

Does martian soil release reactive halogens to the atmosphere?



Suniti Karunatillake ^{a,b,*}, Yu-Yan Sara Zhao ^a, Scott M. McLennan ^a, J.R. Skok ^b, Nicole E. Button ^b

^a Stony Brook University, Department of Geosciences, Earth and Space Sciences Building, Stony Brook, NY 11794-2100, United States

^b Department of Geology and Geophysics, Louisiana State University, Baton-Rouge, LA 70803, United States

ARTICLE INFO

Article history:

Received 21 July 2012

Revised 10 July 2013

Accepted 12 July 2013

Available online 23 July 2013

Keywords:

Atmospheres, chemistry

Mars, atmosphere

Mars, surface

Photochemistry

ABSTRACT

Detailed statistical examination of Cl, Br, and S distributions, in martian soil profiles at Gusev Crater and Meridiani Planum, indicates decreasing Br abundance and weakening Br-S association towards the surface. All three elements decrease towards the surface in the order Cl < S < Br. Furthermore, Br variability decouples from potential cations such as Mg at the surface relative to the subsurface. These observations support a relative loss of surficial Br compared to S and Cl, all highly mobile elements in aqueous environments. We propose that Br may have converted preferentially to gas phases (e.g., BrO), driven either by UV photolysis or by chemical oxidants. Such volatilization pathways may in turn impart a global signature on Mars by acting as controls on oxidants such as ozone and perchlorates. S/Cl mass ratios vary with depth (~4–5 in the subsurface; 1.8–3.6 on the surface) as well, with a strong correlation of S and Cl near the surface but more variable at depth, consistent with differential vertical mobility, but not volatilization of Cl. Elevated S/Cl in subsurface soil also suggests that the ratio may be higher in bulk soil – a key repository of martian geologic and climatic records – than previously thought.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

The halogens chlorine and bromine are probably the most mobile elements known on Mars. Halogen distributions reveal constraints on surficial processes; indeed Br is perhaps the most important trace element used to evaluate evaporative processes on Earth (Warren, 2006). To date, 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 (Clark et al., 2005; Knoll et al., 2008; Marion et al., 2009; Rao et al., 2009; Yen et al., 2005).

On Earth, halogens remobilize by both aqueous and atmospheric processes. Recent work (Hönninger et al., 2004; Risacher et al., 2006) further suggests that atmospheric processes can also affect rock/sediment geochemistry in highly arid evaporative settings. Accordingly, even though aqueous processes may explain variations in the Mars soil data, these recent studies in terrestrial settings question the exclusion of atmospheric effects in the martian context (Zhao et al., 2013).

To evaluate the potential for volatility effects, we examine the geochemical relationships among Br, Cl, and other mobile elements in martian soils to evaluate whether atmospheric processes could

have affected their distribution. Such pathways typically yield reactive halogen species known to destroy ozone (Finlayson-Pitts, 2010), though not yet incorporated into models of oxidant distribution on Mars, such as for perchlorates (Marion et al., 2010), H₂O₂ (Hurowitz et al., 2007), and atmospheric ozone (Lefèvre et al., 2008). For our analysis, we use geochemical data obtained by the Mars Exploration Rovers Spirit and Opportunity at Gusev Crater and Meridiani Planum, respectively.

In assessing halogen volatility, we also examine whether the S/Cl ratio may vary substantially more in the martian soil profile than suggested previously (Gellert et al., 2006). This analysis helps to assess the volatility of Cl, as well as to constrain the extent to which the proposed compositional uniformity of martian soil (e.g., Yen et al., 2005) holds true both at depth and across the surface. Soil excavations by the rovers enabled us to generate continuous profiles of compositional variation with depth at specific locations (e.g., Squyres et al., 2006).

Both aspects of our investigation relate to soil as a key repository of many complex processes operating at the surface of Mars over geological time. Its varying composition reflects complex interactions among impact, volcanic, eolian, glacial, aqueous, and atmospheric influences. While a daunting task, unraveling the relative importance of such processes can shed considerable insight into the geologic and climatic evolution of the planet.

