Evaporation and freezing modeling to predict microbial habitability of potential Martian brines

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OVERVIEW

Liquid water is typically unstable at the surface of Mars due to the combination of low temperatures and pressures. However, the presence of dissolved salts on the Martian surface could lead to substantial freezing point depression, making it likely water could remain stable and expand the range of potential microbial habitability (Altheide et al., 2009). We modeled evaporation and freezing of various brine chemistries using two thermodynamic models at various conditions relevant to the Martian surface to help determine the possible limits of life in a cold, hyperarid Martian environment.

INTRODUCTION

Sulfates, chlorides, perchlorates, and carbonates have been detected by various Mars missions; including gypsum, kieserite ($MgSO_4 \cdot H_2O$), and polyhydrated sulfates (Vaniman et al. 2004; Langevin et al. 2005; Gendrin et al. 2005; Flahaut et al. 2010; Chevrier and Mathé 2007; Hecht et al. 2009; Clark and Kounaves 2016). Characteristics that might limit habitability include: activity of ions (a_i); activity of water (a_w); salt precipitation parageneses; ionic strength (I); pH; and chaotropic vs. kosmotropic effects of salts. Chaotropic agents are thought to induce stress on cells because they disrupt the structure of water and macromolecules, whereas kosmotropic agents facilitate water-water interactions to stabilize macromolecules (Zhang and Cremer, 2006). The lower limit of a_w to allow biochemical reactions is debated, but is estimated as a_w = 0.611 by Fox-Powell et al. (2016) and Stevenson et al. (2015), and as a_w = 0.5 by Jones et al. (2018).

We have evaluated water chemistries in equilibrium with a number of possible Martian mineral assemblages to help determine geochemical constraints on microbial life in a hyperarid Martian environment. Calculated equilibrium brine compositions were allowed to further evaporate or freeze and evolved brine compositions were also evaluated for the potential persistence of microbial life under possible extreme cold and evaporative conditions.

METHODS

Modeling of brines in equilibrium with possible Martian mineral assemblages was performed with Geochemist's Workbench (GWB) and FREZCHEM with Pitzer parameters, and a fixed $P(CO_2)$ of 6 or 600 mbar (Bethke et al., 2018). Mineral assemblages were based on identified minerals on the Martian surface, and model the Martian locations Valles Marineris (VM), the Southern Highlands (SH), and Meridiani Planum (MP). Primary mineral assemblages, and minerals that precipitated during evaporation and freezing are listed in Tables 1 & 2.

Initial brine compositions described in Table 2 include various brines of Ca-Mg-Na-K sulfates, chlorides, and carbonates. Evaporation calculations were performed at 298.15 K as modern temperatures near the equator on Mars can reach this temperature (Ojha et al. 2015). Freezing calculations were performed at temperatures between 298.15 K and 173.15 K and final freezing temperature (T_E) is included in the FREZCHEM model output (Table 4). Freezing temperature (T_E) of the residual solution after each evaporation run in GWB (Table 3) was calculated using Eqs. (26) and (28) found in supplemental information Figure S2 (Chevrier and Altheide, 2008).

Mineral	Abbreviation	Formula
Sulfates		
Gypsum	Gy	$CaSO_4 \cdot 2H_2O$
Anhydrite	An	$CaSO_4$
Epsomite	Ep	$MgSO_4 \cdot 7H_2O$
Kieserite	Ki	$MgSO_4 \cdot H_2O$
MgSO4 Dodecahydrate	Msd	$MgSO_4 \cdot 12H_2O$
Polyhalite	Po	$K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$
Leonite	Le	$K_2Mg(SO_4)_2 \cdot 4H_2O$
Schoenite	Sch	$K_2Mg(SO_4)_2 \cdot 6H_2O$
Glaserite	Gs	$K_3Na(SO_4)_2$
Arcanite	Ar	K_2SO_4
Syngenite	Sg	$K_2Ca(SO_4)_2 \cdot H_2O$
Bloedite	Bl	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Mirabilite	Mr	$Na_2(SO_4) \cdot 10H_2O$
Glauberite	Gl	$Na_2Ca(SO_4)_2$
Labile Salt/ Eugsterite	Ls	$Na_4(Ca(SO_4)_3 \cdot 2H_2O$
Chlorides		
Halite	Ha	$NaCl$
Sylvite	Sy	KCl
Antarcticite	At	$MgCl \cdot 6H_2O$
MgCl Dodecahydrate	Mcd	$MgCl_2 \cdot 12H_2O$
Carbonates		
Calcite	Ca	$CaCO_3$
Magnesite	Mg	$MgCO_3$
Nahcolite	Nah	$NaHCO_3$
Lansfordite	Lf	$MgCO_3 \cdot 5H_2O$
Nesquehonite	Ns	$MgCO_3 \cdot 3H_2O$
Natron	Nat	$Na_2CO_3 \cdot 10H_2O$
Ikaite	Ik	$CaCO_3 \cdot 6H_2O$

