



# The Water Activity of Mars-relevant Multicomponent Brines: The Changing Influence of Perchlorate on Habitability over Time

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## Abstract

Low water activity limits the habitability of aqueous environments, and salts present on Mars are known to reduce water activity. As environmental brines are not pure solutions of a single salt, predicting their water activity is difficult without direct measurement. Martian brines are likely complex and dominated by ions including sulfates and perchlorates, unlike typical terrestrial aqueous environments dominated by sodium chloride. We used the Pitzer model to predict the water activity of multicomponent brines and tested against laboratory-produced brines, including for the first time perchlorate salts that are known to exist on Mars. Our calculations match measurements of single-salt solutions and predict the water activity of multicomponent brines with an accuracy dependent on the quality of thermodynamic data available for a given ion combination. We tested the hypothesis that some salts will dominate the water activity, and therefore habitability, of multicomponent brines. Some salts, such as sodium and magnesium sulfates, did not strongly modulate the water activity of the solution, whereas others such as magnesium chloride and some perchlorates did. Applied to the history of Mars, the data suggest that sulfates and sodium chloride present in Noachian and early Hesperian environments would not have limited habitability. Perchlorates produced photochemically later in the Amazonian could impose a water activity limit at high concentrations that is not significantly changed by other salts. Overall we found that magnesium and calcium chlorides mixed with perchlorates can reach the lowest water activity values and therefore the lowest habitability of the brines tested.

*Unified Astronomy Thesaurus concepts:* [Astrobiology \(74\)](#); [Habitable planets \(695\)](#)

## 1. Background

The habitability of an environment is restricted by the thermodynamic availability of water (water activity,  $a_w$ ). This restriction is thought to place a fundamental limit for life at just less than 0.6  $a_w$  (Stevenson et al. 2014). This water activity limit could have presented a significant problem for any life that may have existed on Mars due to high levels of dissolved salts in Martian aqueous systems (Tosca et al. 2008). In addition, the seemingly widespread presence of perchlorate salts that can strongly suppress water activity (Toner & Catling 2016) suggests that water activity can be a significant barrier to the habitability of liquid water on Mars, whether it exists on the surface (Chevrier et al. 2009; Hecht et al. 2009; Rivera-Valentín et al. 2020) or deep subsurface (Orosei et al. 2018), in addition to many other factors that can make Martian environments inhospitable for life. However, through its history the aqueous systems of Mars likely had spatially dynamic compositions, with dilute chloride fluids in the Noachian and Hesperian (Osterloo et al. 2010; Hynek et al. 2015), sulfate-rich fluids forming through the Hesperian (Bibring et al. 2006) and later emplacement of a global veneer of perchlorate added later in the Amazonian through photochemical production in the atmosphere (Catling et al. 2010).

Recent observations imply that transient aqueous environments may exist at or near the Martian surface, but also that these environments will contain complex mixtures of different salts including sulfur, chlorine, and oxychlorine species

(Marion et al. 2010; Ojha et al. 2015). Our understanding of how the physicochemical properties of such multicomponent brines vary is limited, especially at the high ionic strengths expected in these Martian environments (Marion & Kargel 2008), but since surface or subsurface brines present the likely only remaining habitable environment or most recent habitable environment on Mars, understanding their habitability is key in the search for life beyond Earth.

Previous work has investigated the dynamic chemistry of similar environments and modeled the precipitation of various minerals to understand how they formed (Marion et al. 2010). Here we approach the problem of measuring biologically relevant characteristics of extraterrestrial environments by using the Pitzer model to calculate water activity from the concentration of dissolved ions, as might be measured by a spacecraft probe with ion-specific electrodes. Such a measurement would contribute one aspect to an instantaneous habitability metric that could be determined by a planetary probe without requiring a complete understanding the full complexity of a planetary environment. This aligns with the ongoing development of miniaturized sensors that could, for example, measure ion concentrations and allow calculation of properties such as water activity (Shang et al. 2019) or measure water activity directly (Desai et al. 2021). Building such a metric would eventually lead toward a potential “habitability sensor.” We pay particular attention to the influence of perchlorate salts that have otherwise not been well explored in the context of a multicomponent environment until recently (Chevrier et al. 2022a, 2022b). Modeling these brines allows us to put constraints on the possibility of extant life in Martian surface brines, as well as understanding the history of habitability in past aqueous systems, with implications for the



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search for life, and for planetary protection and the definition of Special Regions (Rummel et al. 2014). Data can also be applied to the oceans of icy moons, which are thought to have similarly complex solute chemistries (Vance et al. 2018).

## 2. Methods

### 2.1. Water Activity Model

We produced a standalone Python script that predicts the water activity of multicomponent brines using the water activity components of the Pitzer model, following FREZ-CHEM (Marion & Kargel 2008) and including the extended perchlorate Pitzer coefficients of Toner et al. (2015b). The only environmental information required to calculate the water activity is the concentration of each ion under scrutiny and the temperature, streamlining the process of water activity calculation.