1.1. Halogen atmospheric chemistry: Implications for Mars

In terrestrial settings, Br may convert from soluble bromide (Br⁻) to a variety of gas phase bromine species (e.g., Br, Br₂, BrO,

* Corresponding author. Address: Geology & Geophysics, Louisiana State University, E300 Howe-Russell BLDG (Postal: E235), Baton Rouge, LA 70803, United States.

E-mail address: wk43@cornell.edu (S. Karunatillake).

URLs: <http://www.linkedin.com/pub/suniti-karunatillake/7/56b/8b6>, <http://www.researcherid.com/rid/A-5934-2009> (S. Karunatillake).

HBr, HOBr) and enter the atmosphere via numerous chemical pathways, many of which include photochemical reactions (Simpson et al., 2007). Salt aerosols, released from frost flowers on newly formed sea ice or lake ice and blowing snow especially in polar regions (Buys et al., 2012; Kaleschke, 2004; Yang et al., 2008), offer a primary natural mechanism for such transport. Modified analogs of this may occur on Mars, from atmospheric moisture as hoarfrost or from phase changes in brine films associated with soil. As another mechanism with obvious potential relevance for Mars (e.g., Smith, 2008) halogens may transfer from thin water films on eolian dust (Sander et al., 2003). Similar processes also mobilize chlorine into the atmosphere, but terrestrial marine brines that remain after ice formation and form the aerosols are relatively enriched in Br compared to Cl (Vogt et al., 1996; Yang et al., 2008). As a consequence, Br converts preferentially into the gas phase compared to Cl, which in turn fractionates Br/Cl ratios significantly.

Despite evidence for a limited role for aqueous activity on Mars through much of its geological history (Hurwitz and McLennan, 2007), Br/Cl fractionation may remain in effect for brine films on eolian dust. Beyond the known volatilization of Br from aerosols at the marine boundary layer, recent studies also indicate preferential Br transfer into the atmosphere during simple evaporation of brines (Smoydzin and Von Glasow, 2009; Wood and Sanford, 2007) and possibly directly from salt pans in arid environments (Hönninger et al., 2004). In one experiment, Wood and Sanford (2007) evaporated Br-spiked Abu Dhabi sabkha brines mixed with sand under vacuum and UV light at 80 °C. While Cl concentrations remained constant, they found that a remarkable 83% of the Br migrated to the atmosphere and that the Cl/Br ratio in the re-dissolved salts increased by nearly a factor of 6 over the original brine. These observations indicate that surface-atmosphere transfer of Br in hyper-arid regions such as Andean salt pans, analogous in terms of aqueous activity to the typical surface conditions on Mars, may influence the Br mass balance and fractionate Cl/Br ratios (Risacher et al., 2006).

On Earth, the mobility of Br via the atmosphere is of limited relevance to the overall global aqueous balance of the element. Br resides in the atmosphere only briefly (several minutes to several days) and at low concentrations (10's of ng/g) (Simpson et al., 2007; von Glasow and Crutzen, 2007). In contrast, Br resides in the oceans about 10⁸ times longer at concentrations about 10⁶ times greater (Broecker et al., 1982). The immense size of oceans diminishes the importance of saline lakes to global mass balance.

Compared to Earth, several factors make halogen atmospheric mobility on Mars possible. Mars presents compelling evidence for evaporite minerals at the surface despite insufficient evidence for ancient marine environments. Its surface experiences high solar UV-C (200–280 nm), UV-B (280–315 nm), and to a lesser degree UV-A (315–400 nm) fluxes (Cockell et al., 2000; Rontó et al., 2003). The martian surface has also been exposed to the atmosphere and to dust storms over long timescales, perhaps exceeding 10⁹ years (Carr, 2008). Accordingly, the atmosphere may affect the near surface environment significantly. The amount and composition of the martian atmosphere certainly differs fundamentally from Earth's, with outstanding questions on sedimentary processes (e.g., Grotzinger et al., 2013) and unknown implications to the halogen atmospheric chemistry. Nevertheless, volatilization may only require thin films of brine forming from the deliquescence of salts at low temperatures (Fairén et al., 2009; Zorzano et al., 2009) in salt pan analogs or on dust grains as discussed above. Subsurface H₂O ice, as recently shown in situ at the Phoenix site (Smith et al., 2009) and locally within craters (Byrne et al., 2009), may further facilitate such processes.