Table 1. Minerals in black were initially set in equilibrium with waters. Minerals listed in blue were only produced by evaporation. Minerals listed in red were only produced by freezing.

RESULTS

Evaporation

Waters evolved into $Mg-SO_4$, $Na-SO_4$, $Mg-Cl$, and $Na-Cl$ dominant hypersaline brines. Table 3 shows that in waters initially in equilibrium with $P(CO_2)$= 6mbar and initial pH of 7-8, a_w remains above 0.61 even at very high I. Specifically, SH4 is the only water that has a_w< 0.71, and decreases to 0.64 as it evolves into a concentrated Mg-Cl brine. Brines that evolved at different values of $P(CO_2)$ and initial values of pH produced similar results with respect to I and a_w, although evolution of pH varied by environmental conditions (Table 3). The final value of I ranges from 6.5 - 16.6 mol/L. Brines SH3, SH1, and MP3 reached a final pH<5 for an initial pH 5 and $P(CO_2)$= 6 mbar. SH3 was the only brine that reached a final pH<5 with initial $P(CO_2)$= 600 mbar. Sulfates mostly dominated the mineral precipitation parageneses (Fig. 1) and freezing temperatures ranged between 225.2 K - 260.9 K, with lower eutectic temperatures correlating with a higher concentration of Cl^- in the final brine composition.

Brine	Initial Composition
MP1	Gy-Gl-Ki-Po
MP3	Gy-Ep-Po
SH1	Gy-Ar-Ha
SH3	Gy-Ar-Gl-Le
SH4	An-Ki-Ha
VM4	An-Ca-Ha

Table 2. Mineral assemblages initially set in equilibrium with waters.

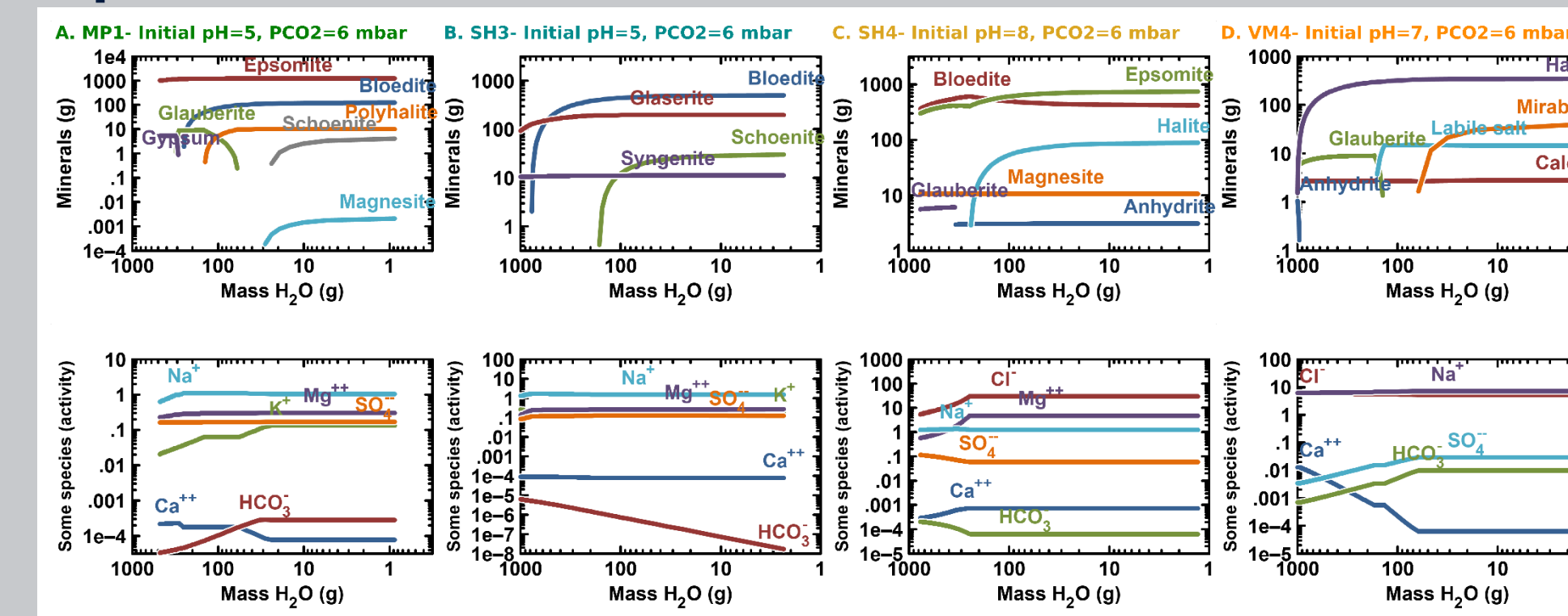Figure 1. Minerals and activity of aqueous species with PCO2=6 mbar and initial pH 5-8.

