

**HALOGEN SIGNATURES IN GALE, GUSEV, AND MERIDIANI SOILS: EVIDENCE FOR SURFACE-ATMOSPHERE INTERACTIONS.** D. Laczniak<sup>1</sup>, S. Karunatilake<sup>2</sup>, Y. S. Zhao<sup>3</sup>, D. R. Hood<sup>2</sup>, D. Susko<sup>2</sup>, <sup>1</sup>Department of Geoscience, University of Nevada Las Vegas, Las Vegas, NV 89154-4010 ([dllaczniak@gmail.com](mailto:dllaczniak@gmail.com)), <sup>2</sup>Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803, <sup>3</sup>Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Science, Guiyang, China.

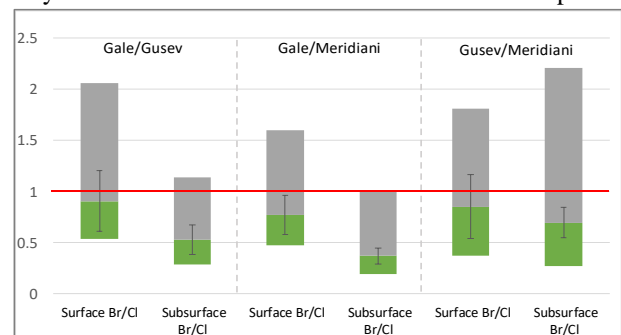
**Introduction:** Being a byproduct of various weathering processes—volcanic, aqueous, atmospheric, eolian, and impact gardening to name a few—soil records the complex evolution of the surface of Mars. Specifically, the examination of halogen distributions—particularly the highly mobile elements of Br and Cl—in martian soils provides insights into weathering processes that influence, not only the planet's local and global soil composition, but also its atmospheric composition. Prior investigations of martian soils attribute varying Br and Cl abundances solely to aqueous near-surface processes [1-5]. However, other studies suggest that in arid, evaporative environments (i.e., sabkhas, salt pans, etc.), interactions between the surface and atmosphere alter soil chemistry through volatilization of halogens [6-9]. Through a thorough examination of halogen variation (Br, Cl, and S) in soil samples within different landing sites, we address three pertinent questions: (1) how are halogens distributed at Gale; (2) how do halogen distributions at Gale Crater, Gusev Crater, and Meridiani Planum compare; and (3) are surface-atmosphere interactions—specifically volatilization—altering martian soil chemistry? Findings from this study will advance our limited understanding of the halogen cycle of Mars.

**Methods:** To conduct this geochemical and spatial analysis, we collocated Alpha Particle X-Ray Spectroscopy (APXS) element and oxide compositions for Gale Crater soils from the Planetary Data System Geosciences Node (PDS). Additionally, we added APXS compositions to Gusev and Meridiani soil datasets previously compiled by [6]. Soil samples from each rover landing site were categorized by their nature (i.e. undisturbed or disturbed). Undisturbed samples consist of soils that had no contact with rover wheels. Disturbed samples consist of soils whose upper-most layers (mm-scale) were mixed or removed by rover wheels [10]. Gale scoop samples—which excavate a cm-scale portion of loose sediment using Curiosity's Sample Acquisition, Processing, and Handling (SA/SPaH) subsystem—were included in the undisturbed category [11]. Here, it is assumed that undisturbed soil samples represent surface soil trends while disturbed soils represent shallow subsurface trends. It should be noted that trends observed at Gale may be affected by its less comprehensive dataset (n=26) compared to Gusev (n=73) and Meridiani (n=54).

Halogen mass fraction ratios (i.e., Br/Cl, S/Cl, Br/S) and elemental abundances were analyzed to evaluate differences among landing sites and changes in soil chemistry between the surface and shallow subsurface.