The fate of any volatilized halogens remains an additional unknown on Mars. However, volatile halogens on Earth exchange

easily between solid, aqueous, and gaseous phases (Simpson et al., 2007), likely enabling a steady state to be reached over the ~2.5–3.5 Ga geologic ages of Meridiani (Andrews-Hanna et al., 2007) and Gusev (Parker et al., 2010). Even though modern Mars seems to lack sabkhas and playas, their analogs could have existed cyclically in places like Meridiani (e.g., Hayes et al., 2011) and Gusev (Wang et al., 2008) enabling a steady state. Factors such as wind patterns, atmospheric temperature profiles, and atmospheric dust load may also offer varying environments for volatile phases to condense and redistribute.

Terrestrial BrO_x species exist only for several hours during daytime (Simpson et al., 2007). The reactive species BrO in the terrestrial troposphere would eventually convert to BrCl or BrONO₂ within a few hours after sunset (Wayne et al., 1995). Clouds and aerosols enable subsequent surface deposition. Despite the unknown significance of such pathways on Mars, the dearth of removal agents such as clouds might extend the atmospheric lifetime of volatilized halogens, facilitating long-distance transportation. Fine particles suspended by dust storms or dust devils may offer adsorption surfaces with which to convert from gas to solid phases, depositing subsequently on the martian surface under dry conditions.

What evidence supports an atmospheric effect on halogen chemistry in surface materials of Mars? The 2007 Phoenix lander discovered significant quantities of perchlorate (ClO₄⁻) in the water-soluble fraction of soils at the Phoenix polar landing site. The mineralogy hosting the perchlorates is uncertain, but data are consistent with Mg(ClO₄)₂·nH₂O. Measurements indicate that perchlorates may contain most of the chlorine in polar soil (Hecht et al., 2009). Analysis of Rocknest soil at Gale Crater also supports perchlorate presence (Archer et al., 2013; Sutter et al., 2013). Although aqueous processes may influence perchlorate geochemistry on Mars (Marion et al., 2010), the perchlorate ions on Mars may ultimately originate atmospherically (Catling et al., 2010). Terrestrial perchlorates, found in the stratosphere and as mineralization in hyperarid environments, result from photochemical oxidative processes involving volatile chlorine species (Catling et al., 2010) as discussed by Bao and Gu (2004).

2. Data and methods

For this analysis, we examined Alpha Particle X-ray Spectrometer (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). MERAnalyst makes both data sets available to the public (http://an.rsl.wustl.edu/mer/MERB/merb_apxsoxide.htm), including introduction, key work (e.g., Gellert et al., 2006; Ming et al., 2008), notes on data evolution, and oxide data as *.csv files. The *.csv file header row includes sol identifier (spectrum), team consensus on target type (type), stoichiometric oxide mass fraction, and corresponding uncertainty at two standard errors. Target type contributed to our own classification by distinguishing soil targets from rocks and by identifying different soil preparation methods. Several different sampling methods of soil at the two sites show varying effects of local mineralogy. For example, local alkaline volcanics make some soils in Gusev Crater P-rich, and bedrock-derived hematitic spherules make some Meridiani Planum soils Fe-rich.

Soil excavations constitute a critical component of the data at both Gusev and Meridiani. In the Columbia Hills of Gusev Crater, some surface soils and associated subsurface soils exposed by a failed rover wheel differ dramatically (Yen et al., 2008). For this study, we term such excavations "involuntary." The mission also sampled soil intentionally as "trenches" by rotating a single rover

