BRINES WITHIN BASAL ICE OR SEDIMENTS CAN EXPLAIN THE MARSIS BRIGHT BASAL REFLECTIONS IN THE SOUTH POLAR LAYERED DEPOSITS. D.E. Stillman[1], E. Pettinelli[2], S.E. Lauro[2], E. Mattei[2], B. Cosciotti[2], K.M. Primm[3], and G. Caprarelli[4], [1]Southwest Research Institute (dstillman@boulder.swri.edu), [2]Mathematics and Physics Department, Roma Tre University, [3] Planetary Space Institute, [4]Centre for Astrophysics, University of Southern Queensland, Australia.

Introduction: The MARSIS radar sounder has detected strong radar returns from the basal ice in the region of Ultimi Scopuli (81°S, 193°E), within the South Polar Layered Deposits (SPLD) [1-2]. Here, we discuss possible materials that could create a large reflection at Ultimi Scopuli and our laboratory measurements of these materials to better constrain possible reflectors.

Radar Background: Radar waves are reflected at sharp interfaces (with respect to the radar wavelength) with differing electrical or magnetic properties (magnetic interfaces can likely be ruled out [3]). The magnitude of the reflected energy increases with the magnitude of the contrast in electrical and magnetic properties at an interface. Unfortunately, MARSIS reflectivity data do not allow to separately compute real (ε') and imaginary (ε'') parts of the complex permittivity, but only the apparent permittivity (ε_a) [1-2], which is a real single quantity that accounts for both polarization and conductive processes. *Lauro et al.* [2] found that the reflectivity was likely caused by material with an ε_a = 33.

Ultimi Scopuli Background: The anomalous reflector is under ~1.5 km of ice. Temperatures estimated at this location are heavily dependent on the assumed heat flow and thermal conductivity of the SPLD. Assuming a temperature-dependent thermal conductivity of pure H_2O ice for the SPLD, a heat flow >84 mW/m^2 is needed to allow liquid brine to form via calcium perchlorate [4]. This research [4] suggests a basal temperature of ~171-176 K, assuming a more realistic heat flow range of 14-25 mW/m^2 [5].

Hypothesized Basal Reflecting Material: The high ε_a value significantly limits the possible materials that could be responsible for such a reflection. In order to produce this magnitude of reflectivity (ε_a = 33), the reflector must be able to store a significant amount of charge (high ε′) or dissipate a large amount of charge (high ε''). Below we introduce three categories of materials that have been hypothesized to produce the high reflectivity.

Brine Mixtures: Salts, when mixed with H_2O form a mixture of phases (anhydrous salt, hydrated salts, brines, and ice) that depend on the parameters of the salt (type and concentration) and the environment (temperature and pressure). Above the melting temperature of the salt-H_2O mixture only the brine phase exists. Below the melting temperature, ice forms and brines are stable as long as the temperature does not fall below the eutectic temperature (the minimum temperature at which a stable salt-H2O mixture can have brine). Below the eutectic temperature, brine forms into hydrate salt, anhydrous salt, or ice depending on the salt type. Anions such as chloride (Cl^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-) significantly reduce the eutectic temperature, however even the lowest eutectic temperature of 198 K of $Ca(ClO_4)_2$ is too high based on previous models [4].

Liquid brine has a high ε' of ~80 and is highly conductive thus increasing ε''. Such values of 100 vol% of brine would produce reflections that are much greater than the measured ε_a. However, a brine mixture with regolith or ice could produce an ε_a = 33.

Dry Minerals: *Bierson* [6] suggested that hematite or jarosite could have a high electrical conductivity in the absence of water at predicted basal temperatures. Thus, a rocky unit at the base of the SPLD could cause a large contrast in ε'', thus creating an ε_a = 33.

Clay with Adsorbed Water: *Smith et al.* [7] suggested that the dielectric relaxation of clay with adsorbed water at the base of the SPLD could produce a material with a high ε_a at predicted basal temperatures.

Methodology: Over the last two decades, hundreds of measurements on Martian analog materials have been made at SwRI [8-9] and Roma Tre University [10-11]. We have gone back through our previous measurements and made new measurements [12-13] to further constrain the salt type, salt concentration, and temperatures that could produce the necessary ε_a at Ultimi Scopuli.

We start our measurements by pouring pre-mixed brine samples into a three-electrode sample holder with an attached Teflon cup. For regolith mixtures, the cup is pre-loaded with regolith that is then mixed with a spatula to ensure even mixing throughout. The sample holder is then placed in an ultra-low freezer and the temperature is dropped. Measurements are conducted during freezing to monitor metastability and warming to measure the stable properties of the ice-brine-regolith mixtures.

Results: *Figure 1* shows a handful of perchlorate samples as a function of temperature. This shows that without metastable effects the temperature of the basal unit would have to approach or exceed the eutectic temperature of the salt. Additionally, we have not found any binary mixture of salt that dramatically lowers the eutectic temperature below that of $Ca(ClO_4)_2$.

