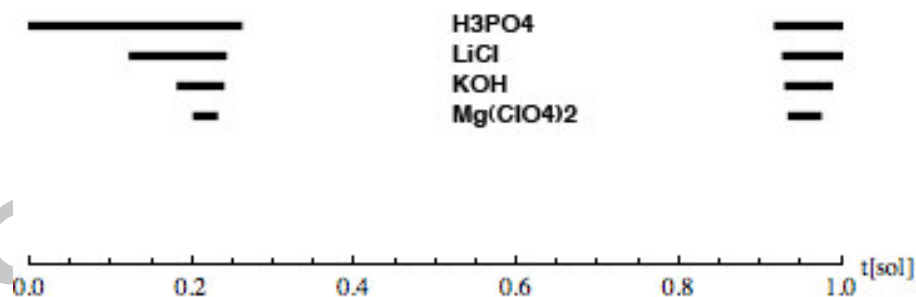
5 The stability of some cryobrines at northern martian latitudes is shown in the following. In
6 particular the arbitrarily chosen longitude of 0° E is used though there are longitudinal
7 variations in the water vapour distribution on Mars, these are small enough relative to the
8 latitudinal changes that a representative latitude 0° E has been chosen for these investigations.
9 Local effects like the presence of appropriate salts will more efficiently modify the
10 liquefaction conditions of cryobrines. So, the results for the landing site of NASA's Phoenix
11 mission with a longitude of 234° E do not essentially differ from that at the same latitude but
12 at the longitude 0° E (cf. Figs. 5).

13 The temporary presence of the liquid phase of cryobrines formed by the deliquescence of the
14 salts listed in Table 1 is calculated using Eqs (2) and (3). The horizontal bars in Figures 2
15 describe the periods of the day on which the different cryobrines can form and remain liquid.
16 Obviously, the formation of liquid cryobrines depends strongly on season and latitude. Higher
17 latitudes are preferred, and only a few salts liquefy under these martian conditions. However,
18 mixtures of various salts might be able to deliquesce at more extreme conditions (Renno et
19 al., 2009). The preference of high latitudes is a consequence of the latitudinal distribution of
20 water vapour in the martian atmosphere, which peaks in the northern hemisphere at high
21 latitudes shortly after northern spring between $L_S = 90^\circ$ and $L_S = 150^\circ$ and between 60° N and
22 about 80° N, and to a smaller extent in the southern hemisphere shortly after southern spring
23 between $L_S = 270^\circ$ and $L_S = 300^\circ$ for latitudes higher than about 60° S (cf. Smith, 2002). At
24 low and equatorial latitudes, atmospheric humidity is largest around northern summer (L_S
25 around 180°) but clearly smaller than the maximum relative humidity at the high latitudes.
26 Therefore, the calculations have been performed here for these spring-time conditions only.

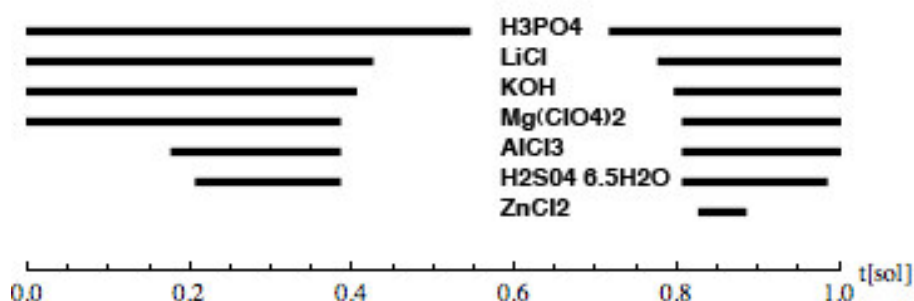
27 The relative humidity is generally larger during night. This effect is mainly because of
28 the remarkable decrease in the temperature-dependent saturation vapour pressure during the
29 cooler night hours, as indicated by Eq. (1). On the other hand, the temperature $T(t)$ exceeds
30 the eutectic temperature of cryobrines ($T > T_{\text{eut}}$) during the warmer daytime periods.
31 Therefore, the small overlapping time calculated with the aid of Eqs. (2) and (3) limits the
32 presence of the liquid phase of cryobrines of the pure salts described in Table 1 at the surface.
33 Figures 2 illustrate this behaviour for the latitudes 60° N, 70° N and 80° N and for one sol.



