



## Soluble sulfate in the martian soil at the Phoenix landing site

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[1] Sulfur has been detected by X-ray spectroscopy in martian soils at the Viking, Pathfinder, Opportunity and Spirit landing sites. Sulfates have been identified by OMEGA and CRISM in Valles Marineris and by the spectrometers on the MER rovers at Meridiani and Gusev. The ubiquitous presence of sulfur has been interpreted as a widely distributed sulfate mineralogy. One goal of the Wet Chemistry Laboratory (WCL) on NASA's Phoenix Mars Lander was to determine soluble sulfate in the martian soil. We report here the first in-situ measurement of soluble sulfate equivalent to  $\sim 1.3(\pm 0.5)$  wt% as  $\text{SO}_4$  in the soil. The results and models reveal  $\text{SO}_4^{2-}$  predominately as  $\text{MgSO}_4$  with some  $\text{CaSO}_4$ . If the soil had been wet in the past, epsomite and gypsum would be formed from evaporation. The WCL-derived salt composition indicates that if the soil at the Phoenix site were to form an aqueous solution by natural means, the water activity for a dilution of greater than  $\sim 0.015$  g  $\text{H}_2\text{O}/\text{g}$  soil would be in the habitable range of known terrestrial halophilic microbes. **Citation:** Kounaves, S. P., et al. (2010), Soluble sulfate in the martian soil at the Phoenix landing site, *Geophys. Res. Lett.*, 37, L09201, doi:10.1029/2010GL042613.

### 1. Introduction

[2] Sulfur has been detected by X-ray spectroscopy in martian soils at the Viking [Clark, 1993], Pathfinder [Wänke et al., 2001], Opportunity [Clark et al., 2005] and Spirit [Rieder et al., 2004] landing sites. Spectroscopic detection of sulfur minerals from orbital and landed missions has added to the evidence for potentially widespread occurrence of sulfates on Mars [Christensen et al., 2004; Bibring et al., 2007]. Sulfates have been identified by OMEGA in Valles Marineris [Gendrin et al., 2005], Meridiani [Arvidson et al., 2005], and in a large dune field approximately 700 km north of the Phoenix landing site where gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )

was detected [Langevin et al., 2005]. The Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) has identified sulfates in numerous sites including thin stratified deposits at several locations and km-deep sulfate-rich canyons and mounds [Bishop et al., 2009; Murchie et al., 2009]. The Mars Exploration Rover (MER) Spirit in the Columbia Hills area of Gusev Crater has identified shallow soils enriched in Mg-sulfates [Yen et al., 2005; Wang et al., 2006; Gellert et al., 2004] as well as other soils containing mixtures of Fe-, Ca-, and Mg-sulfates [Johnson et al., 2007; Yen et al., 2008; Ming et al., 2006]. The MER Mini-TES and Mössbauer instruments have also both detected sulfates [Glotch et al., 2006; Morris et al., 2006]. The ubiquitous presence of sulfur in soils has been interpreted as a widely distributed sulfate mineralogy [Yen et al., 2005].

[3] One goal of the Wet Chemistry Laboratory (WCL) [Kounaves et al., 2009a] on board NASA's 2007 Phoenix Mars Lander [Smith et al., 2009] was to measure and directly confirm the identity and solubility of the sulfur species in the martian soil. The earlier analysis of the data for the acquired samples showed the presence of several ionic species with average solution concentrations of 3.3 ( $\pm 2$ ) mM  $\text{Mg}^{2+}$ , 2.4 ( $\pm 0.5$ ) mM  $\text{ClO}_4^-$ , 1.4 ( $\pm 0.3$ ) mM  $\text{Na}^+$ , 0.6 ( $\pm 0.3$ ) mM  $\text{Ca}^{2+}$ , 0.5 ( $\pm 0.1$ ) mM  $\text{Cl}^-$ , and 0.4 ( $\pm 0.1$ ) mM  $\text{K}^+$ , with a moderate pH of  $\sim 7.7$  ( $\pm 0.3$ ), and an average conductivity of  $\sim 1.4$  ( $\pm 0.5$ ) mS/cm. The charge balance, calculated ionic strength, and conductivity, showed a discrepancy, suggesting that the solution contained unidentified anionic species at a minimum of several mM [Hecht et al., 2009; Kounaves et al., 2010].