Water activity was calculated via the Pitzer equation for the osmotic coefficient (Equation (1)), with neutral species excluded:

$$\phi = 1 + \frac{2}{\sum m_i} \left\{ \begin{aligned} & \frac{-A_\phi I^{3/2}}{1 + bI^{1/2}} \\ & + \sum \sum m_c m_a (\beta_{ca}^\phi + (\sum m_i |z_i|) C_{ca}) \\ & + \sum \sum m_c m_c' (\Phi_{cc'}^\phi + \sum \sum m_a \psi_{cc'a}^\phi) \\ & + \sum \sum m_a m_a' (\Phi_{aa'}^\phi + \sum \sum m_c \psi_{ca'a}^\phi) \end{aligned} \right\}, \quad (1)$$

where  $\phi$  is the osmotic coefficient;  $m_i$  is the molality of cation (c) or anion (a) species  $i$ ;  $z$  is the ion charge;  $I$  is the ionic strength;  $A_\phi$  is the Debye–Hückel limiting law slope (calculated to be  $0.3886 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  at 293.15 K to match laboratory measurements; Spencer et al. 1990);  $b$  is a constant ( $1.2 \text{ kg}^{-1/2} \text{ mol}^{-1/2}$ ; Toner et al. 2015a); and  $\beta$ ,  $C$ ,  $\Phi$ , and  $\psi$  are functions calculated using the coefficients below for given combination of cations (c) and anions (a) that measure the interactions between them. Sums are calculated over all combinations of cations and anions in the mixture. Full details of how to calculate these functions are given by Marion & Kargel (2008).

The water activity ( $a_w$ ) is then given by

$$a_w = e^{\left(\frac{-\phi \sum m_i}{55.50844}\right)}. \quad (2)$$

Pitzer coefficients used in the calculations are shown in Tables 1–3. These ions were selected because of their relevance to Mars and to align with prior measurements of their biological impacts (Stevens & Cockell 2020). These coefficients are temperature dependent and those listed are calculated at 298.15 K. They could be recalculated for a reduction to 293.15 K to match laboratory measurements, but such a recalculation is beyond the scope of this work so we accept the small error introduced by this 5 K difference. One of the coefficients ( $\Psi_{\text{CaSO}_4\text{ClO}_4}$ ) from Toner et al. (2015b) produced highly anomalous results compared to the other values and appeared to be a transcription error, as it is 1 order of magnitude larger than similar coefficients, so it was reduced by a factor of 10 to bring it in line with the values for other ion mixtures. Water activity values were calculated for solutions with a single cation and anion, as well as mixtures with two cations and two anions.

**Table 1**  
 $\beta$  and  $C$  Parameters in the Na–Ca–Mg–Cl–SO<sub>4</sub>–ClO<sub>4</sub> System from FREZCHEM Used in This Study

Ion Pair	$\beta_0$	$\beta_1$	$\beta_2$	$C_\phi$	Reference
Na_Cl	7.63E-02	2.80E-01		1.27E-03	1
Na_ClO <sub>4</sub>	5.54E-02	2.76E-01		−1.18E-03	1
Na_SO <sub>4</sub>	2.62E-02	1.05E+00		2.80E-03	1
Ca_Cl <sub>2</sub>	3.04E-01	1.71E+00		−1.99E-03	1
Ca_ClO <sub>4</sub>	4.51E-01	1.76E+00		−5.01E-03	1
Mg_Cl	3.52E-01	1.82E+00		6.51E-03	1
Mg_ClO <sub>4</sub>	4.96E-01	2.01E+00		9.58E-03	1
Mg_SO <sub>4</sub>	1.27E-01	3.49E+00	−6.24E+00	5.29E-02	1

**Reference.** (1) Marion & Kargel (2008).

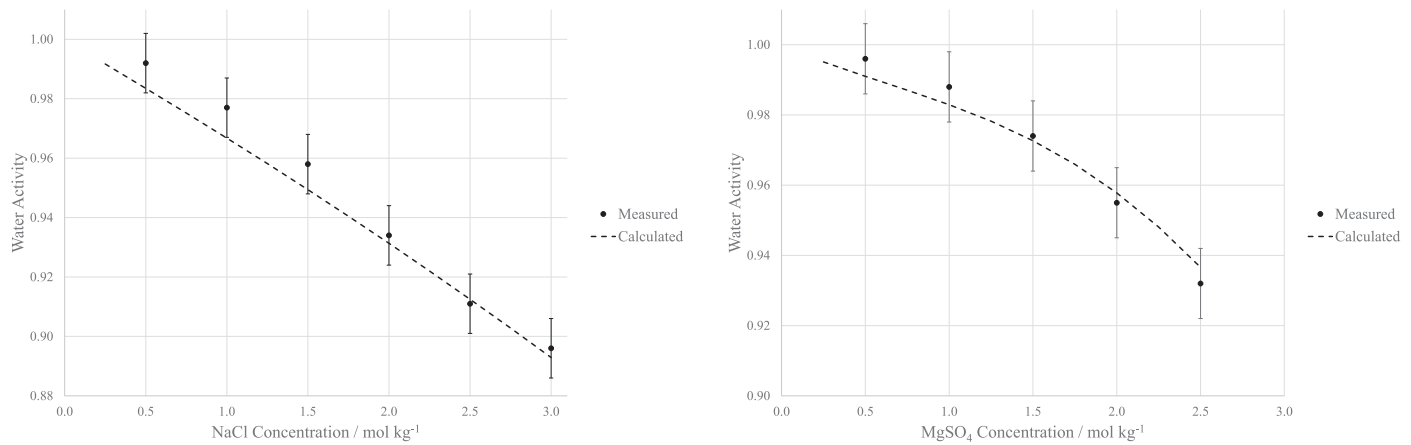
**Table 2**  
 $\theta$  Parameter for the Na–Ca–Mg–Cl–SO<sub>4</sub>–ClO<sub>4</sub> System Used in This Study