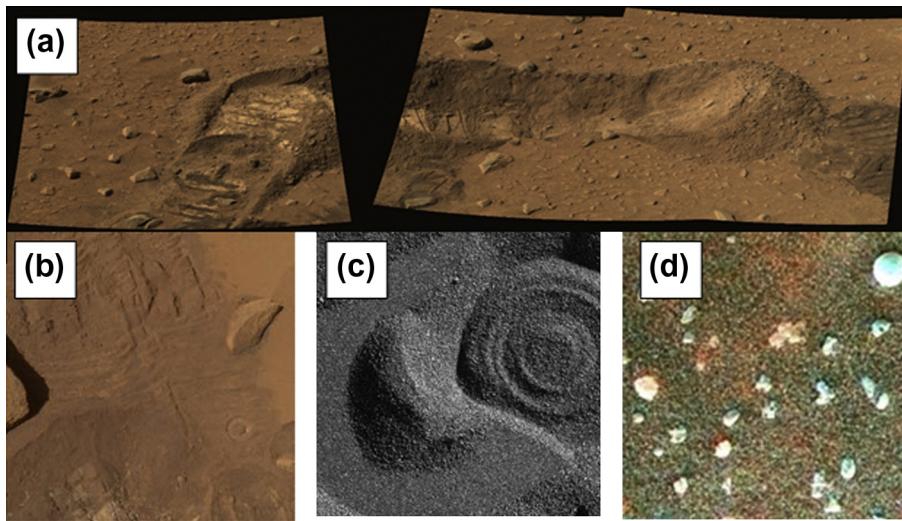


Fig. 1. Examples of different soil sampling methods we used to distinguish soil types: (a) trench activity at Gusev shown by a Pancam mosaic generated of Boroughs on Sol 142 (available online 1). Boroughs is approximately 20 cm wide and 11 cm deep. (b) Disturbed soil sample at Gusev imaged by the Pancam on Sol 343 (online 2) bearing the Mossbauer contact plate imprint roughly 5 cm across. (c) MI $\sim 3 \times 3$ cm on Sol 236 of Meridiani soil sample brushed with the RAT (online 3). (d) MI on Sol 10 of undisturbed soil at Meridiani colorized with Pancam data (online 4). Photo credits: JPL/NASA/Cornell/USGS, MER-Analyst (online 5), and Pancam Images (online 6). Online 1: http://pancam.astro.cornell.edu/pancam_instrument/142A_new.html. Online 2: http://pancam.astro.cornell.edu/pancam_instrument/images/True/Sol343A_P2573_1_True_R-AD_thumb.jpg. Online 3: http://pds-geosciences.wustl.edu/mer/mer1-m-mi-3-rdr-sci-v1/mer1mi_1xxx/extras/sol0236/B0236auk_rawenh.tif. Online 4: http://pancam.astro.cornell.edu/pancam_instrument/images/merges/images/1MP010I0F02ORT24P2933L256F1_ec-th.jpg. Online 5: <http://an.rsl.wustl.edu/mer/>. Online 6: http://pancam.astro.cornell.edu/pancam_instrument/images.html.

wheel in place (Fig. 1a), as “disturbances” by brief wheel rotation scuffs (Fig. 1b) or wheel motion over soil, as “brushed” by spinning the Rock Abrasion Tool’s brush mechanism against the soil (Fig. 1c), or as pristine surface samples undisturbed by the rover (Fig. 1d). Microscopic Images (MI) taken before and after subsurface soil exposure generally accompanied subsurface sampling. For sufficiently deep trenches, APXS observations of the adjacent surface, interior wall, and floor (Wang et al., 2006) offered the best chemical insight to date of the martian soil profile. Trenches in particular were expected to characterize the bulk soil for comparisons with depth-sensitive chemical remote sensing by the Mars Odyssey Gamma Ray Spectrometer (GRS) at regional scales (Karunatillake et al., 2007).

With the goal of identifying relationships among the elements of interest in the context of atmosphere–surface interactions, we subdivided the Gusev soils ($n = 60$) 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). The details of these categories follow:

1. The moderate S category consisted of all soil with elemental S mass fractions less than 4%.
2. In addition to the S threshold, basaltic soil excluded potential sinter/bleached soil and hydrothermally altered samples such as those discussed by Ruff et al. (2011) and Yen et al. (2008), respectively.
3. Trench soil excluded involuntary excavations, such as Paso Robles soil, made by the Spirit Rover’s immobile wheel. For additional insight into the soil profiles we compared surface, wall, and floor samples at each of the three Gusev trench sites.
4. Disturbed soil included all shallow subsurface samples, such as wheel scuffs and involuntary excavations, but excluded trench soil.
5. On the other hand, disturbed normal soil also excluded Paso Robles (hydrothermal origin) and Kenosha Comets (sinter/bleached) samples.
6. Surficial soil consisted of normal soil from undisturbed surfaces.