[4] We report here for the first time the presence of soluble sulfate, its concentration, and possible phases, in the soil at the Phoenix landing site. Calculations based on the results of the soil salt composition indicate that the water activity of brines formed at this location would be tolerable for terrestrial microbes.

### 2. Analytical Methodology

[5] The Phoenix WCL received three  $\sim 1$  cm<sup>3</sup> soil samples on mission sol 30 (cell-0, surface, Rosy Red), sol 41 (cell-1, subsurface, Sorceress-1), and sol 107 (cell-2, subsurface, Sorceress-2), where "sol" measures Martian solar days elapsed from the landing, and the names refer to the samples and sampling sites assigned by the Phoenix team. Phoenix did not measure soil density; however, density of the Phoenix soils was estimated at 1.0 g/cm<sup>3</sup> based on the Viking-2 data for the bulk density of the martian fine granular material of 1.1 g/cm<sup>3</sup> [Clark et al., 1977]. The two subsurface samples were sublimation lag scraped off the ice table at  $\sim 5$  cm depth. The location, acquisition, and delivery of samples by the robotic arm has been previously described [Arvidson

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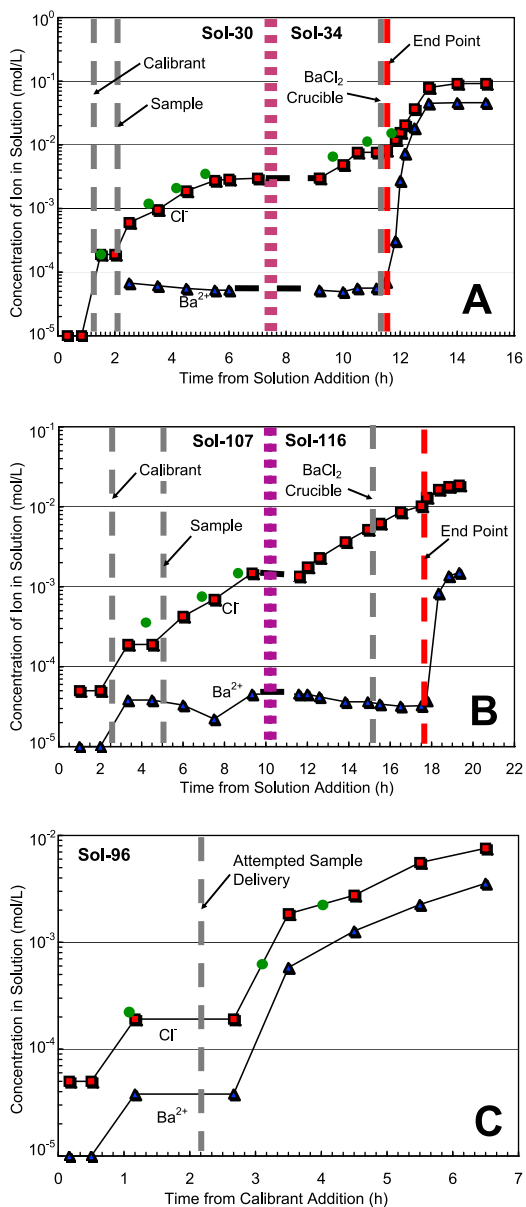
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**Figure 1.** Concentrations of the barium and chloride in the leached soil samples as measured by the  $\text{Ba}^{2+}$  ISE ( $\blacktriangle$ ),  $\text{Cl}^-$  ISE ( $\blacksquare$ ), and chronopotentiometric  $\text{Cl}^-$  ( $\bullet$ ) in each of the WCLs. Results are shown for (a) “Rosy Red” sample in cell 0 on sols 30 and 34, (b) Sorceress-2 sample in cell 2 on sols 107 and 116, and (c) “blank” in cell 3 on sol 96. In all cases it’s clear that although  $\text{BaCl}_2$  was being added to the solution, the concentration of  $\text{Ba}^{2+}$  remained at or below its calibration level.