Ion Pair	$\theta$	Reference
Na_Ca	4.85E-02	1
Na_Mg	7.00E-02	1
Ca_Mg	1.24E-01	1
Cl_ClO <sub>4</sub>	3.10E-02	2
Cl_SO <sub>4</sub>	4.60E-02	1
SO <sub>4</sub> -ClO <sub>4</sub>	1.69E-01	2

**References.** (1) Marion & Kargel (2008), (2) Toner et al. (2015a).

### 2.2. Laboratory Verification

Calculated values were compared to measurements of laboratory-mixed brines of the same composition using pairwise combinations of NaCl, Na<sub>2</sub>SO<sub>4</sub>, NaClO<sub>4</sub>·(H<sub>2</sub>O), MgCl<sub>2</sub>, MgSO<sub>4</sub>·(7·H<sub>2</sub>O), and MgClO<sub>4</sub>·(6·H<sub>2</sub>O) salts from a range of commercial sources (Acros Organics, Fisher Chemical, Sigma Aldrich, and Alfa Aesar). The range of salts was restricted compared to the calculated values because every additional salt included doubled the number of measurements required. Because of the amounts required, stock availability, and the large number of measurements made, we were unable to use the same source of salt for all measurements. The salts were mixed with deionized water to a desired molal concentration, accounting for any water included in the hydrated salts, to a final volume of around 100 ml, using magnetic stirrers where necessary. The water activity of the solutions was measured at approximately 20°C using a Rotronic HC2-AW (Rotronic, UK) calibrated with saturated single-salt solutions of MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, NaCl, KCl, and KH<sub>2</sub>PO<sub>4</sub> with known water activity of 0.33, 0.44, 0.76, 0.85, and 0.965, respectively (Winston & Bates 1960). Due to the length of time required and number of measurements required, only one measurement of water activity was made at each concentration.



**Figure 1.** Comparison of calculated and measured water activity for NaCl solution and MgSO<sub>4</sub> solution. Error bars are estimated 0.01  $a_w$  measurement error.

### 3. Results

#### 3.1. Validation

To confirm the proper operation of our code, we compared our results to measured water activity values for some single-salt solutions that have been determined using existing systems—sodium chloride and magnesium sulfate. Our results are accurate to within 0.01  $a_w$ , and follow the shape of the measured curve well (Figure 1).

Given our addition of recently produced perchlorate coefficients into the Pitzer model (Toner et al. 2015b), we also validated our calculations for single perchlorate salt solutions with those measured using a different method by Toner & Catling (2016; Figure 2). Our modeled water activity is in good agreement with these data up to the solubility limits for these single salts.

#### 3.2. Multicomponent Brines

Having validated our code for single salts, we move to calculating the water activity of multicomponent brines, which are more relevant to real environmental brines because they are unlikely to be pure solutions of single salts. There is a dearth of available water activity measurements for mixed brines, so we made direct measurements of a range of mixed brines of different composition and concentration to compare to.

Residuals between calculated values and measurements are shown (Figure 3) using the solution's ionic strength as a virtual variable that combines the concentration values of the two salts in each mixture, allowing the residual to be easily plotted on one axis. Note that because the ionic strength is not unique for the whole range of concentrations of a given combination of salts this virtual variable should not be used to imply patterns of water activity of a particular mixed brine, but is useful for comparison's sake.

Most modeled values (two-thirds) are within 0.01  $a_w$  of measurements, suggesting our model is accurate, as we would expect a variation of around 0.01 per degree due to temperature fluctuations in the lab, depending on the specific solute (Winston & Bates 1960). There is a general trend that the error between the model and measurements increases with ionic strength, which is expected from the limitations of the Pitzer model, which is known to break down at high ionic strength (Marion & Kargel 2008). Some modeled values show much higher divergence from measurements, but there does not appear to be any specific combinations of ions that generally

**Table 3**

$\Psi$  Parameter for the Na–Ca–Mg–Cl–SO<sub>4</sub>–ClO<sub>4</sub> System Used in This Study

