Introduction: The identification of hydrated MgSO$_4$ on Mars [1,2,3,4,5,6,7] provides a potential reservoir for retaining martian water in the solid phase [8]. A clarification of the stability fields and phase transition pathways of the MgSO$_4$·nH$_2$O salts above 0 °C (Fig. 1) helped in determining the potential candidates that might exist in the martian environment [9, 10,11,12,13]. The recent report on the discovery of a low temperature hydrated sulfate meridianiite MgSO$_4$·11H$_2$O [14] makes it even more imperative that the studies on the stability field and phase transition pathways of the hydrated Mg-sulfates be extended below 0 °C. This is especially important in light of the Phoenix mission for verifying the existence of meridianiite at the Mars polar region. The study we report here was undertaken to extend our study on Mg-sulfates to -10 °C over a wide range of relative humidities (RH) in order to: (a) establish the stability field of meridianiite; and (b) determine what other stable hydrated Mg-sulfates exist at -10 °C.

Low T experiments: Five hydrated Mg-sulfates -- MgSO$_4$·H$_2$O (LH-1w), amorphous MgSO$_4$·~2H$_2$O, starkeyite MgSO$_4$·4H$_2$O, epsomite MgSO$_4$·7H$_2$O, and meridianiite MgSO$_4$·11H$_2$O [14] were used as starting phases. See ref. 13 for details on sample preparation. Meridianiite was prepared by dissolving MgSO$_4$ in water (> 14 H$_2$O/SO$_4$) placing the open sample dish over a tray of crushed water ice and maintaining all in a sealed container at -10 °C. The formation of meridianiite was confirmed by XRD, Raman, and gravimetric measurements made before and after a 400 °C baking of the sample to verify the water content. Each of five starting phases was put into six humidity buffers at -10 °C. The RH values of these buffers were determined by extrapolating from their RH ~ T curves in Greenspan (1977) [15] to -10 °C. Only the humidity buffers (i.e. LiBr, LiCl, MgCl$_2$, KI, NaCl, and KCl) that show minimum curvatures in their extrapolations at T< 0 °C were chosen for our experiments. Raman measurements were made on the intermediate products at regular time intervals using a Kaiser Holoprobe RXN Raman system fitted with a fiber optic stand off probe having a 2.5” focal length. Low temperature diffuse reflectance VIS-NIR spectra (0.35 and 2.5 μm) were collected on a few selected samples using an Analytical Spectral Device (ASD) spectrometer. Both measurements were made with the sample bottles placed in a bed of dry ice (-40 °C).

A Low Temperature polymorph of MgSO$_4$·7H$_2$O (LT-7w): The Raman spectra (Fig. 2) obtained from the low T Mg-sulfates in our experiments showed two phases that were not observed at RT. One is meridianiite [14]. Another phase was found to contain only seven H$_2$O per SO$_4$, but it has distinct Raman and VIS-NIR spectra. This LT-7w polymorph can be easily produced by storing epsomite in a sealed sample vial at -10 °C, but it can also be made from any of the five starting Mg-sulfates at -10 °C using mid to high RH buffers (20% -80% RH). This LT-7w is

![Figure 1. Phases and phase boundaries for hydrated magnesium sulfates above 0 °C compared to the low temperature phases observed in this study.](image-url)
therefore the most common Mg-sulfate phase at - 10 ºC. The major Raman spectral differences among 7w, LT-7w, and 11w are the positions and overall shapes of water peaks at 3000-3600 cm⁻¹. The LT-7w shows peak shifts and multiplicity of the OH stretching modes that seem to be more complex than just the low temperature sharpening of the 7w water modes. The VIS-NIR spectrum (Fig. 3) of LT-7w also shows distinctions in absorption bands among the three phases RT-7w, LT-7w and 11w.

Stability fields of MgSO₄·nH₂O at -10 ºC: The hydrated magnesium sulfates were put in the six RH buffers at -10 ºC for 12 to 14 months. Most experiments at > 20% RH appear to have reached the equilibrium. The current phases at -10 ºC are shown in Fig 1 and compared with the stable phases above 0 ºC [13]. In this phase diagram, the known phase boundaries above 0 ºC [12] have been extrapolated down to -10 ºC. The 11w-7w phase boundary below 0 ºC was predicted by Chou [16]. After ~10,000 hours exposure in six RH buffers (8-91%RH) at -10 ºC, we obtained the following major results.

- Above 90% RH at -10 ºC, all five starting phases converted to meridianite (11w).
- From 34% to 80% RH at -10 ºC, all five starting phases converted to the newly found low temperature polymorph of MgSO₄·7H₂O (LT-7w). Our experiments suggest that LT-7w would be the most common hydrated magnesium sulfate around -10 ºC.
- Below 11% RH at -10 ºC, both meridianiite and epsomite converted to LT-7w. Starkeyite and LH-1w remain unchanged, but amorphous MgSO₄·~2H₂O shows evidence for partial conversion to a 7w structural form. We anticipate it to be LT-7w based on the conversion of epsomite (RT-7w) to LT-7w in the experiments started from epsomite, although the high background fluorescence in the Raman spectrum prevents a more definitive identification. It is very possible that after ~10,000 hrs, equilibrium has not been reached, and these experiments are continuing.

Conclusion: The results of these experiments at -10 ºC show that meridianite (11w) readily dehydrates to the very stable phase LT-7w phase at RH < ~85%. The lower hydrates of MgSO₄ readily rehydrate to the same stable LT-7w at RH>20%. At and below 11% RH, LH-1w and starkeyite show no tendency for rehydration, while amorphous MgSO₄·2H₂O partially rehydrates to 7w. It is very unlike the rehydration pathway of amorphous phase at >0 ºC, where it converted to starkeyite (4w) first, then to 6w/7w. Therefore, the rehydration pathway of amorphous phase at -10 ºC appears to indicate an extended stability field (to low RH) of MgSO₄·7H₂O. Results from our continuing experiments at 8 - 11%RH and -10 ºC will provide answer to this question.

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