*et al.*, 2009]. Each soil sample was added to 25 mL of a leaching solution in a WCL cell and analyzed for solvated ionic species, pH, and solution electrical conductivity [Kounaves *et al.*, 2010].

[6] Analysis of soluble  $\text{SO}_4^{2-}$  in the martian soil after addition to the WCL solution was performed by precipitation with  $\text{Ba}^{2+}$  added as  $\text{BaCl}_2$ . Each WCL cell was equipped with a reagent dispenser that could release up to three individual  $\sim 0.11$  g additions of powdered  $\text{BaCl}_2$ , each contained

within a miniature cylindrical crucible. The dissolution of the  $\text{BaCl}_2$  allows the  $\text{Ba}^{2+}$  to react with the soluble  $\text{SO}_4^{2-}$  in the sample and precipitate as  $\text{BaSO}_4$  [Kounaves *et al.*, 2009a; Lukow, 2005]. Each  $\text{BaCl}_2$  addition allowed for determination of  $\text{SO}_4^{2-}$  up to 5 wt %, or for a total of 15 wt % if all three additions were used.

[7] The concentrations of the added  $\text{Ba}^{2+}$  and  $\text{Cl}^-$  are monitored by their respective ion selective electrodes (ISEs) and the  $\text{Cl}^-$  also by chronopotentiometry (CP). Under the analytical conditions existing in the solution during the analysis on Mars, the  $\text{BaSO}_4$  precipitation technique is rapid and highly selective for  $\text{SO}_4^{2-}$  (solubility product,  $K_{sp}$ , at  $7^\circ\text{C} \sim 5 \times 10^{-11}$ ) with no interference from  $\text{BaCO}_3$ . Thus, monitoring  $[\text{Ba}^{2+}]$  indicates when there is no longer any  $\text{SO}_4^{2-}$  remaining to precipitate the  $\text{Ba}^{2+}$ , while monitoring the  $[\text{Cl}^-]$  gives the total amount of  $\text{BaCl}_2$  added. The  $\text{Ba}$ -ISE response is not used for quantifying the  $\text{Ba}^{2+}$ , but solely as an indicator of when the end point has been reached. The amount of  $\text{SO}_4^{2-}$  precipitated is equal to half the difference between the concentrations of  $\text{Cl}^-$  just before the addition and when the endpoint is reached. As described below, the addition process for the  $\text{BaCl}_2$  unexpectedly deviated from the original plan, but the overall analytical methodology can be applied to understanding the sulfate abundance in the soil.

### 3. Results

[8] Over the course of the WCL analyses, the chloride concentration slowly increased at a rate of  $\sim 1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ h}^{-1}$  (Figure 1a and 1b) in all samples, except for cell-0, where it stabilized by the end of the sol. This was initially thought to result from the sample itself releasing chloride. However, no other cation was observed to increase simultaneously with the chloride. During several attempts to deliver sample to the fourth WCL cell (cell-3) on sol 96, the soil became lodged on top of the delivery funnel and none was dispensed into the solution. The analysis run on cell-3 thus constituted a “blank”. As shown in Figure 1c, the  $\text{Ba}^{2+}$  and  $\text{Cl}^-$  sensors both showed an increase in concentration at a  $\text{Ba}:\text{Cl}$  ratio of 1:2. Similar increases were not seen for other ions. The independent CP analysis for  $\text{Cl}^-$  also confirmed the increase.