We list the sol, feature name, and APXS-derived composition for samples of each soil category in the worksheet “Gusev” of the [Supplementary Excel file “S1SoilCategories.”](#) The first two worksheets of this file contain the first 1368 sols of data for each landing site extracted from the MERAnalyst *.csv files. Remaining worksheets enumerate sol and target names for each soil category at the two landing sites. Columns in the first two worksheets include the classification as soil (header: “soil?”). For samples identified as soil, several additional columns of moderate S, basaltic, trench, disturbed, disturbed normal, and undisturbed surficial soil identify classification into each of the six overlapping categories. Remaining columns present oxide – elemental, in the case of Br and Cl – percentage mass fractions. $\mu\text{g/g}$ mass fractions describe the abundances of minor elements Br, Ni, and Zn. We assessed available images (MIs, panoramic camera, navigation camera, hazard camera) and mission reports to assign a given sample to each category. This also enabled us to identify samples uniquely even in cases of ambiguous or conflicting target names.

Compositional complexities from the presence of hematitic spherules (aka “blueberries”) – considered sedimentary in origin – prompted us to divide Meridiani soil ($n = 38$) into seven overlapping categories. As with Gusev data, we identify samples of each category in the worksheet “Meridiani” of the [Supplementary Excel file “S1SoilCategories.”](#) Most categories remain similar to those used at Gusev, as evident below:

1. Moderate S content soil ($n = 37$).
2. Basaltic soil (23) which, in addition to moderate S content, excluded soil enriched in hematitic spherules.
3. Trench soil (4).
4. Disturbed soil (8).
5. Disturbed soil with moderate S content and low hematite content (5). Such soil contained less than 20% FeO_T with negligible hematitic spherule visibility in available MI and Pancam images.
6. Surficial soil (26). All contained moderate sulfur mass fractions, at less than 4%.
7. Surficial soil without excessive hematite (15).

As key statistical parameters, 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. Standard errors of the correlation coefficients (r) decreased primarily with the number of data and increased with relative scatter of data from a least squares line fit (Karunatillake et al., 2012). Adjusted coefficient of determination (R^2) as well as standard errors of regression slopes and intercepts varied accordingly (Karunatillake et al., 2012). We computed these detailed statistical parameters not only for each elemental pair, but also for each of the 13 soil categories at Gusev and Meridiani. As with Br–S in Section 3, we communicate the results summarily with scatter plots of mutually dependent regression parameters of correlation and slope. To provide context, we describe the underlying data with scatter plots of Br–S and Br–Mg for strong and weak correlation extremes. In addition to highlighting key observations, our methodology prevents a bewildering array of 97 scatter plots and corresponding regression results.

Given our primary interest in elemental trends rather than specific values, and evidence for high instrumental precision (Rieder et al., 2004), we included data with lower Br concentrations, where specifically reported, in our statistical analysis. Nevertheless, even in the context of elemental trends, our results may be sensitive to the greater uncertainties associated with Br. The trace element Br is a special case usually assigned a detection limit of about 30 µg/g despite lower reported values in the literature (Rieder et al., 2004).

3. Results and discussion

Our observations of Gusev trench soil indicate broad consistency with the loss of surficial Br to the atmosphere, driven by UV photolysis (Wood and Sanford, 2007), by chemical oxidants perhaps including –OH radicals (Urbansky, 1998), or by the auto-catalytic pathway involving HOBr (Simpson et al., 2007). 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, roughly in the order Br > S > Cl, yield higher Br/Cl, lower S/Br, and higher S/Cl ratios in the subsurface. Table 1 illustrates this trend by comparing averages of surface ratios (undisturbed) with subsurface (trench) ratios.

