

**DOES MARTIAN SOIL RELEASE REACTIVE HALOGENS TO THE ATMOSPHERE?** Suniti Karunatillake<sup>1,2</sup>, Yu-Yan Sara Zhao<sup>1</sup>, Scott M. McLennan<sup>1</sup>, J. R. Skok<sup>2</sup> <sup>1</sup>Stony Brook University, NY 11794, <sup>2</sup>Geology and Geophysics, Louisiana State University, LA 70803 (wk43@cornell.edu).

**Introduction:** The halogens chlorine and bromine are probably the most mobile elements that have been analyzed on Mars. They provide important constraints on surficial processes; indeed Br is perhaps the most important trace element used to evaluate evaporative processes on Earth.<sup>1</sup> Excluding experiments by Zhao et al.,<sup>2</sup> Cl and Br variations in Martian soils and rocks have been interpreted almost exclusively with their behavior in aqueous fluid – mineral systems, including aqueous alteration, evaporative processes, and post-depositional fluid migration.<sup>3,4</sup>

However, on Earth halogens are remobilized by atmospheric processes as well. Recent work<sup>5,6</sup> also suggest atmospheric influences on rock/sediment geochemistry in highly arid evaporative Martian-analog settings.<sup>2</sup> Accordingly, we assessed the consistency of halogen variation in Martian soil -- at Gusev and Meridiani -- with terrestrial analogs such as volatilization of surficial bromide in Sabkhas<sup>7</sup> and in polar environments at the polar sunrise.<sup>8</sup> We also examined whether the S/Cl ratio may be more variable in the Martian soil profile than suggested previously.<sup>9</sup> In addition to constraining the volatility of Cl, this revealed the extent to which Martian soils are compositionally uniform.

**Methods:** We examined APXS-derived geochemical relationships among Br, Cl, Mg, Na, and S in soils from Gusev Crater (sols 14-1368) and Meridiani Planum (sols 11-1368). The soils at the two sites have been sampled in several different ways and show varying effects of local mineralogy.

With the goal of identifying relationships among the elements of interest in the context of atmosphere-surface interactions, we subdivided the Gusev soils (number of samples,  $n = 60$ ) into six categories, with some overlap allowing samples to appear in more than one category: moderate S content soils ( $n = 53$ ), basaltic soils (45), trench soils (6), disturbed soils (29), disturbed normal soils (15), and surficial soils (25). For additional insight into the soil profiles, we also compared surface, wall, and floor samples at each of the three Gusev trench sites.

Similarly, we divided Meridiani soil ( $n = 38$ ) into seven overlapping categories: moderate S content soils ( $n = 37$ ); basaltic soils (23) which, in addition to mod-

erate S content, excluded soils enriched in hematitic spherules; trench soils (4); disturbed soils (8); disturbed soils with moderate S content and low hematite content (5); surficial soils (26); and surficial soils without excessive hematite (15).

We used linear correlation coefficients, slopes, and intercepts, along with their error bounds for Br-S, Br-Cl, Br-Mg, Br-Na, Cl-S, Cl-Mg, and Cl-Na pairs to determine halogen volatility. Detailed statistical parameters, including elemental ratios, were computed not only for each elemental pair, but also for each of the 13 soil categories at Gusev and Meridiani. Scatter plots of mutually dependent regression parameters summarize our results.

**Results and Discussion:** Elemental systematics in Gusev trench soil broadly support the loss of surficial Br to the atmosphere, driven either by UV photolysis<sup>7</sup> or by chemical oxidants, perhaps including perchlorates.<sup>10</sup> First, the Br concentration is consistently higher in the subsurface relative to the surface at Gusev. Second, while Br, S, and Cl increase in the subsurface, the proportional increase relative to the surface is roughly in the order  $Br > S > Cl$ , consistent with higher Br/Cl and Br/S ratios in the subsurface. This trend is illustrated by Table 1 comparing averages of surface ratios (undisturbed) with subsurface (trench) ratios.