[9] The most consistent model for explaining the above results, is that the powdered  $\text{BaCl}_2$ , contained in three separate containers (crucibles) in the WCL reagent dispenser and intended for the second sol analysis, leaked into the WCL solution during the first sol. The high relative humidity present in the WCL, after the leaching solution was dispensed, would most likely have caused water to condense on the reagent dispenser and allowed the  $\text{BaCl}_2$  to creep or drip into the WCL cell. The same is seen to occur during the other analyses, not only on sols 30 and 107, but also on the following sols (34 & 116) where sulfate analyses were to take place. Unfortunately, the  $\text{Ba}^{2+}$  sensor in cell-1 failed and thus no analyses were possible on sols 41 and 43.

[10] After the initial solution and calibrants were added, a delay was observed, suggesting that  $\text{BaCl}_2$  leakage did not begin in cells 0, 1 and 3 until after soil addition. Furthermore, there was no observed increase indicated by the ISE, CP, or conductivity sensors during the pre-sample calibration periods. The barium chloride leakage was not seen in pre-flight testing, and we are currently investigating pos-

**Table 1.** Summary of Results for All WCL Cells<sup>a</sup>

WCL Cell	Sol(s) Analyzed	Sample	SO <sub>4</sub> <sup>2-</sup> in Solution (mM)	% as SO <sub>3</sub> in Soil
0	30, 34	Rosy Red	4.8 (±1.5)	1.0 (±0.3)
1	41, 43	Sorceress-1	n.p. <sup>b</sup>	n.p. <sup>b</sup>
2	107, 116	Sorceress-2	5.9 (±1.5)	1.2 (±0.3)
3	96	Blank	-	-

<sup>a</sup>Concentration in soil assumes delivery of a 1 g sample with a density of 1 g/cm<sup>3</sup>.

<sup>b</sup>Barium sensor failed thus sulfate analysis was not possible.

sible causes. However, at present the results of the analysis along with the consistent behavior from cell to cell, gives us confidence that the values obtained for the sulfate are reliable.

[11] Figures 1a and 1b show the titration curves used to determine the total soluble sulfate, [SO<sub>4</sub><sup>2-</sup>]<sub>T</sub>, present in the WCL cell-0 (sols 30 and 34) and cell-2 (sols 107 and 116) after delivery of martian soil. The addition of the BaCl<sub>2</sub> is indicated by and proportional to half the increasing Cl<sup>-</sup> concentration. The [Ba<sup>2+</sup>] remains relatively constant until the second sol when the crucible containing additional powdered BaCl<sub>2</sub> was added. A short time after this addition, both the [Ba<sup>2+</sup>] and [Cl<sup>-</sup>] rapidly increase, indicating that the Ba<sup>2+</sup> was no longer being precipitated by SO<sub>4</sub><sup>2-</sup>. Thus the total sulfate present, [SO<sub>4</sub><sup>2-</sup>]<sub>T</sub>, is equal to Δ[Cl<sup>-</sup>]/2 (i.e., the change in [Cl<sup>-</sup>] from immediately after the sample addition response to the start of the Ba<sup>2+</sup> increase that indicated all the SO<sub>4</sub><sup>2-</sup> had been titrated). For cell-0 this gives [SO<sub>4</sub><sup>2-</sup>]<sub>T</sub> = 4.8 (±1.5) mM in solution. Assuming a 1 cm<sup>3</sup> sample with a density of 1 g/cm<sup>3</sup>, and that all the SO<sub>4</sub><sup>2-</sup> was dissolved, this is equivalent to 1.2(±0.5) wt % SO<sub>4</sub><sup>2-</sup> in the soil. For cell-2 this gives [SO<sub>4</sub><sup>2-</sup>]<sub>T</sub> = 5.9 (±1.5) mM equivalent to 1.4(±0.5) wt % SO<sub>4</sub><sup>2-</sup>. On average this is equivalent to approximately 1.1(±0.5) wt % sulfur reported as SO<sub>3</sub> in the soil. Results of analyses are summarized in Table 1.

