HETEROGENEOUS ADSORBED AND SALTY LIQUID WATER AT THE PHOENIX LANDING SITE, MARS. D. E. Stillman and R. E. Grimm, Department of Space Studies, Southwest Research Institute, 1050 Walnut Street, Suite 300, Boulder, CO 80302, (dstillman@boulder.swri.edu).

Introduction: The real part of the dielectric permittivity ε′ was measured by the thermal and electrical conductivity probe [TECP: 1,2] on the Phoenix Lander. We interpret these data using our laboratory measurements of ε′ as a function of temperature, H_2O content, specific surface area, salinity, and salt type. We focus on data taken at one locality ("Vestri") over multiple sols, three separate times. Daytime increase in ε′ at Vestri on sols 46 and 69-71 suggests progressive melting of a salty ice beginning at ~239 K. This temperature is near the eutectic of $NaClO_4$ (~239 K) and just below that of $MgCl_2$ (240 K). We also determined a eutectic temperature for $Mg(ClO_4)_2$ (215.9±0.2 K) that is higher than reported elsewhere, but there is no evidence of this phase in the ε′ data. However, no melting behavior was evident for an insertion on sols 54-55, just centimeters away from the other sites. A large increase in ε′ at Vestri occurred at night on sol 70-71. Surface frost was also detected that night by other instruments [2]. The jump in ε′ can be matched by an increase in adsorbed H_2O from <1 monolayer, the normal state at low H_2O partial pressure, to ≥3 monolayers at saturation (the frost point), in a Viking-analog soil. However, the amount of adsorbed H_2O is an order of magnitude larger than that inferred to have precipitated during the night so adsorbing materials are likely present on only a fraction of the local surface.

Background: Previous interpretations of TECP data [2] recognized "several puzzling signals and an overnight increase in permittivity in the latter half of the mission contemporaneous with H_2O adsorption". Zent and colleagues [2] used the Topp equation [3] to estimate the amount of nighttime adsorbed water, but described their own quantitative results as "implausible." This is because the Topp equation cannot estimate water content in fine-grained soils [4], because the dielectric signature of adsorbed water dominates the free water signature [5]. Here we interpret the TECP data based on our laboratory measurements.

Analysis and Results: The raw TECP data are corrected to ε′ via an empirical formula that was determined by testing the TECP on four materials with an ε′ of 1, 8, 11, and 20 [1]. All the calibration ε′ values lie outside the range observed on Mars (ε′ = 2-4). The calibration function is a third-order polynomial. Relative differences of a few tenths of permittivity unit—comparable to Mars-observed excursions of interest—can be introduced by fitting with fewer parameters or focusing on the smaller ε′.

The ε′ measurements also suffer from imperfect coupling of the TECP to the ground. Because the measurement is between two needles that are 15 mm long and separated by 7 mm, even a small void space will cause a decrease in ε′. Conversely, over-insertion will increase the bulk density and hence ε′. Therefore, ε′ data sets longer than ½ sol are needed to set control points to correct for insertion errors. There are only 3 insertion points of sufficient length and they are all at the "Vestri" [2] site.

Vestri-1 (Sol 46-47). At the warmest part of the sol, the ε′ is 0.2 units above its value during the coldest part of the night. It is unclear when this change occurs due to lack of data between 7.27 and 12.19 LMST but the decrease in ε′ starts at 18.95 LMST when subsurface temperatures drop <245 K. By 21.9 LMST at 222.5 K, the ε′ plateaus. The ε′ data concludes at 7.27 LMST at a subsurface temperature of 233.5 K and does not indicate a trend to a higher value of ε′.

We infer that these changes in ε′ that are directly correlated with temperature are caused by melting of salty ice during the day. Because the TECP data here were taken largely during cooling, there is the possibility of supercooling hysteresis. The data indeed hint at such hysteresis as the warming data at 7.27 LMST on sol 47 are 0.05 units below the cooling data. Without the warming data and specific evidence of premelting, we can only limit the eutectic temperature of the salt-ice mixture to ≥233.5 K.

Vestri-3 (Sol 69-71). The warmest part of the sol and the coldest part of the night have permittivities 0.2-0.35 units above the minima that are reached shortly after sunrise and sunset, respectively.

Overall, the daytime data (Fig. 1) behave similarly to Vestri-1. The minimum ε′ probably occurred between 7 and 7.4 LMST (233 and 237 K, respectively), when data were not collected. The ε′ increases sharply between 7.4 and 7.7 LMST, after which it continues to slowly increase. We interpret this slope break as the pre-to-post eutectic melting transition, and therefore we can assign a eutectic temperature of ~239 K. The gradual increase in ε′ with temperature above the eutectic temperature indicates that melting is continuing and therefore the frozen mixture is not a eutectic composition. The ε′ decreases after 11 LMST (253 K), which may be a signature of evaporation. A similar behavior occurred in the afternoon of the previous sol, when the TECP time series began, although it is displaced in both ε′ and temperature.

A very different pattern evolved overnight. After linearly decreasing from 17.7 to 20.8 LMST (247 to

233 K, respectively), the ε′ begins increasing with decreasing temperature (Fig. 2). This is interpreted as adsorbed water [2]. The Phoenix MET mast and lidar indicated frost formation at ~23 LMST, while orbital CRISM data detected frost at 3 LMST on sol 71 [2]. Results from CRISM indicate 10 pr µm was adsorbed.