1
2 Fig.2 a - 60° N Horizontal bars indicate for 60° N periods on which the liquid phases of
3 H₃PO₄ (upper bars), LiCl and KOH are stable in course of a sol shortly after northern spring
4 ($L_S = 90^\circ - 120^\circ$) at 0° longitude. The condition $rh(t) > DRH$ can be reached only during night
5 and early morning hours. Eqs (2) and (3) are simultaneously satisfied only for the shown salts.
6 Other salts in Table I do not simultaneously satisfy the deliquescence conditions.



7
8 Fig.2 b - 70° N Horizontal bars indicate for 70° N liquid phases of H₃PO₄, LiCl, KOH,
9 and Mg(ClO₄)₂ in course of one sol and shortly after northern spring ($L_S = 90^\circ - 120^\circ$) at 0°
10 longitude. The condition $rh(t) > DRH$ can be reached only during night and early morning
11 hours. Eqs (2) and (3) are simultaneously satisfied only for the shown salts. Other salts as
12 mentioned in Table I do not simultaneously satisfy the deliquescence conditions.



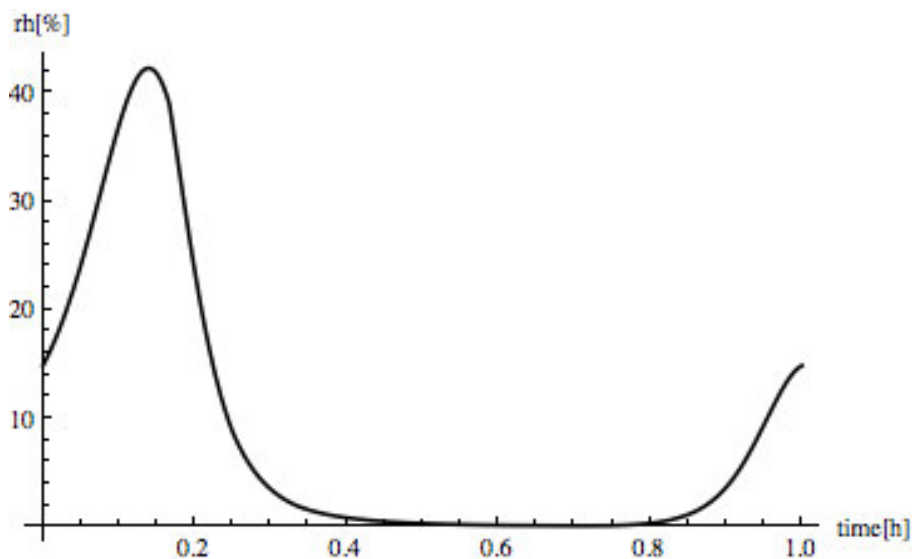
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2 Fig.2 c – 80°N Horizontal bars indicate for 80° N liquid phases of H₃PO₄, LiCl, KOH,
 3 Mg(ClO₄)₂, AlCl₃, H₂SO₄ x 6.5 H₂O, and ZnCl₂ in course of one sol and shortly after northern
 4 spring ($L_S = 90^\circ - 120^\circ$) at 0° longitude. The condition $rh(t) > DRH$ can be reached during
 5 evening, night and morning hours. Eqs (2) and (3) are simultaneously satisfied only for the
 6 shown salts. Other salts as mentioned in Table I do not simultaneously satisfy the
 7 deliquescence conditions.

8

9 The results, described by Figs. 2 refer to higher latitudes in the northern hemisphere. As has
 10 been already described by Smith (2002), the southern hemisphere has slightly smaller water
 11 content than the northern one. This is the reason for comparably lower rh -values (cf. Fig. 3).
 12 The relative humidity, as shown in Fig. 3 for a latitude of 60° S, reaches values which
 13 temporarily permit liquefaction of phosphoric acid over a few hours in the morning hours.
 14 Higher relative humidity is required to have deliquescence of others of the salts mentioned in
 15 Table I. This result indicates possible thermo-physical conditions for deliquescence also at
 16 higher southern latitudes, but this can be expected to happen there on a lower level than in
 17 northern latitudes.