#### 4. Discussion

[12] With minor exceptions [Clark *et al.*, 2005; Ming *et al.*, 2006], soils at previous landing sites have been reported to contain 4 to 8 wt % SO<sub>3</sub> [Clark, 1993; Wänke *et al.*, 2001; Clark *et al.*, 2005; Rieder *et al.*, 2004], and have a nearly uniform S/Cl molar ratio of ~4:1. Based on the previous data for the S/Cl ratio, one would predict that given a total of 2.9 mM Cl in the WCL solution, it should then have contained ~12 mM SO<sub>4</sub><sup>2-</sup>, assuming all of the SO<sub>4</sub><sup>2-</sup> was soluble. The molar ratio of sulfur (as SO<sub>4</sub><sup>2-</sup>) to total chloride (Cl<sup>-</sup> + ClO<sub>4</sub><sup>-</sup>) as measured by the WCL for the Phoenix soils is ~2:1. This factor of 2 discrepancy may be due to: (1) some of the sulfur measured by XRF in previous missions is in a form that is non-soluble, or only sparingly soluble, within the time frame of the WCL analyses; or (2) the Phoenix soil is simply different from those analyzed at other locations and sulfate or perchlorate are lower or higher, respectively, in these soils.

[13] The Phoenix Thermal and Evolved Gas Analyzer (TEGA) analyses found that the Phoenix soil contained 3–5% CaCO<sub>3</sub> [Boynton *et al.*, 2009; Kounaves *et al.*, 2009b], however, as of this point in time the TEGA data with respect to possible evolution of SO<sub>2</sub> is still being evaluated. Such types of analyses may be complicated by inter-

mediate product reactions during the pyrolysis process and also highly dependent on temperature and sulfate phases present.

[14] There are several plausible soluble mineral phases that may be responsible for the SO<sub>4</sub><sup>2-</sup> measured by WCL. These include a variety of K-, Na-, Fe-, Mg-, and Ca-sulfates. However, several can be excluded from being present in any significant amounts. Soluble Fe-sulfates are eliminated since pre-flight characterization tests clearly showed that the presence of >0.1 mM Fe<sup>2+/3+</sup> would have poisoned several of the ion selective electrode (ISE) sensors and would have been detected by cyclic voltammetry (CV). In addition, Fe-sulfates would have buffered the solution at a more acidic pH. Since none of the above responses were observed with any sample, the presence of soluble Fe-sulfate at >0.1 mM in the WCL samples is not likely. Both K and Na forms are plausible, but with only 0.4 mM K<sup>+</sup> and 1.4 mM Na<sup>+</sup> present in the sample solution, they would account for only a fraction of the sulfate species. This leaves MgSO<sub>4</sub> and CaSO<sub>4</sub> as the most probable phases present in the soil.

[15] In order to further constrain the sulfate mineral phase (s) present in the soil samples, we performed equilibrium calculations using *Geochemist's Workbench* (GWB)®. To obtain the measured concentrations observed for the WCL analysis [Hecht *et al.*, 2009; Kounaves *et al.*, 2010] using GWB requires that SO<sub>4</sub><sup>2-</sup> was initially <0.1 mM and was dissolving during the analysis at a rate greater than the addition of the BaCl<sub>2</sub>. If [SO<sub>4</sub><sup>2-</sup>] ≥ 6 mM, then [Ca<sup>2+</sup>] and [Mg<sup>2+</sup>] would need to be ≥3 mM or ≥7 mM, respectively, concentrations 3–10 times greater than actually measured. The GWB model calculations show that the addition of

**Table 2.** Concentration of Species Likely Present in Solution After Adding 1 g of the Phoenix Mars Soil into 25 mL of Pure H<sub>2</sub>O, and the Amounts of the Minerals or Species Required in the Soil to Give the Measured and Calculated Ionic Concentrations<sup>a</sup>