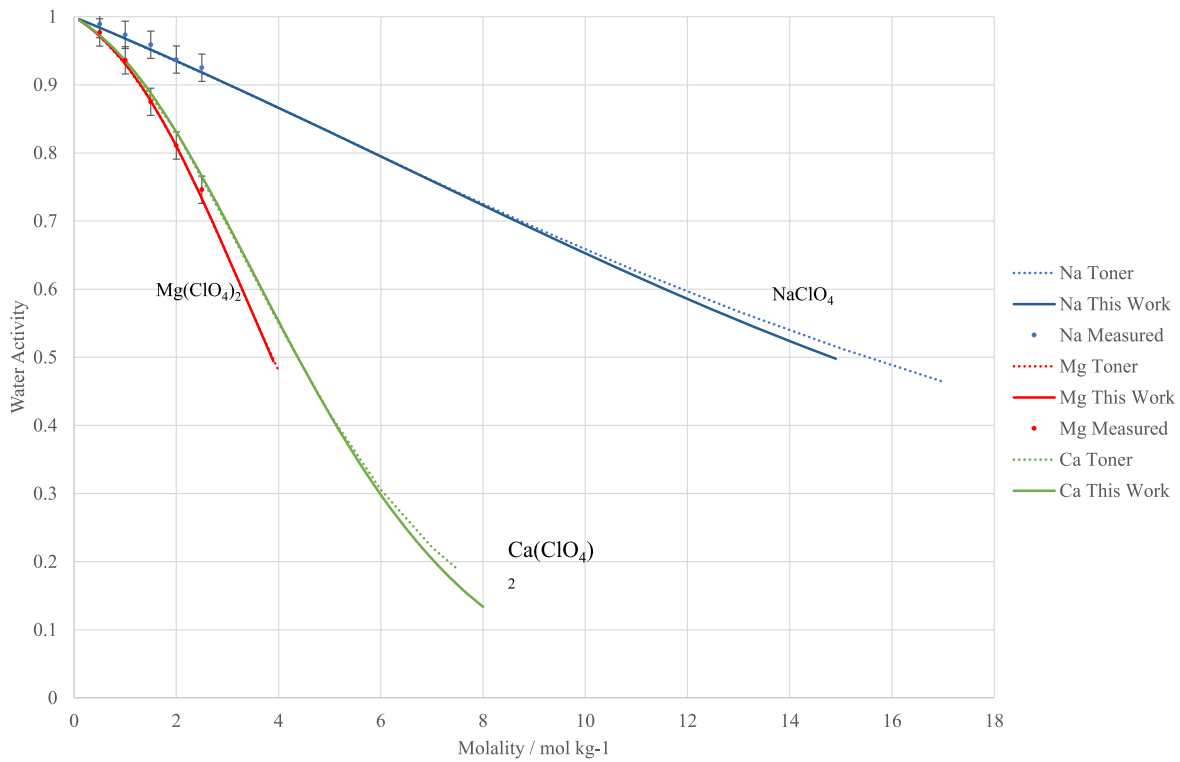
Ion Triplet	$\Psi_{IJK}$	Reference
Na_Cl_ClO <sub>4</sub>	−5.47E-03	2
Ca_Cl_ClO <sub>4</sub>	−3.91E-03	2
Mg_Cl_ClO <sub>4</sub>	−7.62E-04	2
Na_Cl_SO <sub>4</sub>	−1.45E-03	1
Ca_Cl_SO <sub>4</sub>	−5.44E-02	1
Mg_Cl_SO <sub>4</sub>	−1.83E-02	1
Na_SO <sub>4</sub> _ClO <sub>4</sub>	−1.41E-02	2
Ca_SO <sub>4</sub> _ClO <sub>4</sub>	−8.14E-02	3
Mg_SO <sub>4</sub> _ClO <sub>4</sub>	−7.49E-02	2
Na_Ca_Cl	−3.30E-03	1
Na_Mg_Cl	−2.48E-02	1
Ca_Mg_Cl	−2.38E-02	1
Na_Ca_SO <sub>4</sub>	−7.34E-02	1
Na_Mg_SO <sub>4</sub>	−9.91E-03	1
Ca_Mg_SO <sub>4</sub>	2.40E-02	1
Na_Ca_ClO <sub>4</sub>	−1.18E-02	2
Na_Mg_ClO <sub>4</sub>	−2.83E-03	2
Ca_Mg_ClO <sub>4</sub>	−2.29E-02	2

