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### 1 Abstract

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

### 1 **1.** Introduction

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

Deliquescence is the liquefaction of salts, which is driven by the sorption of atmospheric water by the salts. This liquefaction process starts when the atmospheric humidity exceeds a critical threshold value, known as the deliquescence relative humidity, DHR. This threshold relative humidity value (rh = DRH) is a characteristic parameter for each salt. Therefore, and if T(t) > T<sub>eut</sub>, cryobrines can remain liquid as long as rh(t) > DRH. Frequently, "water activity" a<sub>w</sub> is also used to describe relative humidity. Water activity and relative humidity rh(t), what is measured in %, are related via the expression rh[%] = 100 a<sub>w</sub>.

On Mars, temperature and relative humidity depend on season, areographic longitude and latitude, and the position in the diurnal cycle, measured along the orbit of Mars by the solar longitude L<sub>s</sub>. Here, we study the influence of these parameters on presence and distribution of liquid cryobrines on present day Mars.

18

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

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

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

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Deliquescent	Eutectic temperature	DRH
material	[K]	[%]
H <sub>3</sub> PO <sub>4</sub>	203	41
LiCl	206	48
КОН	210	50
Mg(ClO <sub>4</sub> ) <sub>2</sub>	212	53
AlCl <sub>3</sub>	214	53
$H_2SO_4$ 6.5 $H_2O$	215	53
ZnCl <sub>2</sub>	221	58
CaCl <sub>2</sub>	226	60
NiCl <sub>2</sub>	230	64

1

Table I. Properties of non-organic salts with comparatively low DRH-values at eutectic
temperatures below 230K. These properties were calculated with the Extended UNIQUAC
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  $p_{tot}(t)$  and water vapour mixing ratio Mr(t) to calculate via  $rh(t) = p_{tot}(t) Mr(t)/p_{sat}$  the 13 atmospheric humidity as a function of time rh(t). The water vapour saturation pressure  $p_{sat}(t)$ 14 according to the expression described by Marti and Mauersberger (1993) is for the relevant 15 temperatures given in a good approximation by

16 17

$$\mathbf{p}_{\text{sat}}[\mathbf{Pa}] = \mathbf{a} \, \mathrm{e}^{-\mathbf{b}/\mathbf{T}[\mathbf{K}]} \,, \tag{1}$$

18

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

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



Fig. 1 Diurnal variation of the near surface relative humidity in the northern pre-spring interval  $L_s = 60^\circ - 90^\circ$  at,  $60^\circ$  N latitude and  $0^\circ$  E longitude. The horizontal bars indicate saturation (rh = 100 %). The rh(t)-values have been evaluated by using MCD-data (advised model, version 4.3) (Forget et al., 2008) for total atmospheric pressure p(t), H<sub>2</sub>O-vapour mixing ratio Mr(t), and temperature T(t).

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6

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

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rh > DRH. (2)

18 19

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

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20

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

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

3

### 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  $0^{\circ}$  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  $0^{\circ}$  E (cf. Figs. 5).

The temporary presence of the liquid phase of cryobrines formed by the deliquescence of the 13 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  $60^\circ$ 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 then 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.

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



2 Fig.2 a - 60° N Horizontal bars indicate for 60° N periods on which the liquid phases of

3  $H_3PO_4$  (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.



9 and Mg(ClO<sub>4</sub>)<sub>2</sub> 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.



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

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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.



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

6

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Note that not all of the cryobrines in Table.I deliquesce under the thermo-physical conditions
as described here. Particularly, the water activity for some of them is already too small when
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  $0^{\circ}$ , 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.

It is interesting to note that the presence of liquid brines may be accompanied by chemical reactions on Mars also today if a sufficient amount of atmospheric water vapour will be present. From this point of view, higher latitudes are preferred to temporarily permit a waterbased chemistry on Mars, but with slowed down reaction rates due to the lower temperatures. Note that magnesium perchlorate is a strong oxidant and may destroy organic matter. Also,

the temporarily present liquid acids are another challenging aspect. Furthermore, the
hydration of many salts is an exothermic reaction that might temporarily support the stability
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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- 16

17Fig. 4aModel surface temperature T(t) (in fractions of a day) – thick line - at the18Phoenix site  $L_S = 101^{\circ}$  (Phoenix sol 55) as described by Zent et al., 2010) and MCD-model-19temperatures for the interval  $L_S = 90^{\circ} -120^{\circ}$  (Forget et al., 2008) – thin line – for the same20location and time. Time is LMST (Mean Local Solar time).

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



4 Fig. 4b Diurnal variation of the atmospheric relative humidity at the Phoenix site, 5 estimated from MCD  $p_{tot}(t)$ - and Mr(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 %.

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



15 =  $101^{\circ}$  (sol 55), based on the MCD-model data for  $p_{tot}(t)$ , Mr(t), and T(t) (Forget et al., 2008).



Fig 5b Liquid phases of H<sub>3</sub>PO<sub>4</sub>, LiCl, KOH, and Mg(ClO<sub>4</sub>)<sub>2</sub> for the Phoenix site at L<sub>s</sub> =  $101^{\circ}$  (sol 55), based on MCD-model data for p<sub>tot</sub>(t) and Mr(t) (cf. Forget et al., 2008) but using the model surface temperature of Zent et al. (2010).

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

10

#### 11 6. Summary

12 The latitudinal and seasonal dependence of the formation and stability of the liquid phase of 13 cryobrines 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 located between 60° N and 80° N (and higher) latitude, and to a smaller extend in 15 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 cryobrines 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 cryobrines 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.
- 4

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- 10

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5	Research highlights		
6	Rescurent ingringins		
7	Brings can temporarily liquefy on Mars by uptake of atmospheric water		
0	(deliguescence)		
0	(deliquescence).		
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10	This liquefaction process is most effective in the cooler dusk to dawn hours.		
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12	Best conditions for liquid brines to evolve are around spring.		
13			
14	The conditions for temporary liquefaction increase with latitude.		
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