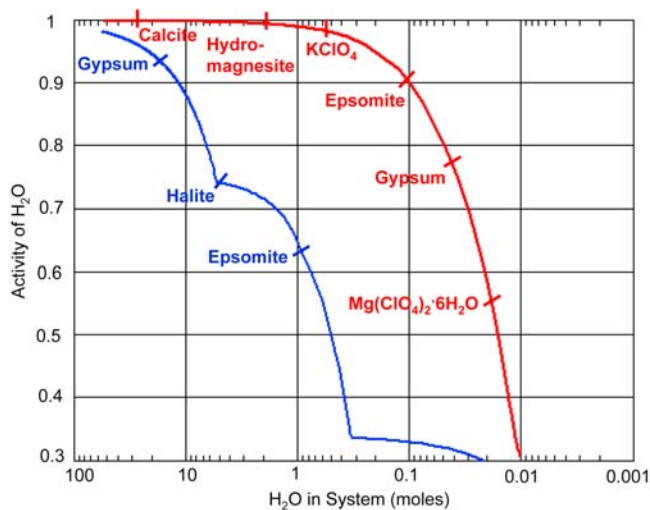
Species	Equilibrium Concentration in Solution (mM)	Concentration in Soil (wt %)
CaCO <sub>3</sub> (calcite)	Saturated	3 – 5 <sup>b</sup>
MgCO <sub>3</sub> (magnesite)	Saturated	≥ 1.8 <sup>c</sup>
MgSO <sub>4</sub> (epsomite)	Dissociated	3.3 <sup>d</sup>
ClO <sub>4</sub> <sup>-</sup>	2.5	0.6
Na <sup>+</sup>	1.4	0.08
Cl <sup>-</sup>	0.40	0.04
K <sup>+</sup>	0.40	0.04
Mg <sup>2+</sup>	6.4	–
SO <sub>4</sub> <sup>2-</sup>	3.9	–
HCO <sub>3</sub> <sup>-</sup>	5.4	–
MgSO <sub>4</sub> (aq)	1.2	–
Ca <sup>2+</sup>	0.75	–
CaSO <sub>4</sub> (aq)	0.17	–

<sup>a</sup>Equilibrium calculated using GWB *React* at 7°C and a 4 mbar CO<sub>2</sub> headspace. Composition differs from that previously reported in that it corrects for BaCl<sub>2</sub> leakage. Addition of Ba<sup>2+</sup> precipitated SO<sub>4</sub><sup>2-</sup> and shifted the equilibrium to values different than if the soil had been added to pure water. The rate of Ba<sup>2+</sup> addition appears to have been sufficient in all analyses to maintain [SO<sub>4</sub><sup>2-</sup>] < 0.5 mM and fully dissociate all SO<sub>4</sub><sup>2-</sup>.

<sup>b</sup>As determined by TEGA and WCL.

<sup>c</sup>Minimum required by model to give saturated Mg<sup>2+</sup> in 25 mL of solution.

<sup>d</sup>Equivalent to 5.3 mM total SO<sub>4</sub><sup>2-</sup> in solution. At such concentrations, other hydrates give similar values.



**Figure 2.** Water activity ( $a_{\text{H}_2\text{O}}$ ) and precipitated minerals as a function of evaporating 1 L (55 moles) of terrestrial seawater under ambient conditions (blue), and 1 L (55 moles) of a solution containing the salts found in 40 g of the Phoenix soil at  $7^\circ\text{C}$  and  $P_{\text{CO}_2} = 4$  mbar (red). Minor salts precipitating at  $<0.01$  moles  $\text{H}_2\text{O}$  are not shown.

$\text{BaCl}_2$  during the sol, coupled with the dissolution of  $\text{SO}_4^{2-}$ , would result in an increase in  $[\text{Mg}^{2+}]$  and a decrease in  $[\text{Ca}^{2+}]$  only if a  $\text{MgSO}_4$  phase was being added to the WCL solution. This was clearly observed during the sol 107 analysis, though present but less so, during the sol 30 and 41 analyses [Kounaves et al., 2010]. The addition of soluble  $\text{CaSO}_4$  would have caused an increase in  $[\text{Ca}^{2+}]$  and no change in  $[\text{Mg}^{2+}]$ , which is not observed. This result suggests that a major fraction of  $\text{SO}_4^{2-}$  was added as a  $\text{MgSO}_4$  phase.