Trends across soil categories confirm the vertical variations in Br observed at the trenches. That Br correlates strongly with S in the subsurface is evident in Fig. 2 summary plot showing the twin regression parameters of correlation and slope. Fig. 3 provides bivariate scatter plot context for the strongest elemental association in summary plots of correlation and slope (e.g., Fig. 2). For example, the Br–S scatter plot for the trench category at Gusev (Fig. 3a) generates the trench datum in Fig. 2. Despite few data, the correlation coefficient of 0.9 (± 0.2 at 1 standard error) corresponds to 73% of the Br variability modeled by S alone, as indicated by the adjusted coefficient of determination (R^2) (Karunatillake et al., 2012).

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. Differences between surface and depth (trench) indicate variability of Br and S relative to Cl. The values indicate that Br, but not S, increases approximately 2× more than Cl at depth.

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

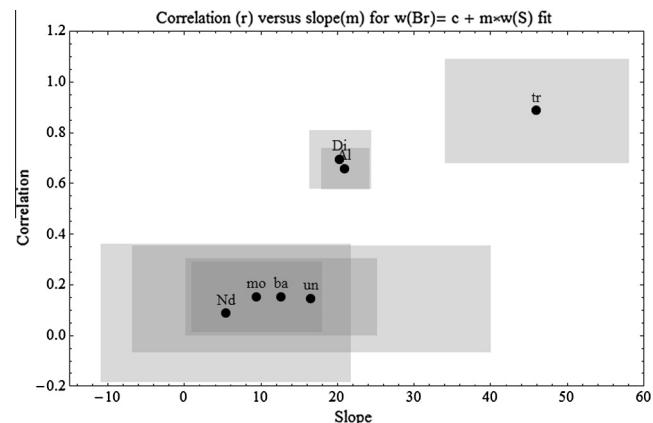


Fig. 2. Plot of correlation coefficient versus slope of linear regressions for Br–S in different soil classes at Gusev. These mutually dependent regression parameters summarily illustrate Br–S mass fraction trends. Labels indicate soil type as described in detail in Section 2: trench (tr), disturbed (Di), all data (Al), moderate S (mo), undisturbed surface soil (un), basaltic soil (ba), normal disturbed soil (Nd). The Supplementary Excel file "S1SoilCategories" identifies samples of each type. Shaded rectangles correspond to 1 standard error in each parameter.

Fig. 3b shows the scatter of Br with Mg in Gusev's Trench soil category, where 90% of Br variability can be modeled with Mg alone. Fig. 3c shows MIs of corresponding samples. Our one standard error bars (using gray shading to avoid visual clutter) for slope and correlation in Fig. 2 account both for data scatter and the number of data, where fewer data cause higher uncertainty than evident visually in scatter plots (e.g., Fig. 3a and b).

In summary, the Br/Cl ratio is lower at the surface (Table 1), Br correlates strongly with S at depth yielding a higher Br/S ratio, and nearly all of the variability in Br can be modeled by S and Mg variations alone (Figs. 2 and 3a and b) in subsurface (trench) soil. The substantially stronger correlation of Br with Mg (Fig. 3b) compared to that with S (Figs. 2 and 3a) suggests coupling between Br and Mg beyond indirect association from subsurface Mg and S correlation. Such indirect variation arise, for example, from the presence of Mg-sulfates in soil along with co-migration of halides and sulfates during aqueous processes.

Fig. 4 shows an example of a bivariate scatter plot to provide context for the weakest association between Br and S, found in the Meridiani surficial soil category. Beyond the visual contrast with the scatter plot from the Gusev trench (Fig. 3a), a factor of 4 higher uncertainty in slope (translating to a factor of 23 higher relative uncertainty), despite more data, reflects our analytical approach that integrates both scatter and the number of data in uncertainty estimates (Karunatillake et al., 2012). Fig. 5, a plot of correlation coefficients versus regression slopes, summarizes the data in Fig. 4 as the surficial soil type at Meridiani.

