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► **To cite this version:**

E. B. Hughes, F. Rivera-Hernández, W. Rapin, J. R. Johnson, P. Gasda, et al.. HYDRATED NA-MG-SULFATE SUGGESTS WARMER CONCENTRATED FLUIDS INFILTRATED THE SULFATE UNIT, GAME CRATER, MARS. Lunar and Planetary Science Conference, Lunar and Planetary Institute, Mar 2024, The Woodlands (Texas), United States. pp.2288. hal-04800413

HAL Id: hal-04800413

<https://hal.science/hal-04800413v1>

Submitted on 24 Nov 2024

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HYDRATED NA-MG-SULFATE SUGGESTS WARMER CONCENTRATED FLUIDS INFILTRATED THE SULFATE UNIT, GALE CRATER, MARS. E. B. Hughes¹, F. Rivera-Hernández¹, W. Rapin², J. R. Johnson³, P. Gasda⁴, D. Das⁴, E. Sklute⁴, O. Gasnault², N. Lanza⁴, L. C. Kah⁵, B. Tutolo⁶, P.Y. Meslin², E. Dehouck⁷, R. Y. Sheppard^{8,9} ¹Georgia Institute of Technology (ehughes36@gatech.edu), ²Institut de Recherche en Astrophysique et Planétologie, ³Johns Hopkins University, Applied Physics Laboratory, ⁴Los Alamos National Laboratory, ⁵University of Tennessee, ⁶University of Calgary, ⁷Université Claude Bernard Lyon 1, LGL-TPE, ⁸Planetary Science Institute, ⁹Institut d'Astrophysique Spatiale, Université Paris-Saclay

Introduction: The *Curiosity* rover is currently exploring a sequence of alternating light-toned and dark-toned bands within the Sulfate Unit in Gale crater, Mars. These bands may represent changes in brine fluid, environmental conditions, or diagenesis, following a drying-out period after extensive clay deposition [1]—yet the formation history of such material is unknown. Here, we suggest that a likely explanation for the darker materials is secondary (i.e., post primary evaporitic crystallization), possibly differently sourced fluids infiltrating the bedrock [2]. We identify the presence of a highly hydrated Na-Mg-sulfate phase nearly exclusive to darker materials in this region, which may represent warm ($T > \sim 7^\circ\text{C}$) late-stage fluid infiltration.

From sol ~ 3600 to the time of writing, the *Curiosity* rover has encountered flaky dark-toned laminated material, in addition to lighter-toned materials in the Sulfate Unit. These darker materials became particularly abundant as the rover encountered the Light-Dark sequence, and appear to be present throughout the region but possibly in higher abundances in the dark bands observed from orbit. *Curiosity's* ChemCam instrument has obtained geochemical data from both the darker and lighter materials in this layered unit.

Methods: To distinguish light rocks from dark rocks we rely on ChemCam passive relative reflectance spectra between ~ 400 and ~ 840 nm [3]. The maximum reflectance value for each passive spectrum is used to determine whether the material is “dark”, “light”, or “intermediate”, after excluding points that appear to be too dusty, are soil/sand targets, or are in shadow, by validating each point visually using co-located images from the Remote Micro Imager. Our spectral classes are: <0.27 relative reflectance units (“Dark”), between 0.27 and 0.30 reflectance units (“Intermediate”), and >0.30 reflectance units (“Light”).

Each passive spectrum is acquired after a Laser Induced Breakdown Spectrometer (LIBS) analysis in a five-point raster. Thirty laser shots are taken at each LIBS point; the last 25 are averaged together to derive the chemistry. The “shot-to-shot” (STS) data—the chemistry derived from each of the 25 laser shots—provide information on how oxides correlate on a micron scale. STS uncertainties are higher than the average value, but this dataset is useful for evaluating the composition of individual minerals and grains.

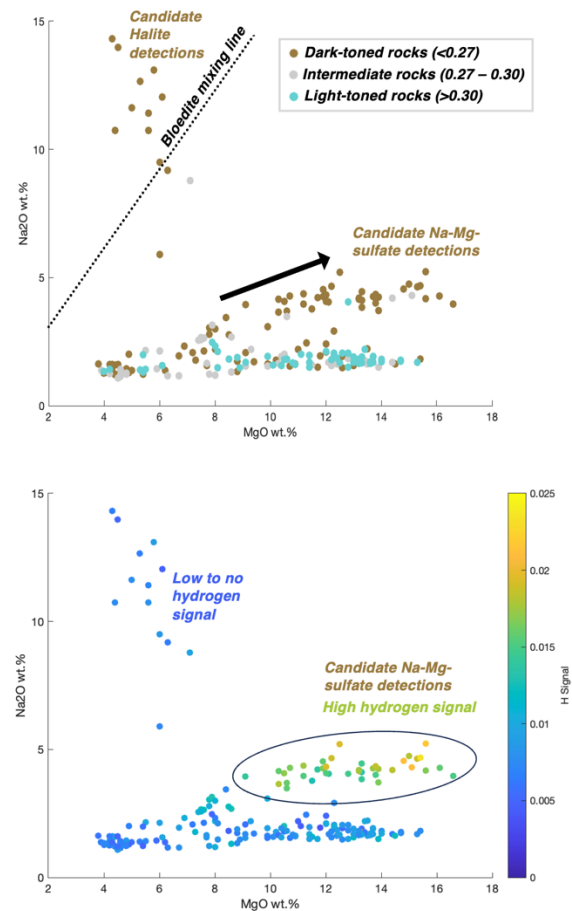


Figure 1. Top: MgO versus Na₂O in targets from sols 3949 – 3999 sorted by rock brightness, indicating a correlated trend in dark rocks. **Bottom:** Hydrogen signal is derived from the methods of [4], indicating notably high hydrogen in the correlated Na₂O/MgO targets.