**References.** (1) Marion & Kargel (2008), (2) Toner et al. (2015a), (3) modification of Toner et al. (2015a).

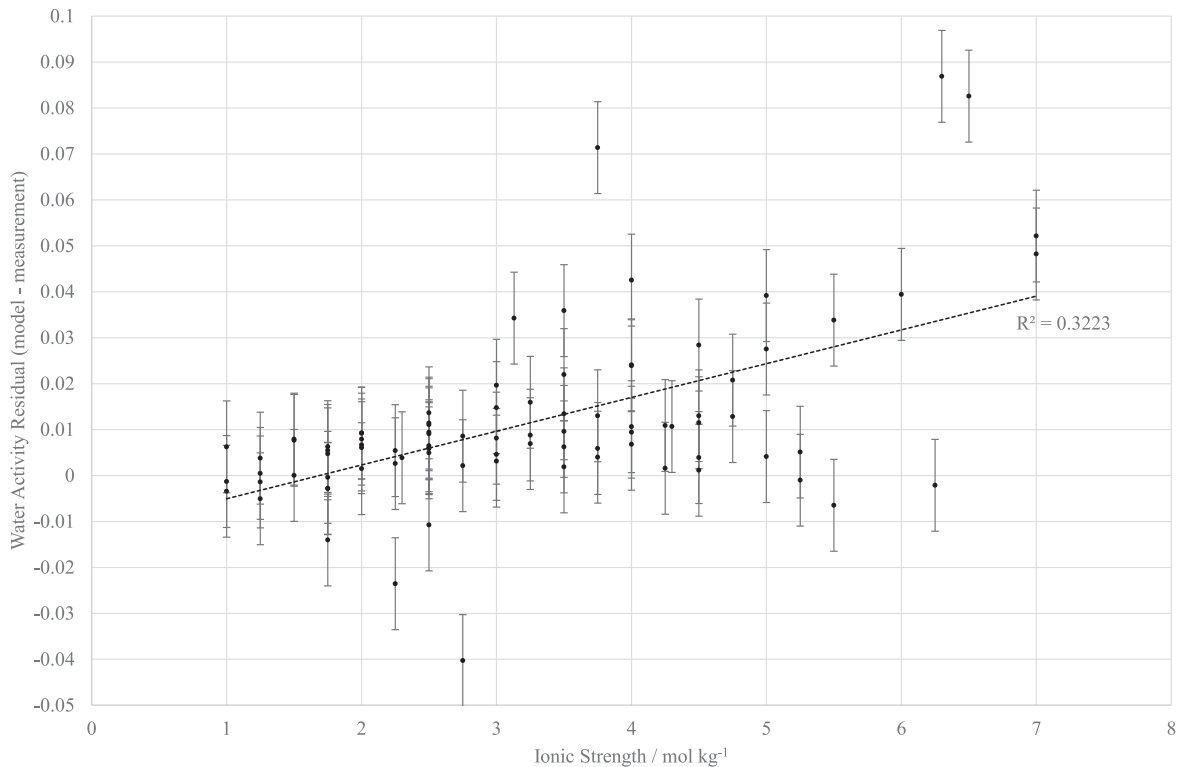
produce less accurate results (Figure 4), and this could be due to the interpolated nature of the coefficients used (Toner et al. 2015a), especially at higher ionic strength where errors are compounded.

#### 3.3. Mapping the Limits of Life Imposed by Water Activity

Having demonstrated the accuracy of our model, we can use it to predict the concentrations of mixed brines that will limit life by assuming a water activity limit to biological activity of



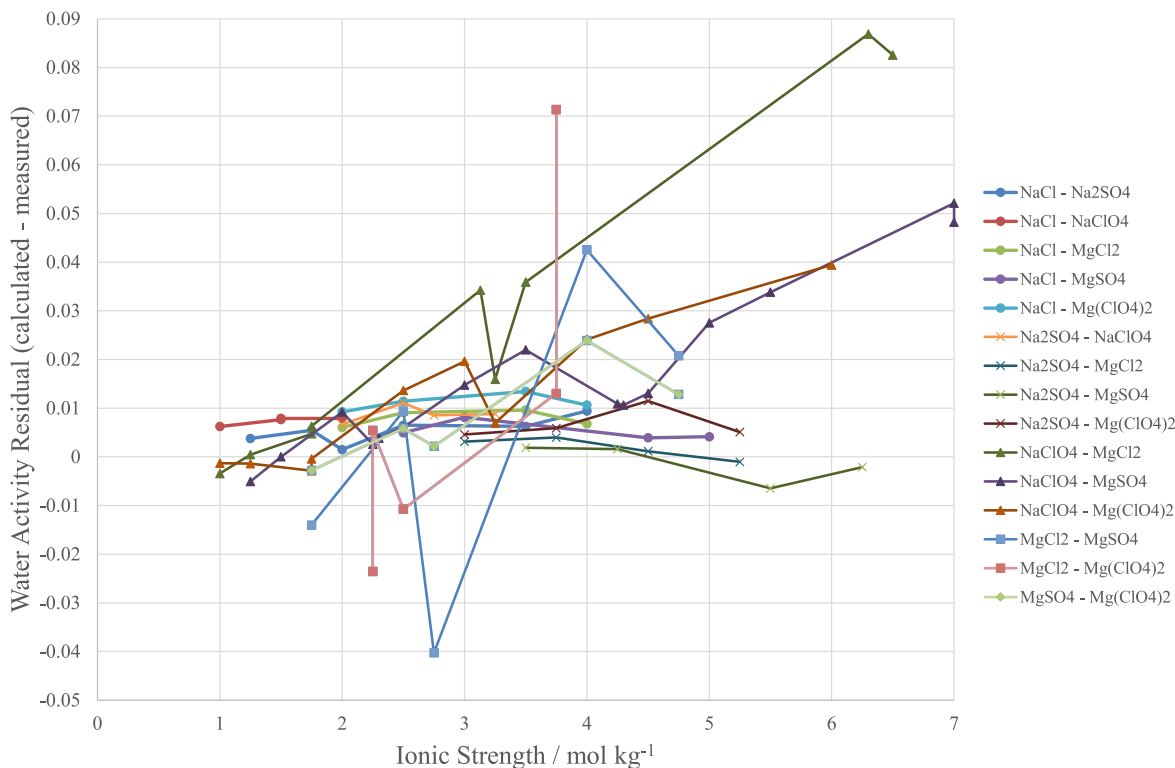
**Figure 2.** Comparison of calculated water activity from our model vs. those calculated using a different method from experimentally measured heat capacities of Toner & Catling (2016).