18



1

2 Fig. 3 Relative humidity at post-spring conditions ($L_S = 270^\circ - 300^\circ$) at a latitude 60° S and
 3 a longitude 0° E, based on MCD-data (cf. Forget et al., 2008). The relative humidity is
 4 remarkably smaller than under comparable post-spring conditions ($L_S = 90^\circ - 120^\circ$) in the
 5 northern hemisphere.

6

7 Note that not all of the cryobrines in Table.I deliquesce under the thermo-physical conditions
 8 as described here. Particularly, the water activity for some of them is already too small when
 9 the temperature reaches and is above their eutectic temperature.

10 It should be cautioned that the results presented above mainly refer to the one longitude 0° , as
 11 an example only, and they are based on results of a single atmospheric model, a few single
 12 salts and only the presence of brines, in the absence of shadows and on local features such as
 13 the presence of neighbouring water ice with the consequence of locally enhanced relative
 14 humidity. Indeed, variations in the local temperature and atmospheric water vapour content
 15 can modify the behaviour described above and alter the stability of liquid cryobrines. More
 16 detailed and locally dedicated investigations are necessary to complete the picture.
 17 Nevertheless, the main result that only a limited number of cryobrines can liquefy by
 18 deliquescence on Mars, and that higher latitudes and evening/night and morning hours are the
 19 preferred time for the presence of these liquids on present Mars, can be taken as accurate.

20 It is interesting to note that the presence of liquid brines may be accompanied by chemical
 21 reactions on Mars also today if a sufficient amount of atmospheric water vapour will be
 22 present. From this point of view, higher latitudes are preferred to temporarily permit a water-
 23 based chemistry on Mars, but with slowed down reaction rates due to the lower temperatures.

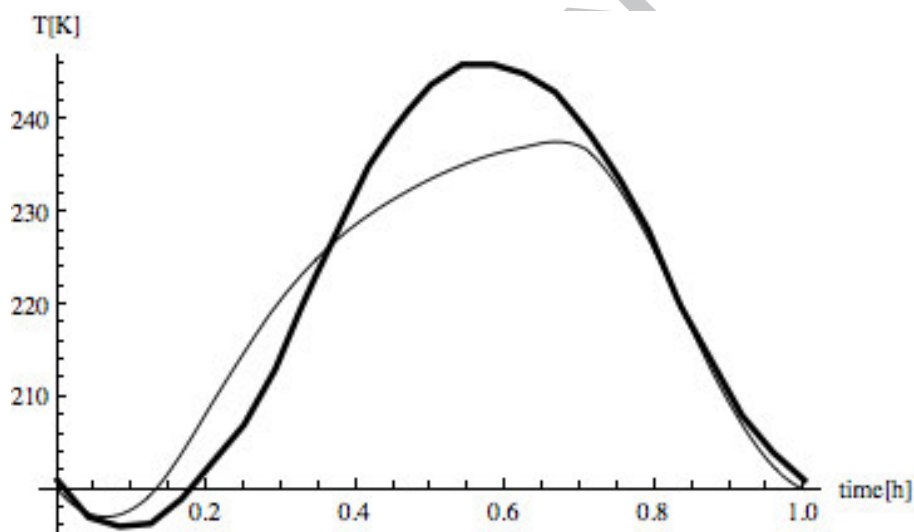
24 Note that magnesium perchlorate is a strong oxidant and may destroy organic matter. Also,

1 the temporarily present liquid acids are another challenging aspect. Furthermore, the
 2 hydration of many salts is an exothermic reaction that might temporarily support the stability
 3 of their liquid phases at the colder environmental temperatures (Zorzano et al., 2009).

4

5 **5. Conditions for deliquescence at the Phoenix landing site**

6 The Phoenix spacecraft landed at the martian coordinates 125.70546 W longitude and
 7 68.28952 N latitude. The question of if and when liquid cryobrines can temporarily exist at
 8 the Phoenix landing site on Mars is open since indications for the existence of perchlorates
 9 have been found (Hecht et al., 2009) and temporarily liquid droplet-like phenomena on a strut
 10 of Phoenix have been imaged (Renno et al., 2009). Unfortunately, there are no reliable
 11 measurements of the surface temperature given for the Phoenix landing site, and the available
 12 model temperatures (Zent et al. (2010) model surface temperature and the MCD-model-data)
 13 differ (cf. Fig. 4a).