Results: There is an emergent trend in the darker-toned rocks with correlated MgO and Na₂O abundances, high sulfur, and high hydrogen, that is absent in the lighter-toned rocks (**Fig. 1, Fig. 2**). This material is highly hydrated (**Fig. 1**)—far more so than other materials in this part of the sulfate unit, including light-toned materials with similarly high MgO. Within 5-point LIBS rasters on darker-toned rocks, correlations between MgO and Na₂O are often present that are absent in the lighter-toned rocks (e.g., **Fig. 3**). STS data shows the same trend; of the 36 candidate

detections of the Na-Mg-sulfate between sol 3949 and 3999, 19 show $R^2 > 0.30$ between MgO and Na₂O in STS data, and none of the remaining detections are anti-correlated (as would be expected for two distinct mineral phases). All 36 detections show a lack of chlorine in the spectra and all show presence of sulfur (**Fig. 2**), indicating these are unlikely to be mixed Mg-sulfates and halite detections, and are likely a hydrated Na-Mg-Sulfate phase.

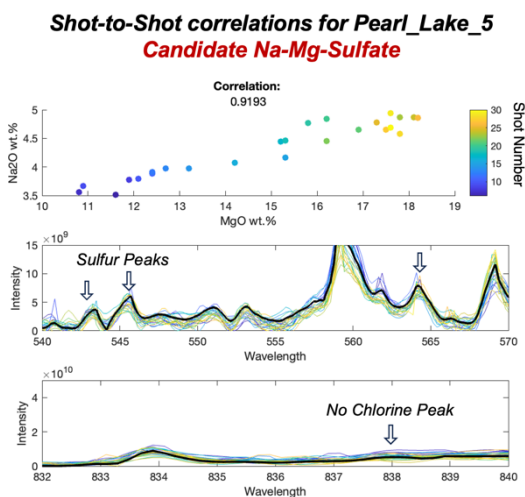


Figure 2. Top: STS correlation between MgO and Na₂O in a candidate Na-Mg-sulfate, demonstrating an R^2 of 0.91. Color corresponds to number in shot sequence. **Middle:** Presence of sulfur peaks in LIBS spectra. **Bottom:** Lack of chlorine peak in LIBS spectra.

Discussion: The dark-toned material is associated with higher MgO than the mixing line of the multication sulfate, bloedite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) (**Fig. 1**). Given the difference in wt. ratio between this material and bloedite, it is possible this is an amorphous material, which might have formed rapidly and not encountered fluids since, preventing crystalline ordering, or might have become amorphous after

formation. It is also possible that Mg-sulfates altered into bloedite are co-located with unaltered Mg-sulfates, indicating either rapid fluid loss or minor fluid infiltration. In either case, *the lack of evidence for this material in the light-toned rocks indicates an alteration event took place that solely enriched the dark-toned rocks with Na₂O and produced a Na-Mg-sulfate phase.* Such a phase is likely to have formed from a concentrated solution, as geochemical pathways for evaporation on Mars indicate that solutions rich in Mg, Na, SO₄ (and possibly Cl) are late in an evaporation sequence [5]. Indeed, this may have also been a warmer-temperature solution, as bloedite preferentially forms under moderately warm conditions (above $\sim 7^\circ\text{C}$) [6]. We therefore interpret the presence of this material as indicative of secondary fluid events mobilizing highly concentrated Na-rich brines into the light-toned bedrock, altering the already-present Mg-sulfates into Mg-Na-sulfates, including possibly bloedite, or an amorphous material. The presence of this highly hydrated new phase indicates complex brine systems and extended hydrologic activity were present in the Gale crater Sulfate Unit, and may indicate fluid events occurred under different temperature conditions [e.g., 7, 8].

References: [1] Sheppard R.Y. et al. (2021) *JGR*, 126, 2 [2] Das et al. (2023) 54th LPSC, #2440 [3] Johnson J.R. et al. (2015) *Icarus*, 249, 74 – 92 [4] Rapin W. et al. (2017) *Spectro. Acta Part B: Atomic Spec.*, 130, 82 – 100 [5] Tosca N.J. & McLennan S.M. (2006) *EPSL*, 241.1-2, 21-31 [6] Warren J.K. (2006) *Evaporites: sediments, resources and hydrocarbons*. Springer. [7] Rampe et al. (2020) *JGR*, 125 [8] Martin et al. (2017) *JGR*, 122, 2803–2818

Figure 3. Examples of a darker-toned rock (Saddlehorn) near to a lighter-toned rock (Kern River) demonstrating a strong, positive MgO/Na₂O correlation occurs only in the points in the darker-toned raster.