In addition to using classical statistics, our analyses rely on the evaluation of (1) modified-box-and-whisker plots which provide a robust graphical method for summarizing compositional variation (maximum, minimum, and central tendencies) between regions [12]; (2) bivariate scatterplots comparing elemental mass fraction abundances which demonstrate geochemical relationships; and (3) a bivariate scatterplot comparing Cl and Br abundances to a normal evaporation/freezing Cl-Br trendline. Least-squares trendlines, Pearson correlation coefficient ( $r$ ), and the coefficient of determination, ( $r^2$ ), are selectively added to plots to determine the goodness-of-fit of our linear regression models. Specifically,  $r^2$  represents the fraction of response variability modeled by the predictor.

**Discussion:** Examination of the data, specifically the modified boxplots (e.g., Fig. 1), show that Gale, Gusev, and Meridiani all exhibit similar halogen distributions. Noted minor differences, specifically at Gale, may be indicative of local variations in alteration pro-



**Figure 1.** Modified boxplots comparing Br/Cl ratios between sites.

cesses or rate of alteration. In a broad sense, the overlapping ranges in Br/Cl and S/Cl ratios at all three landing sites support the widely held notion of a globally homogenous martian soil unit, likely resulting from a common basaltic crust source or a globally distributed provenance [2,10]. Compared to Br/Cl, S/Cl ratios are more uniform between landing sites and surface versus subsurface soils. This suggests that S and Cl bearing phases (e.g., minerals or amorphous compounds) are more stable in the soil—or reacting similarly to alteration processes—at all locations while Br counterparts are less stable and responding differently to alteration processes.

Upon closer evaluation, halogen ratios at Gusev and Meridiani are more similar and lower in value than those at Gale. Gale's distinct halogen distribution may suggest either a different alteration process or a different

rate of alteration. In addition, differences in typical Br/Cl and S/Cl ratios between locations are consistently less in surface than in subsurface soils, implying that surface soils are more homogenous, likely due to eolian mixing.

Scatterplots graphing halogen mass fractions show: (1) a lack of Br-Cl and Br-S correlation in subsurface and surface soils at all three landing sites; and (2) spatial coupling of S and Cl in all soils at Gale and Meridiani. Again, these trends suggest Br responds differently than S and Cl to alteration processes in both surface and subsurface soils. S and Cl correlation in Gale and Meridiani soils suggests that both elements respond similarly to weathering, thus negating the idea of aqueous-driven soil alteration which likely would distribute S and Cl differently [14]. Gusev data lacks this same S-Cl correlation at depth. This observation may be due to the presence of two distinct soil lithologies—high-S and low-S—representing contribution from differing local rock composition or alteration processes [15]. Considering that subsurface soils represent shallow mm-depths and that Br variation controls halogen ratios, the spatial decoupling of Br from S and Cl at all three locations is indicative of preferential Br volatilization in surface and near-surface soils rather than aqueous processes.

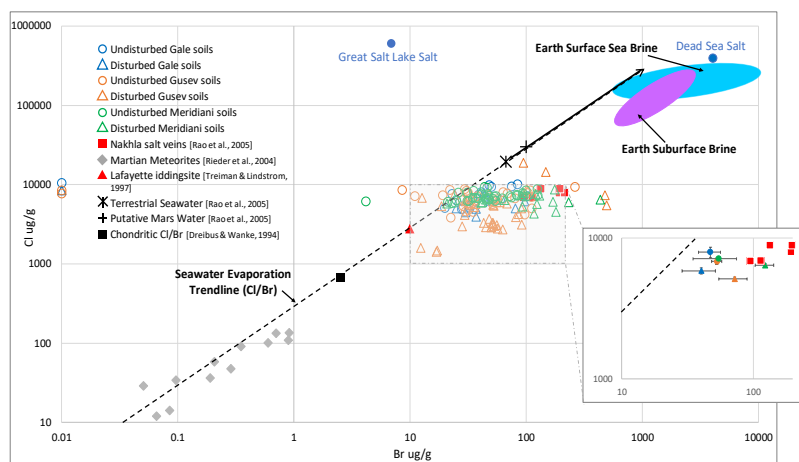
Br and Cl abundances relative to an evaporation/freezing Cl-Br trendline are shown in figure 2. At Gale, Gusev, and Meridiani, Br concentrations vary approximately 2-3 times more in magnitude than Cl, as indicated by the horizontal spread of data. This spread suggests that Br is driving changes in Br/Cl ratios at each location. Relative to the Cl-Br trendline—which represents the expected constant change in both Cl and Br concentrations in response to evaporation and/or freezing—subsurface soils are, generally, slightly more Br-enriched than surface soils, suggesting a decrease in