[16] TEGA and WCL results suggest that the soil may have been wet in the past because the relatively large quantity of carbonate detected is difficult to form under dry conditions [Boynton et al., 2009; Kounaves et al., 2009b]. If the soil was once wet, then salts deposited from evaporating the WCL solution (Table 2) could provide a guide to minerals present in the soil. Evaporation models over temperature ranges of  $0$ – $25^\circ\text{C}$  and partial pressures of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ) of  $0.004$ – $1$  atm, showed that the evaporites are dominated by calcite ( $\text{CaCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ),  $\text{KClO}_4$ , and  $\text{NaClO}_4$ . Depending on the process of evaporation,  $T$ , and  $P_{\text{CO}_2}$ , epsomite exceeds gypsum precipitation by 3 times to 3 orders of magnitude. We have not considered the formation of phases at temperatures of  $<0^\circ\text{C}$ , but this would result in other possible species such as meridianite ( $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ ) [Marion et al., 2010]. While by themselves these results show only the possible candidates for the hydrated sulfate phases, these equilibrium model calculations are consistent with the current chemical and mineralogical data obtained by other landers and orbiters.

[17] The presence of soluble sulfate at the Phoenix landing site has implications for the geochemical history and potential past habitability of Mars. With the gypsum dune fields and the edge of the polar ice cap only 700 km to the north, and the Alba Patera volcano 1700 km to the south, the Phoenix site is located between significant sources

of  $\text{SO}_x$  and  $\text{H}_2\text{O}$ . Nearby volcanic eruptions could have provided large quantities of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  which would have been atmospherically oxidized to  $\text{H}_2\text{SO}_4$  [Settle, 1979] and that would have reacted with carbonates and other minerals to produce  $\text{CaSO}_4$  and  $\text{MgSO}_4$ . Subsequently, if liquid water ever occurred, such minerals may have undergone transformations through aqueous speciation. Alternatively, the sulfates may have been brought to the Phoenix site by wind-blown dust, after a volcanic or aqueous origin elsewhere on Mars.

[18] The findings of the Phoenix WCL, and the levels of the dominant salts specifically, have a direct bearing on the question of whether under the right conditions, water activity ( $a_{\text{H}_2\text{O}}$ ) on Mars could have been sufficient to support life. Previous calculations of the maximum water activity at Meridiani Planum and other sites where salts precipitated from martian brines, indicate that it was often below levels tolerated by any known terrestrial organisms [Tosca et al., 2008]. Table 2 shows our best estimate for the chemical composition of a solution consisting of 1 g of the average Phoenix site soil in 25 mL pure  $\text{H}_2\text{O}$ . These values were used with the *GWB React* software package to calculate the precipitation of minerals and water activity ( $a_{\text{H}_2\text{O}}$ ) as a function of decreasing water on evaporation. Figure 2 shows the results for the evaporation of water with the concentrations given in Table 2. Calcite, hydromagnesite, and  $\text{KClO}_4$ , precipitate at a water activity ( $a_{\text{H}_2\text{O}}$ )  $> 0.97$ , while epsomite precipitates at  $\approx 0.9$ , gypsum at  $\approx 0.78$ , and  $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  at  $\approx 0.55$ . In the past, changes in the obliquity and longitude of perihelion of Mars have caused summer surface temperatures to exceed 273 K at the latitude of Phoenix [Richardson and Michna, 2005]. Thus, our findings suggest that if a small portion of the Phoenix soil was wetted, for example by a melting snowpack [Clow, 1987; Christensen, 2003], the water activity for a dilution of greater than  $\sim 0.015$  g  $\text{H}_2\text{O}/\text{g}$  soil (assuming no aqueous interactions with the soil and already fully hydrated salts) would be in the habitable range ( $a_{\text{H}_2\text{O}} \geq 0.75$ ) of terrestrial halophilic microbes [Grant, 2004].

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