**Table 1. Average mass fraction ratios of Br to Cl and S to Cl compared between undisturbed surface and trench soil samples at Gusev Crater. The values indicate that Br, but not S, increases approximately  $\times 2$  more than Cl at depth.**

Mass ratio type	Soil category	Mean ratio	Standard error
Br/Cl	Undisturbed	$0.3 \times 10^{-2}$	$0.1 \times 10^{-2}$
	Trench	$0.6 \times 10^{-2}$	$0.1 \times 10^{-2}$
S/Cl	Undisturbed	3.6	0.1
	Trench	5.1	0.9

Vertical variations in Br within trenches are reinforced by trends in other soil categories. Figure 1,

ly, the more readily volatilized Br shows strong evidence of decreasing concentration and weakening cor-

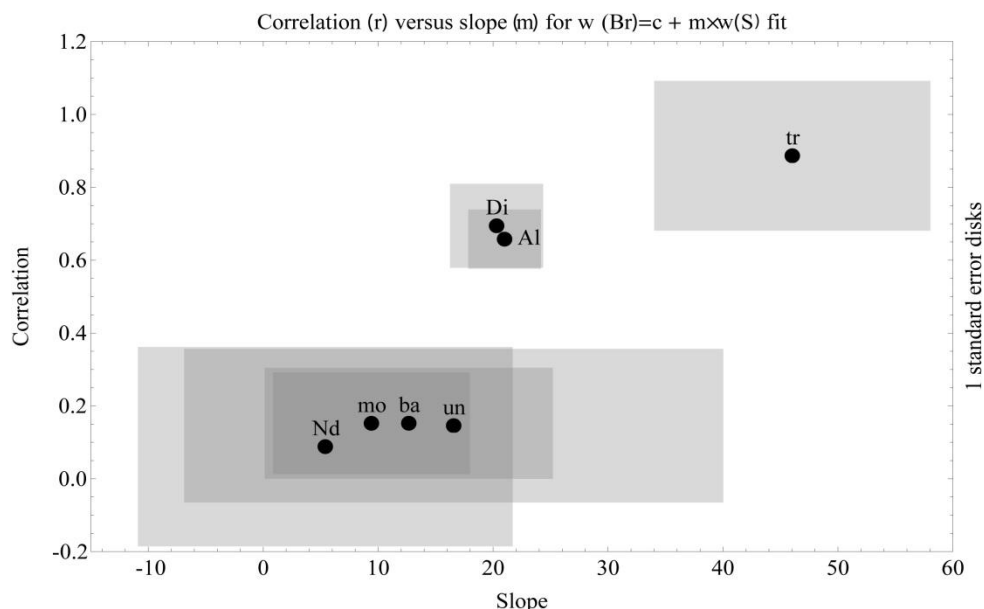


Figure 1 Correlation coefficient versus slope of linear regressions for Br-S in different soils classes. These mutually dependent regression parameters summarily illustrate Br-S mass fraction trends at Gusev. Labels indicate soil type: trench (tr), disturbed (Di), all data (Al), moderate S (mo), undisturbed surface soil (un), basaltic soil (ba), normal disturbed soil (ND).

showing the twin regression parameters of correlation and slope, highlights the compelling association of Br with S in the subsurface. The correlation and the related slope of trench soil exceed those for most other soil categories. Meridiani soil analyses suggest that Br varies at depth in a manner roughly similar to that at Gusev albeit with minor differences in detail.

We also observe a higher S/Cl ratio with depth at both Gusev and Meridiani, from ~3.6 at the surface to approximately 5 in the subsurface (Table 1). Furthermore, positive Cl intercepts, amounting to ~15% of the typical 0.6 – 0.7 % Cl mass fraction in basaltic soil, are observed even in soil categories where S and Cl correlate strongly. Consequently, the two elements may be fractionated significantly in bulk Martian soil at depth scales on the order of decimeters or more. The fractionation is consistent with differential mobility driven more by aqueous processes than the volatilization of Cl, not only because terrestrial analogs indicate much greater Br volatility<sup>12</sup> but also because Cl decreases less towards the surface than both Br and S.

Zhao et al.<sup>2</sup> show the fractionation of Br/Cl and production of perchlorate in UV-exposed brines under a simulated Mars atmosphere. The remarkable Br volatility they observe reinforces our soil observations.

**Conclusions:** Our soil analyses yield two key results. First, halogen variability in the soil profile is consistent with loss to the atmosphere.<sup>cf., 2</sup> According-

ly, the more readily volatilized Br shows strong evidence of decreasing concentration and weakening correlation with S toward the surface. Therefore, analogs of some terrestrial processes that volatilize Br, such as facilitation by frost flowers,<sup>8</sup> low-temperature oxidation with UV-photolysis,<sup>9</sup> and UV-photolysis in salt pans,<sup>7</sup> could be significant on Mars.

Second, the soil profile reveals a more variable S/Cl mass ratio than previously thought. Based on our observations, bulk soil – possibly regionally and to decimeter depths<sup>cf., 13</sup> – bears a bi-modal S/Cl distribution with low values at the surface approximating 3.6, and higher subsurface values of ~5. We posit further that S/Cl variability may be driven more by aqueous processes, unlike the variability in Br/S and Br/Cl that appear to be driven substantially by the atmospheric release of Br.

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