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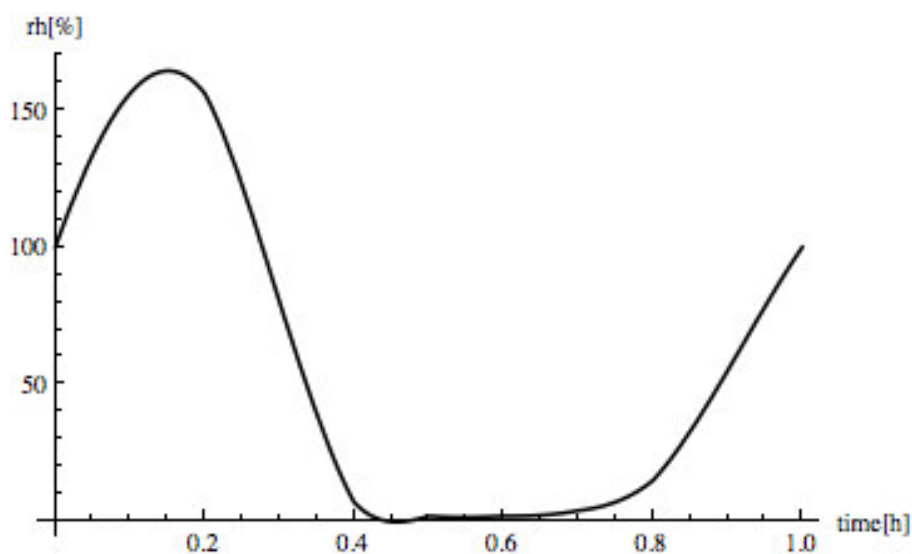
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17 Fig. 4a Model surface temperature $T(t)$ (in fractions of a day) – thick line - at the
 18 Phoenix site $L_S = 101^\circ$ (Phoenix sol 55) as described by Zent et al., 2010) and MCD-model-
 19 temperatures for the interval $L_S = 90^\circ - 120^\circ$ (Forget et al., 2008) – thin line – for the same
 20 location and time. Time is LMST (Mean Local Solar time).

21

22 Fig. 4b shows the calculated atmospheric humidity at the surface of Mars at the Phoenix
 23 landing site. This calculation is based on MCD-data for total pressure and for the mixing ratio
 24 but uses the probably more realistic model surface temperature of Zent et al. (2010) for the
 25 Phoenix landing site.

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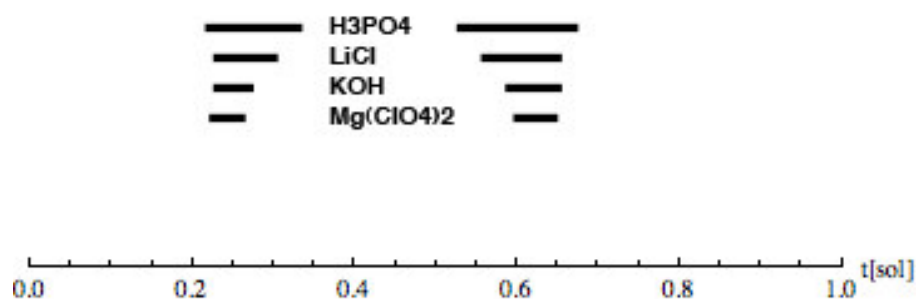
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4 Fig. 4b Diurnal variation of the atmospheric relative humidity at the Phoenix site,
 5 estimated from MCD $p_{\text{tot}}(t)$ - and $M_r(t)$ -data for an area including the Phoenix landing site,
 6 with a typical average values for $L_S = 90^\circ - 120^\circ$, and using the local model surface
 7 temperature of Zent et al. (2010) for $L_S = 101^\circ$ (Phoenix sol 55). Saturation will be reached
 8 around midnight. At this time the onset of condensation can be expected to stop the growth of
 9 $rh(t)$, which then remains at $rh=100\%$.