Br abundance towards the surface. Boxplot comparisons of surface and subsurface Br/Cl ratios at each landing site show a similar decrease in surface soils. Since Br is more reactive than Cl [8,14], this observation, in conjunction with a large fluctuation in Br, supports volatilization of Br at the martian surface. Surface soils at Gusev and Meridiani that plot left of the Cl-Br trendline (depleted in Br) are easily explained by surface-atmosphere volatilization of Br. Contrarily, Br-enriched samples (plotting to the right of trendline) are more difficult to attribute solely to Br volatilization without assuming complementary interactions with middle- or late-stage evaporative brines. More Br-enriched samples (plotting further to the right of trendline) likely interacted with late-stage, highly Cl-fractionated brines while less Br-enriched samples (plotting closer to the trendline) interacted with early-stage, less Cl-fractionated brines. The latter could also represent residual soil from late-stage evaporation that underwent more active volatilization.

**Conclusion:** Regolith formation on the martian surface is a complex process and our data show the difficulty in deciphering the influence of aqueous versus surface-atmosphere processes. Br-enrichment noted in many soils indicates that an interaction with evaporative-formed brines likely occurred at Gale, Gusev, and Meridiani. Observed geochemical relationships, significant Br fluctuation, and an apparent decrease in Br/Cl towards the surface, supports the hypothesis of preferential Br volatilization affecting surface soils. Some data suggest volatilization may be more substantial at Gusev and Meridiani. Thus, volatilization pathways, such as UV photolysis and chemical oxidation [6-9], should be seriously considered as ongoing processes in martian soil. More APXS compositional data, particularly to decimeter depths, would help constrain the relative influence of different alteration processes in the soil surface versus subsurface.

**References:** [1] Clark, B.C. et al. (2005)

- Earth Planet. Sci. Lett.*, 240, 73-94. [2] Yen, S.A., et al. (2005) *Nature*, 436, 49-54. [3] Knoll, A.H. et al. (2008) *JGR*, 113 (E6), E06S16. [4] Marion, G.M. et al. (2009) *Icarus*, 200(2), 436-445. [5] Rao et al. (2009) *Earth Planet. Sci. Lett.*, 286(3), 396-403. [6] Karunatillake, S., et al. (2013) *Icarus*, 226, 1438-1446. [7] Zhao, Y.S., and S.M. McLennan (2014) *8<sup>th</sup> Int. Conf. on Mars.*, Abstract #1378 [8] Zhao et al. (2013) *LPSC XLII*, Abstract #1719 [9] Smith, M.L. et al. (2014) *Icarus*, 231, 51-64. [10] Gellert, R.R. et al. (2006) *JGR*, 111, E02S05. [11] Anderson R.C. et al. (2012) *Space Sci. Rev.*, 170, 57-75. [12] Karunatillake, S. et al. (2011) *J. Sci. Comput.*, 46(3), 439-451. [13] Karunatillake, S. et al. (2014) *Icarus*, 229, 400-407. [14] Wang, A., et al. (2006) *JGR*, 111, E02S17. [15] Yen, A.S. et al., (2008) *JGR*, 113, E06S10.



**Figure 2.** APXS Cl (ug/g) and Br (ug/g) soil concentrations plotted relative to the terrestrial seawater Cl/Br evaporation trendline. Adapted from [7]. The call-out box (lower right) displays the root-mean-square-error for each data category. These error bars are centered on the mean of the corresponding dataset.