**Figure 3.** Water activity residual (modeled value–measured value) for all measured multicomponent brines, plotted against the total ionic strength of the mixed solution. Line of best fit shown for all values. Error bars are estimated 0.01  $a_w$  variation in laboratory measurements.

around 0.6  $a_w$  (Stevenson et al. 2014). Figure 6 shows the water activity isolines for 0.55  $a_w$  and 0.65  $a_w$ , with traffic-light shading between to show the field of habitability for a given combination of brines. The upper limit of each concentration

axis is set as the saturation point for the respective single salt. The green area of each plot shows where water activity is at a habitable level ( $>0.65 a_w$ ) and the red at uninhabitable levels ( $<0.55 a_w$ ). It should be noted that the combined solubility of



**Figure 4.** Same data as in Figure 5, but separated by salt combination. No pattern of a particular ion or ions increasing the error in calculations is evident.

the mixed salts is not accounted for in these plots as this would require full geochemical modeling, which is beyond the scope of this study. Instead, these plots show the lower bounds on the habitability imposed by water activity in multicomponent brines. Real brines with multiple solutes will saturate before reaching the upper right corner of these plots and therefore will not reach the lowest values of water activity shown here.

Because each salt depresses water activity differently, some solutions become saturated before they reach the  $0.55 a_w$ . These combinations of solutes (NaCl/Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>/NaCl, and MgSO<sub>4</sub>/Na<sub>2</sub>SO<sub>4</sub>) therefore never reach this lower habitability limit at any physically achievable concentration under these conditions.

The key metric for habitability is the gradient of the isolines. Salts with smaller effects on the water activity create flatter isolines. For example, Na<sub>2</sub>SO<sub>4</sub> shows almost vertical isolines when mixed with most other salts, implying it has a weak effect on water activity relative to these salts. MgSO<sub>4</sub> is similar, with a lower gradient than most other salt combinations. Other combinations are far more dependent on the specific salts in question, but generally combinations including NaClO<sub>4</sub>, MgCl<sub>2</sub>, Mg(ClO<sub>4</sub>)<sub>2</sub>, CaCl<sub>2</sub>, and Ca(ClO<sub>4</sub>)<sub>2</sub> generate large uninhabitable spaces beyond the  $0.55 a_w$  isoline.

#### 4. Discussion

We built a standalone module that calculates the water activity of multicomponent aqueous solutions using the Pitzer model, allowing us to assess the habitability of these solutions. This can be applied to potential Martian brines, which are likely to be complex and contain mixtures of salts that are rare on Earth.

Our module accurately predicts the water activity of single-solute and multicomponent brines of pairs of Mars-relevant

salts up to their saturation limits, with the accuracy reducing with the total ionic strength of the solution. Our code is limited in its ability to consider solubility curves of mixed brines and changing temperatures. When solubility limits of particular ions are reached they will precipitate out as salts. Tracking solubility effects in multicomponent fluids depends sensitively on the composition and environmental conditions (Tosca et al. 2008), and because our model does not track solubility, Figure 5 shows only the lower limits of water activity for each combination of salts. In reality, precipitation will occur before the solution reaches the low water activity values at the high concentrations of both salts. It would be possible to calculate solubility limits using other more fully featured code that already exists or by extending our module, but this was beyond the scope of our study. Our aim was to be able to rapidly assess habitability with only a few measurements that could be conducted in situ in an aqueous environment, so our focus is on ions in solution only.

The quality of the results produced by the model is controlled by the quality of the input coefficients. As these coefficients must be empirically generated, the scope of the model is limited by what measurements are available. Although we have only included pairwise mixtures of salts, modeling more complex mixtures is possible with the Pitzer model, and existing programs such as Geochemist's Workbench and PHREEQC have this functionality. However, for some ion species the higher-order virial coefficients of the Pitzer model are not necessarily negligible (Pitzer & Press 1991), and because the solution of the Pitzer model used here (and in most other programs) only includes the second-order virial coefficients, their accuracy may be compromised at the high concentrations required to simulate Martian brines. In particular, some relevant salts such as calcium chloride and perchlorates have displayed behavior that deviates from





**Figure 5.** Water activity isolines showing limits of habitability for all tested combinations of salts. Red areas should be uninhabitable as they are below 0.55  $a_w$ , yellow shows where habitability will be possible for the most extreme known organisms ( $0.55 < a_w < 0.65$ ), and green shows where brines of that combination of salts should be habitable ( $a_w > 0.65$ ).