We compared the TECP data directly to laboratory experiments on a sand-clay mixture prepared to have the same specific surface area (A_s = 17 m^2/g) as inferred by Viking measurements [6]. The Vestri-3 nighttime data are nearly exactly bounded by the laboratory measurements with 1 ML and 3 ML adsorbed water (Fig. 2). The problem is that an additional 2 ML to 15 mm depth at 17 m^2/g is ~20 times more water than was inferred to have precipitated. This discrepancy can be reduced because the TECP ε′ response at the surface is approximately 1.4 times the average over the probe length. Calibration error could further reduce the actual ε′ variation and hence adsorbed water requirements. Also, it is unclear how the dielectric response of the adsorbed water changes as a function of mineralogy.

Currently, we can only conclude that direct comparison with laboratory data of Mars-analog materials and conditions is consistent with the inferred precipitate to within an order of magnitude, whereas the Topp equation is off by a factor of 300.

Vestri-2 (Sol 54-56) ε′ data is temperature independent over ~3 sols. These data show that salty solutions measured at Vestri-1 and Vestri-3 are heterogeneous at a measurement scale of centimeters.

Salty Solution Composition. The salty solution has a eutectic temperature of ~239.2 K. This eutectic temperature is near that of sodium perchlorate (~239 K), just below that magnesium chloride (240 K), and much above that of magnesium perchlorate (206, 215.85 K). MECA geochemical modeling suggests that sodium perchlorate was the dominate salt followed by magnesium chloride or magnesium perchlorate, depending on whether the solution is frozen or evaporated [7].

Conclusions: Due to insertion problems only long duration measurements can be used to determine changes due to vapor deposition and eutectic melting. In order to interpret the TECP ε′ data, it is imperative to have a library of permittivity measurements conducted under similar conditions. The TECP ε′ measurements of martian regolith showed that we were able to interpret the eutectic temperature of a salty solution, detect hysteresis of this solution, and determine when additional water monolayers were present.

Future ε′ measurement systems that are flying onboard the Rosetta lander and that are being prototyped [7] have the ability to measure over decades of frequencies and utilize better geometries. This will eliminate the insertion problems and allow mapping of ε′ down to 10s of meters. A greater frequency range and depth of penetration will allow for the determination of depth to the ice table, vol% of the ice in the ice table, the temperature of the ice table, the amount of Cl^- in the ice lattice, and the thickness of the ice table [5,8,9].

References: [1] Zent, A. et al. (2009) *JGR, 114*, E00A27. [2] Zent, A. et al. (2010) *JGR*, *115*, E00E14. [3] Topp, G.C. et al. (1980) *WRR*, *16*, 574-582. [4] Rubin, Y. and S.S. Hubbard, *Hydrogeophysics*, 523 p. [5] Stillman, D.E. et al. (2010) *JPC*, *114*, 6065-6073. [6] Ballou, E.V. et al. (1978) *Nature*, 644-645. [7] Marion, G.M. et al. (2010) Icarus, 207, 675-685. [8] Stillman, D.E. and R.E. Grimm (2008) *39th LPSC*, 2277. [9] Grimm, R.E. and D.E. Stillman (2011) *42nd LPSC.*

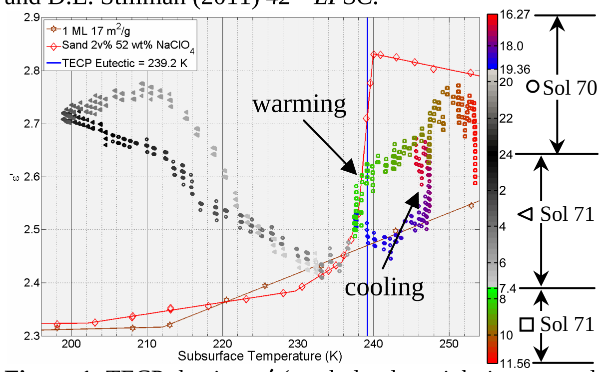

Figure 1. TECP daytime ε′ (symbol color, nighttime grayed out) of Vestri-3 as a function of temperature, overlaid with data from two laboratory samples. One monolayer of adsorbed water (ML) on a sand-clay mixture yields an appropriate background. A $NaClO_4$-H_2O ice in sand melts completely and then evaporates. The TECP data shows that during cooling as the temperature decreases below 248 K the ε′ greatly decreases. This higher apparent eutectic could be caused by evaporation. During warming the temperature rises above the assumed eutectic temperature of 239.2 K.

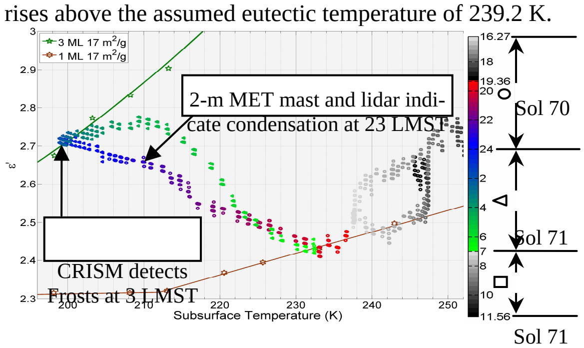

Figure 2. TECP nighttime ε′ (symbol color, daytime grayed out) of Vestri-3 as a function of temperature overlaid with our laboratory data of a sand-clay mixture with a similar surface area to that of martian regolith (17 m^2/g) with 1 and 3 ML of adsorbed water. At 19.36 LMST on Sol 70, ε′ indicates 1 ML. The relative humidity then increases with the decreasing temperature and the number of ML increases to 3 by 1 LMST. At 4 LMST, the temperature increases. The ε′ also increases but the relative humidity begins to remove some of the adsorbed water. By 5 LMST the number of ML is reduced back to 1.