Brine	Initial pH	pH 6 mbar PCO2 start	pH 6 mbar PCO2 end	pH 600 mbar CO2 start	pH 600 mbar CO2 end	I 6 mbar PCO2 start	I 6 mbar PCO2 end	I 600 mbar PCO2 end	a_w 6 mbar PCO2 end	a_w 600 mbar PCO2 end	T_E 6 mbar PCO2 end	T_E 600 mbar PCO2 end	Minerals 6 mbar PCO2 end	Minerals 600 mbar PCO2 end
MP1	5	5.6	6.6	5.6	5.6	13.9	16.5	16.6	0.82	0.82	253.1	250.3	Ep-Bl-Sch-Po-Gl-Mg	Ep-Bl-Po-Sch-Gy-Mg-Gl
MP1	7	6.6	6.6	N/C	N/C	13.9	16.5	N/C	0.82	N/C	253.1	N/C	Ep-Bl-Po-Gl-Gy-Sch-Mg	N/C
MP3	5	5.0	2.1	5.0	5.7	12.7	13.5	12.7	13.6	0.89	0.89	260.8	259.1	Ep-Sch-Sg-Gy-Po	Ep-Sch-Sg-Gy-Po-Mg
MP3	7-8	6.7	6.7	5.7	5.7	12.7	12.7	13.6	0.89	0.89	260.8	259.1	Ep-Sch-Sg-Po-Gy-Mg	Ep-Sch-Mg-Sg-Po
SH1	5	4.8	3.0	5.0	6.4	7.8	7.9	7.8	7.9	0.72	0.72	239.9	235.8	Ha-Sy-Gs-Sg	Ha-Sy-Gs-Sg-Ca
SH1	7-8	7.0	7.4	7.0	7.0	7.8	7.9	8.0	8.1	0.72	0.72	239.9	235.5	Ha-Sy-Gs-Sg-Ca	Ha-Sy-Gs-Nah-Ca
SH3	5	4.9	2.3	4.9	2.0	12.9	16.1	12.9	16.2	0.83	0.82	253.6	250.7	Bl-Gs-Sch-Sg	Bl-Gs-Sch-Sg
SH3	7-8	6.7	6.6	5.7	5.6	12.9	16.1	13.0	16.2	0.83	0.83	253.7	250.9	Bl-Gs-Sch-Sg-Mg	Bl-Gs-Sch-Mg-Sg
SH4	6.5	N/C	N/C	5.4	5.0	N/C	N/C	12.6	12.3	N/C	0.65	N/C	225.9	N/C	Ep-Bl-Mg-Gl-An
SH4	8	6.4	6.0	N/C	N/C	12.8	12.3	N/C	0.65	N/C	230.2	N/C	Ep-Bl-Ha-Mg-Gl-An	N/C
VM4	6	N/C	N/C	6.0	6.9	N/C	N/C	6.5	10.6	N/C	0.72	N/C	236.5	N/C	Ha-Ls-Mr-Nah-Gl-An-Ca
VM4	7	7.0	8.1	N/C	N/C	6.5	10.3	N/C	0.73	N/C	240.9	N/C	Ha-Mr-Ls-Mg-Ca-Gl-An	N/C