Interpretation

Dry Minerals: Previous measurements of hematite and jarosite have shown low electrical conductivity of dry samples [3,9]. However, all these measurements were made on regolith samples, thus it is possible that a consolidated material could have a higher electrical conductivity at these very low temperatures. Albeit, our samples showed no signs of interfacial polarization mechanisms due to charges building up on highly conductive grains. Additionally, one would expect that if hematite or jarosite on Mars was highly electrically conductive that locations outside the SPLD would also have significant radar returns. Thus, hematite or jarosite on Mars may be highly conductive, possibly due to some impurity in its crystal structure that only occurs below the SPLD. We cannot rule out this hypothesis, but suggest it has a low probability.

Clay with Adsorbed Water: Previous and current measurements conducted at SwRI [14-15] and Roma Tre University [12-13] agree that the apparent permittivity of any clay with any type of adsorbed water (deionized or with any type of salt type or concentration) cannot produce a large ε_a at temperatures below 230 K. Thus, we do not believe this hypothesis could be correct.

Brine Mixtures: The volume of brine needed to raise the bulk ε' of a mixture to 33 is ~60%. To raise the ε_a to 33 with only using a difference in ε'' via electrical conductivity, requires a conductivity of 3 mS/m. The bulk conductivity of an ice or regolith can reach this threshold with ~6 or ~17 vol%, respectively (see Fig 1 with solutions >100 mM). This means that as long as the brine is well connected that even a small amount of brine can create an ε_a large enough to create the observed reflection. Thus, ice or regolith does not need to be saturated in perchlorate salts.

The permittivity values of concentrated (~200 mM or higher) liquid brines (*Fig. 1*) indicate that these materials can plausibly explain the bright reflections detected by MARSIS at Ultimi Scopuli. Furthermore, previous work showed that metastable perchlorate brines persist at sub-eutectic temperatures [16-18], possibly expanding their fields of stability within range of the SPLD basal temperatures.

Discussion: It is far from demonstrated that the longevity of metastable brines shown in laboratory settings extends over geologic timescales. Furthermore, the conditions of formation and accumulation of putative brines at the base of the SPLD have not been discussed, and remain a focus of our ongoing investigations of the geologic context and climatic evolution of the SPLD. Deliquescence of perchlorates could be responsible for localized melting of ice in fractures and veins of the deposits, followed by freeze-melting cycles that would lead to further concentration of the brines. An interconnected system of fractures could have then acted as conduits toward the base of the deposits. Deliquescence of perchlorates could have also taken place directly at the interface between the underlying regolith and the base of the ice.

Conclusion: Our experimental work indicates that liquid brines are the most convincing candidates, thus far, as the source of the bright reflections detected by MARSIS at Ultimi Scopuli. We continue to explore the scenarios that may have led to the formation and accumulation of basal brines in Ultimi Scopuli.

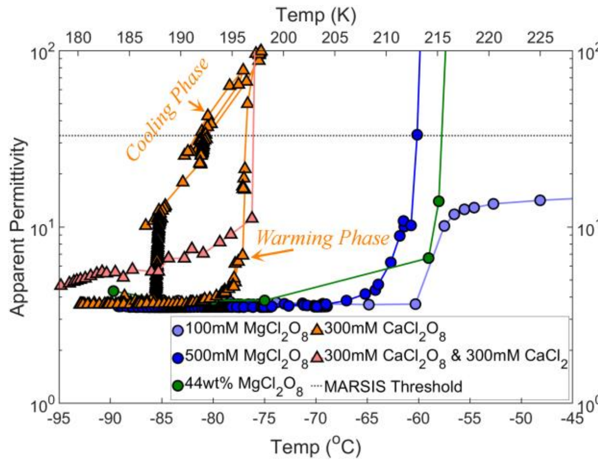

Fig. 1. Apparent permittivity vs. temperature for different perchlorate solutions. Note the 300 mM $Ca(ClO_4)_2$ shows significant metastability. However, this metastability only decreases the temperature by 5 K.

References: [1] Orosei et al. (2018) *Science, 361,* 490-493. [2] Lauro et al. (2021) *Nat. Astron., 5,* 63-70. [3] Stillman & Olhoeft (2008) *JGR*, 113, E09005. [4] Sori & Bramson (2019) *GRL*, *46*, 2018GL080985. [5] Parro et al. (2017) *Nature Sci. Rep.*, *7*, 45629. [6] Bierson et al. (2021) *GRL*, *48*, e2021GL093880. [7] Smith et al. (2021) *GRL*, *48*, e2021GL093618. [8] Grimm et al. (2008) JPCB, 112, 15382-15390. [9] Stillman et al. (2010) JPCB, 114, 6075-6073. [10] Pettinelli et al. (2003) JGR, 108(E4), 2002JE001869. [11] Pettinelli et al. (2007) IEEE Trans. Geosci. Remote Sens., 45, 1271-1281. [12] Mattei et al. (2022), in press, *Earth and Planet. Sci. Let.* [13] Mattei et al. (2022) *LPSC*, #1392. [14] Stillman & Grimm (2011) *JGR*, *116*, E09005. [15] Stillman & Grimm, (2011) *JGR*, *116*, E03001. [16] Primm et al. (2020) *Icarus*, *342*, 113342. [17] Stillman et al. (2022) Modern Brines, #6028. [18] Toner et al. (2014) *Icarus*, *233*, 36-47.