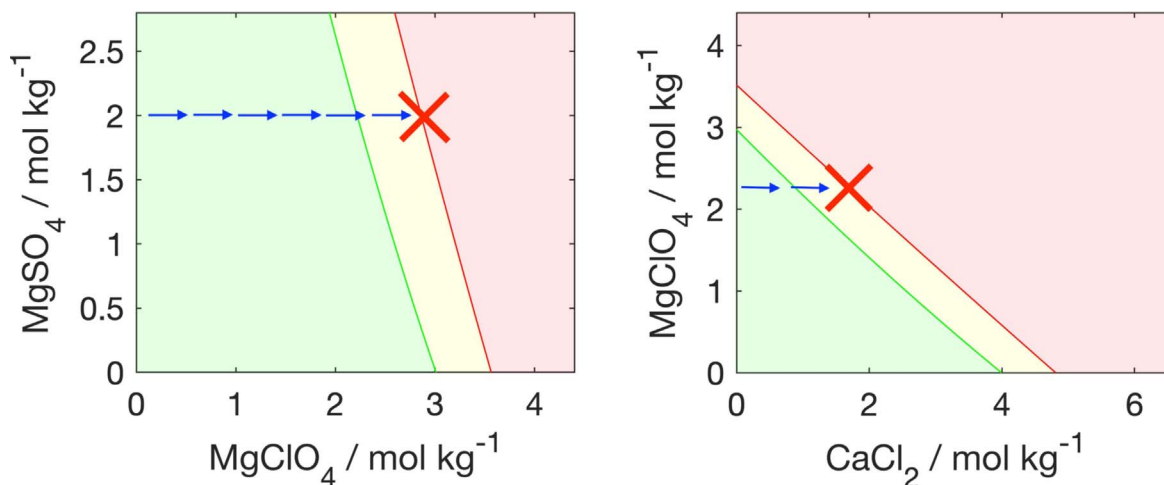
second-order descriptions at high concentration (Phutela & Pitzer 1983; Pitzer & Press 1991) and measurements of higher-order coefficients for relevant salts are sparse, so to extend our code to predict Martian habitability with confidence is no small task. In some cases, where one salt dominates the system, we can use results such as those shown in Figure 5 to determine whether the simulation can be simplified to a one- or two-salt system. This problem is exacerbated when looking at Martian brines because of their likely complex nature (Tosca et al. 2011) and high ionic strength (Fox-Powell et al. 2016).

Generalizing these results to other ions or more complex brines is difficult—while we can make general statements about some salts or ions reducing water activity more or less, in mixed brines the balance of these effects is sensitive to all of their properties. For example, while the influence of  $\text{Na}_2\text{SO}_4$  in a mixed brine can be ignored at all concentrations up to saturation, the influence of  $\text{MgSO}_4$  can only be ignored at low concentrations, but at high concentrations relative to saturation it has a significant effect on water activity. Compare this to  $\text{Mg}(\text{ClO}_4)_2$ , whose influence cannot be discounted at any concentration. These effects cannot be predicted from any single value of coefficient for these ions as there is no direct correlation between the coefficients and the strength of their

impact. Rather, the coefficients that measure the interactions between the different ions clearly have a major impact, making blanket statements about the effect of a particular single solute impossible.

Because the temperatures these results were measured at are well above the temperature of Martian brines at the surface and in the subsurface up to extreme depths where the ambient temperature could reach 20°C (Michalski et al. 2013), they represent a lower limit for the habitability of similar brines at Martian temperatures. Lower temperatures increase the water activity of a given brine, though the size of this effect is solute specific (Winston & Bates 1960), so the habitability isolines shown in Figure 5 will be shifted up and right to a variable extent in each plot, and this is true for brines more generally. The lower temperature would also reduce the solubility limit of dissolved salts, reducing the maximum molar concentration and reducing the uninhabitable area (red) in the plots of Figure 5, therefore relatively increasing the habitability of the brines compared to our data where they exist as a liquid on Mars.

Applying the results of our model to the context of Mars allows us to investigate the habitability of Martian brines over time. The geochemistry of the Martian surface suggests that



**Figure 6.** (a) An initially habitable magnesium sulfate dominated brine becoming enriched in magnesium perchlorate remains habitable until the concentration of perchlorate reaches  $\sim 75\%$  of saturation. (b) An initially habitable magnesium perchlorate dominated brine becoming enriched in calcium chloride becomes uninhabitable well before either salt reaches saturation.

many brines present through the history of the planet would have been sulfate-rich (Vaniman et al. 2004; Bibring et al. 2006; Tosca et al. 2011; Karunatillake et al. 2014). Because sodium and potassium are depleted relative to terrestrial minerals (Clark et al. 2005; McLennan 2012; Hynek et al. 2015), magnesium and iron sulfates would likely be dominant in surface brines. However, chlorides have been detected from early in Mars's history (McLennan et al. 2005; Osterloo et al. 2008), and the depression of freezing-point caused by perchlorates has been implicated in allowing liquid water to exist at the surface (Hecht et al. 2009) and in subsurface reservoirs (Orosei et al. 2018). As Martian perchlorate was likely generated via photochemical alteration of Amazonian-era volcanically generated chlorine (Catling et al. 2010; Wilson et al. 2016), the addition of perchlorate to Martian brines would have happened more recently, with important implications for the continuing habitability of these aqueous systems.

