LOW-TEMPERATURE AQUEOUS FLUIDS ON MARS. V.F. Chevrier¹ and T.S. Altheide¹, ¹W.M. Keck Laboratory for Space Simulation, Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR, 72701, vchevrie@uark.edu, talthei@uark.edu.

Introduction: Numerous geomorphologic features are seen on the martian surface which indicate fluvial activity, both ancient and recent [1,2]. In addition, abundant hydrated minerals have been found across Mars, suggesting a wet past [3,4]. However, given the conditions existing at the surface, liquid water should not have been stable on Mars for any significant period of time.

Yet this instability is only true for pure liquid water. Chloride brines allow liquid water to exist for much longer periods under the harsh surface conditions [5,6,7]. Saturated CaCl2 solutions remain liquid down to around -50°C, which is approximately the average temperature on Mars. But unlike the surface of Earth, chlorides and other halogens are quite scarce on Mars, making such solutions unlikely to have existed in sufficient quantities to cause the observed water-related structures.

Alternatively, magnesium sulfates such as kieserite, are abundant in the martian soils. Other sulfates, including gypsum, have also been found primarily in equatorial regions and in the northern polar regions [8]. However, these minerals are not extremely soluble and can only lower the freezing point of water by less than 5 K [9]. Thus, these solutions should not be liquid at temperatures appropriate to Mars.

We suggest that ferric sulfates may be an important component in martian fluids. Both iron and sulfate are found in abundance on Mars, so solutions of ferric sulfate should not be rare over geologic history. Indeed, jarosite has been detected in Meridiani Planum [10], and other ferric sulfates have been found in concentrations of up to 30% by weight in some soils in Gusev Crater [11]. Here, we present data demonstrating the stability of ferric sulfate solutions under simulated martian conditions.

Materials and Methods: The following solutions were made using DI water and dried ferric sulfate (Fe2(SO4)3): 25.5, 29.8, 34, 38.3, 42.5, 46.8 and 51 wt%. Ferric sulfate n-hydrate was dried in an oven for 48 – 72 hours at 110°C under a total pressure of 0.04 bars to remove the hydrated state. The dried sulfate was analyzed using XRD to confirm the nature of the original phase, which was found to be composed of amorphous Fe2(SO4)3, rhomboclase, mikasaite and coquimbite. Weight loss measurements after additional heating at 400°C showed that the originally dried ferric sulfate contained ~15 wt% H2O, and this was allowed for in calculating concentrations of solutions made from the dehydrated salt, or mikasaite.

The evaporation rate of each solution was measured in our Mars Simulation Chamber, where it was exposed to 7 mbar of CO2 for 0.5 to 3 hours. The average temperature of the atmosphere inside the chamber was 264K. The temperature of each solution tested ranged from 274 to 257K. Humidity inside the chamber was adjusted to approximately 1% by carefully injecting CO2 and pumping during testing. The density of each solution was also determined, which was used to determine the evaporation rate.

Samples were observed over a range of low temperatures in an attempt to observe any potential crystallization. For the 46.8 and 51 wt% solutions, CO2 ice and liquid nitrogen were used to achieve temperatures of 195K and lower.

Results: The evaporation rate for each ferric sulfate solution was determined from the mass loss at low pressure (Fig. 1). Two trends may be noted from these experimental data. First, the evaporation rate strongly decreases at lower temperature. This has been demonstrated under similar conditions for brine solutions of NaCl and CaCl2 [6]. Second, we observe that increasing concentrations decrease the evaporation rate at constant temperature. The 51 wt% concentration demonstrated an evaporation rate 20 times slower than that of pure liquid water at the same temperature.

Figure 1: Evaporation rate of ferric sulfate solutions as a function of the sample temperature for various concentrations from 25.5 to 51 wt%. The top black line indicates the evaporation rate of pure water calculated using the Ingersoll equation [12]. The other lines are calculated for lower water activities.

The observed “crystallization” point seems to be around 201K for an initial concentration of 55.3 wt% Fe2(SO4)3. When exposed to very low temperatures,
these solutions exhibited a strong increase in viscosity with decreasing temperature. This effect was particularly obvious for high concentrations (above 40 wt%).

**Discussion:** Experiments and theoretical treatments have shown that the saturation vapor pressure controls the diffusion of water molecules in the CO₂ atmosphere [6,12]. However, in the case of strongly concentrated solutions, the saturation pressure is affected by the lower water activity resulting from interactions between water and ions in the solution.

The Pitzer ion interaction model for the Fe₃(SO₄)₂·H₂SO₄·H₂O system was used as an independent model to recalculate the water activity [13,14] at very high ionic concentration. The results show that the Pitzer model perfectly fits the activity of water extracted from the evaporation rates, confirming our approach to the evaporation process and the validity of the Pitzer model at very high concentrations.

Figure 2: The evaporation rate of a 55 wt% solution of ferric sulfate (in Log scale) projected on a shaded MOLA topographic map. The black areas correspond to zones below the average freezing temperature (Tᵥ < 201 K).

Using the Pitzer model combined with the Ingersoll equation [13], which describes diffusion of water vapor and buoyancy of water in a heavier CO₂ atmosphere, the evaporation rate of ferric sulfate solution at all concentrations and temperatures may be determined. We use as input data the averaged annual surface temperatures [15] and the MOLA data to calculate total surface pressure. Results for a 55 wt% concentration are shown in Fig. 2. Evaporation rates never get higher than 10⁻¹ mm yr⁻¹ in the warmest regions. Colder regions exhibit Eᵥ around 10⁻² – 10⁻³ mm yr⁻¹. This would allow these solutions to be conserved over geological timescales.

It is interesting to note that the freezing point of ferric sulfate saturated solutions (around 201 K) falls exactly between 30 and 60° of latitude (Fig. 3), where the large majority of flow features, from gullies to viscous flows, are formed. The formation of gullies would therefore result from alternation between freezing and melting depending on the temperature, which would depend on the period of the year. Moreover, the large amplitude of viscosity variation between 201 and 273 K could explain why gullies and viscous flows are found at the same latitude.

Figure 3: Geological features resulting from potentially recent fluid flow activity on Mars: gullies (red circles), viscous flows (blue squares). The dark line represents the 201K isotherm or freezing point of the saturated ferric sulfate solution. The green stars represent gullies we identified in other areas where the 201K isotherm is present.

**Conclusions:** If high enough concentrations of these solutions are reached, a freely flowing liquid is still achieved at temperatures dominating the surface of Mars today. The very low evaporation rates of these solutions at such temperatures and concentrations make them perennial over long timescales as well. We suggest that such solutions could have formed quite easily, and subsequently, may be responsible for formation of liquid-related geomorphologic features on the present-day surface of Mars.

**References:**