Table 3. Result summary of evaporation trajectories for pH, ionic strength (I), activity of water (a_w), freezing temperature in K (T_E), and precipitated minerals for waters set in equilibrium with PCO_2= 6 or 600 mbar and initial pH 5-8. N/C = not calculated

Freezing

Freezing calculations produced water types similar to those produced during evaporation. Table 4 shows that a_w of waters shown also remain above 0.61. SH4 and VM4 are the only waters that have a_w< 0.71, and decrease to 0.69 and 0.68 respectively. The final value of I ranges from 3.94 – 9.89 mol/L. Brine SH3 is the only brine shown that reaches a final pH<5 for an initial pH 5 and $P(CO_2)$= 6 mbar. Highly hydrated minerals such as $MgSO_4 \cdot 12H_2O$ and $MgCl_2 \cdot 12H_2O$ were only precipitated through freezing scenarios. Final freezing temperatures of evolved brines shown ranged between 232.85 K - 268.2 K.

Brine	Initial pH	pH 6 mbar PCO2 start	pH 6 mbar PCO2 end	I 6 mbar PCO2 start	I 6 mbar PCO2 end	a_w 6 mbar PCO2 end	T_E 6 mbar PCO2 end	Minerals 6 mbar PCO2 end
SH1	7-8	8.65	9.26	5.91	7.2	0.78	246.65	Hh-Sy-Mr-Ca-Nat
SH3	5	4.93	0.58	6.01	3.94	0.95	268.2	Mr-Msd-Ar-Gs-Gy
SH3	7-8	8.82	9.56	6	5.2	0.92	264.85	Mr-Msd-Ar-Gy-Nah-Ca-Gs-Ik
SH4	8	7.28	6.75	5.78	9.76	0.69	234	Msd-Hh-Mr-Mg-Gy-Mcd-Ca
VM4	7	7	9.4	4.75	9.89	0.68	232.85	Hh-Mr-Gy

Table 4. Result summary of freezing trajectories for pH, ionic strength (I), activity of water (a_w), freezing temperature in K (T_E), and precipitated minerals for waters set in equilibrium with PCO2= 6 mbar and initial pH 5-8.

CONCLUSIONS

The sustained values of a_w > 0.61 at high ionic strengths in all evolved waters suggests that microbes could survive high extents of evaporation and freezing. Under most conditions, evolved pH values are not exceptionally acidic and should allow for microbial activity (Jin and Kirk, 2018). However, a combination of low a_w and low pH may have a negative synergistic effect on microbial activity. The results indicate that microbial activity could potentially be feasible under modern CO_2 conditions as well as in the past, when Mars was possibly more temperate with a CO_2-rich atmosphere. While microbial activity appears to be feasible in brines set in equilibrium with the mineral assemblages investigated thus far, the effects of chaotropic and kosmotropic solutes requires further investigation. The negative effects of low a_w and high I may be counteracted by the presence of high concentrations of kosmotropic solutes such as NaCl, KCl, or Na-K sulfates (Cray et al., 2013). However, the presence of high concentrations of chaotropic solutes such as Ca-Mg chlorides, together with low aw will have a negative synergistic effect on microbial activity.

FUTURE WORK

Continued modeling efforts will investigate the characteristics of water chemistries in equilibrium with other sulfate, chloride, and perchlorate assemblages at temperatures and environmental conditions relevant to the past and present Martian surface, with particular future attention to geochemical modeling at sub-zero temperatures relevant to modern Martian conditions. We will also investigate the chao/kosmotropic effects on microbial habitability in hyper-saline brines by performing quantitative measurements of chao/kosmotropic effects (c.f. Cray et al., 2013) of mixtures of inorganic salts.

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