In particular, our results allow us to explore the habitability of concentrated brines that might have existed in the Hesperian era, when the hydrological cycle on Mars declined and acid weathering and evaporation generated widespread chloride and sulfate-dominated fluids on the planet. Combinations of sodium chloride and sodium sulfate, sodium chloride and magnesium sulfate, and sodium sulfate and magnesium sulfate remain above the 0.6 water activity threshold at all values above their solubility. Therefore, considering only water activity limits, any of these combinations of salts will not have presented a barrier to life, though at high concentrations other factors such as high ionic strength or kosmotropic effects may have limited habitability (Cray et al. 2013; Fox-Powell et al. 2016). Generally, combinations including sodium or magnesium sulfate retain habitability up to higher values of dissolved salts than other salts investigated here. These results would support the high priority of sulfate deposits as priority targets for life detection missions, with these deposits widespread across the surface (Rapin et al. 2019). The stronger effects of chlorine and oxychlorine species on water activity imply that where evidence suggests the presence of past aqueous environments dominated by these ions (Osterloo et al. 2008) habitability may have been more limited.

The inclusion of perchlorates throughout the Amazonian further complicates the picture. For example, if we imagine a

brine initially dominated by sulfates but gradually being enriched in perchlorate (Figure 6(a)), the water activity of the brine starts above the lower limit of 0.55 for any starting concentration of magnesium sulfate, implying a habitable brine. The addition of perchlorate reduces the water activity until it moves through the lower habitability limit at higher concentrations of  $\text{Mg}(\text{ClO}_4)_2$ . We do not know how abundant perchlorates would have been in past aqueous environments on Mars, but to reach these high concentrations there must have been effective concentrating mechanisms considering that only millimolar levels are observed today in the Martian soil (Hecht et al. 2009). The requirement of near-saturation levels of perchlorate to explain observations of liquid brines under Martian conditions (Orosei et al. 2018) suggests that the concentration of perchlorate may be highly variable across Mars, meaning that to assess the habitability of such perchlorate-containing Martian brines we require specific data about the environment under scrutiny, especially the total abundance of water that will also moderate habitability (Rivera-Valentín et al. 2020).

However, the absolute perchlorate concentration must still be high to reach these low values of water activity. A perchlorate-containing brine does not become uninhabitable (i.e., below an  $a_w$  of 0.55) until the concentration of  $\text{Mg}(\text{ClO}_4)_2$  exceeds  $\sim 3\text{--}3.5 \text{ mol kg}^{-1}$ , and similarly high concentrations are required when adding  $\text{Na}(\text{ClO}_4)$  and  $\text{Ca}(\text{ClO}_4)_2$ . At values below these concentrations, water activity remains above the limits for life, which is consistent with various studies showing growth in perchlorate brines by halophilic and nonhalophilic organisms (Heinz et al. 2019; Stevens & Cockell 2020).

Our results also have implications for a context where ancient sulfate deposits could be dissolving into more recently generated perchlorate brines. For example, if a dilute and habitable perchlorate brine dissolves material from a dissimilar geological unit containing sulfate, the water activity would not be reduced substantially by the addition of sulfate. In contrast, certain salts do moderate water activity strongly when added to others. For example, magnesium chloride and calcium chloride concentrations on their own reduce water activity substantially at high concentrations and when added to perchlorates they would produce combined conditions that might place limits on life, shown by the high gradients of these plots in Figure 5.

These salts have not been detected directly on Mars, but they show how a greater knowledge of the types of salts that exist and existed on Mars and their ionic combinations is required to be able to predict how the mixing of ions from different geological units in aqueous environments will determine local habitability. Other salts that are known to exist on Mars could also have large effects on habitability, for example iron, chlorate, or nitrate ions driving the water activity to uninhabitable levels or introducing other habitability effects well before other salts precipitate (Tosca et al. 2008).

The important thing to note from our results is that the presence of perchlorate in an aqueous environment does not necessarily make it uninhabitable. When at low concentrations or combined with chloride or sulfate salts, perchlorate-containing brines remain at a water activity above habitable limits, but at the high concentrations required to maintain a liquid state at the Martian surface perchlorate brines are likely to be uninhabitable. This means that the habitability of the environment depends sensitively on the composition of the aqueous solution, and because on Mars the composition of any such environments will have varied significantly over time we cannot make definitive statements of habitability without detailed compositional information. High concentrations of perchlorate or chloride salts could have reduced water activity below habitable levels, but in mixed environments such as these potential Martian aqueous systems, the prevalence of sulfate ions could have moderated the restriction of habitability.

We would like to thank David Catling for enlightening discussion on the topic and for John Toner for providing advice and raw data for our comparisons. We also thank two anonymous reviewers for their comments.

### Data Availability

All raw data is available through the University of Edinburgh Datashare doi:10.7488/ds/3755.

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