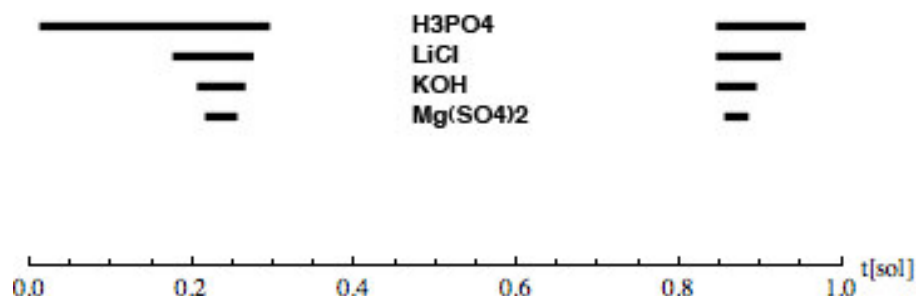
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11 Obviously, $T(t)$ and $rh(t)$ will temporarily permit the formation of the liquid phase of
 12 cryobrine. Figs. 5 describes this graphically for the used Phoenix- and MCD-data.

13



14 Fig. 5a Liquid phases of H_3PO_4 , $LiCl$, KOH , and $Mg(ClO_4)_2$ for the Phoenix site at L_S
 15 $= 101^\circ$ (sol 55), based on the MCD-model data for $p_{\text{tot}}(t)$, $M_r(t)$, and $T(t)$ (Forget et al., 2008).



1
2 Fig 5b Liquid phases of H_3PO_4 , LiCl , KOH , and $\text{Mg}(\text{ClO}_4)_2$ for the Phoenix site at L_S
3 $= 101^\circ$ (sol 55), based on MCD-model data for $p_{\text{tot}}(t)$ and $M_r(t)$ (cf. Forget et al., 2008) but
4 using the model surface temperature of Zent et al. (2010).

5
6 Thus, the known data of temperature and atmospheric water content indicate that indeed the
7 liquid phase of cryobrine can form by deliquescence at the Phoenix site (in this case for sol
8 55, i.e. shortly after northern spring) if the appropriate salts are present there. This
9 liquefaction will preferentially take place in early morning and late evening hours.

11 6. Summary

12 The latitudinal and seasonal dependence of the formation and stability of the liquid phase of
13 cryobrine on Mars is studied for a few non-organic salts likely to exist on Mars. The
14 presence of the liquid phase at northern latitudes occurs around late northern spring and is
15 located between 60° N and 80° N (and higher) latitude, and to a smaller extent in
16 corresponding southern latitudes around the southern spring. This behaviour is caused by the
17 fact that the atmospheric water content peaks at specific solar longitudes and latitude bands
18 but with slightly higher values in the northern hemisphere. The appearance of the liquid phase
19 is in most cases restricted to evening and morning hours.

20 Only a limited number of salts may have the property to at least temporarily liquefy by
21 deliquescence on Mars. Of course, the presence of these salts is a necessary condition. The
22 appearance of liquid phases of cryobrine may have chemical and also rheological
23 consequences. The presence of possibly cryobrine-triggered rheological phenomena on Mars
24 (cf. Renno et al., 2009; Möhlmann and Kereszturi, 2010) may be an indication for the
25 existence of cryobrine on Mars. A cryobrine-driven chemistry on Mars is a yet open

1 challenge. Furthermore, deliquescence on Mars can also be of biological relevance since a
2 liquid phase, which is necessary for the transport of nutrients and waste, can be made
3 available by these processes.

5 **Acknowledgments**

6 This research has been supported by the Helmholtz Association through the research alliance
7 “Planetary Evolution and Life”.

8 I wish to express my thanks to Nilton Renno for improving the manuscript by helpful and
9 critical hints.

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Research highlights

Brines can temporarily liquefy on Mars by uptake of atmospheric water (deliquescence).

This liquefaction process is most effective in the cooler dusk to dawn hours.

Best conditions for liquid brines to evolve are around spring.

The conditions for temporary liquefaction increase with latitude.

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