Br regresses with S at distinctly higher correlation and slope in trench soil than in most other soil categories (Fig. 2) at Gusev. A similar trend at Meridiani (Fig. 5) remains discernable despite insufficient data for trench soil ($n = 4$) inducing substantial uncertainty. Also consistent with stronger coupling of Br and S at depth, only the correlation within disturbed soil exceeds the ~0.5 value of trench soil.

Several factors contribute to subsurface trends. Some subsurface soil may reflect a history of alteration and consolidation over longer periods than eolian infill of secondary crater depressions, termed hollows by the MER team (e.g., Squyres, 2004). Furthermore, compositional trends with depth vary from one trench to another. Such variability makes the depth gradient difficult to quantify across the three trenches (Boroughs, Big Hole, Road Cut) at Gusev. Among these, Boroughs type soil seems areally abundant,

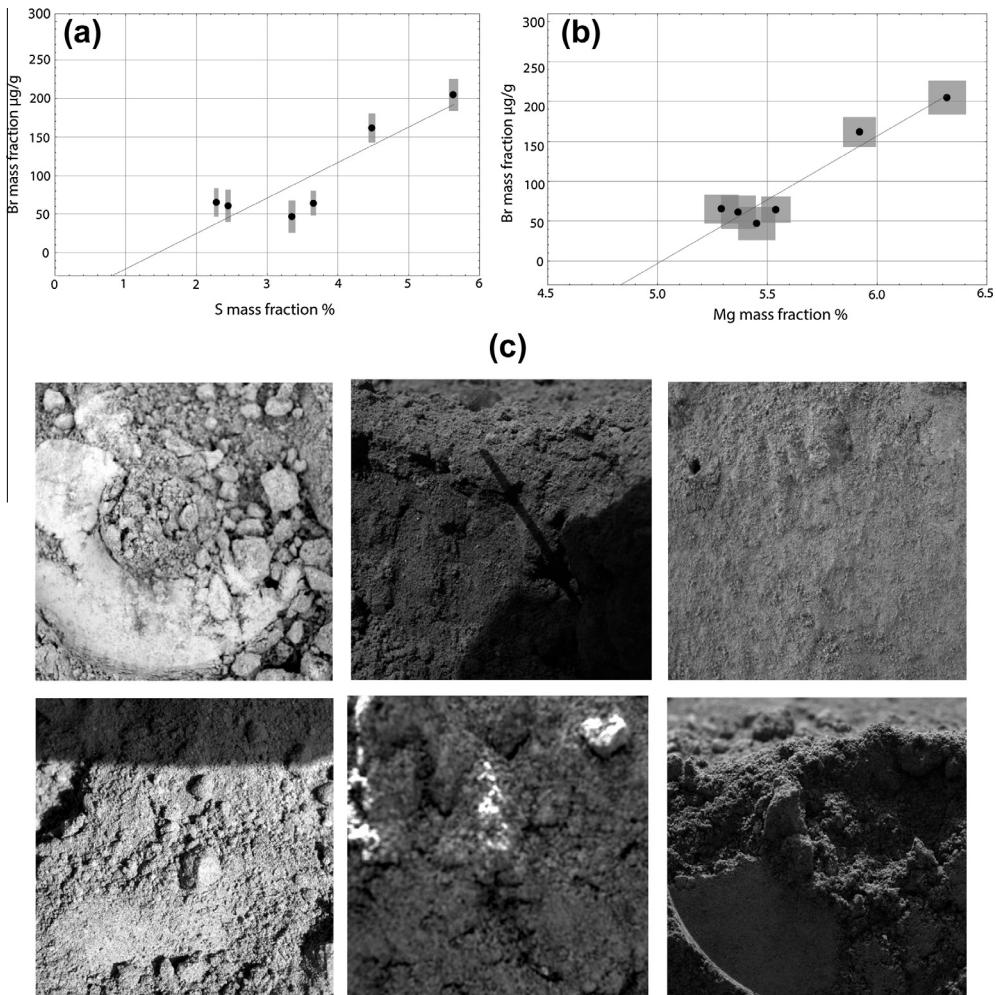


Fig. 3. Correlation of Br ($\mu\text{g/g}$) with S and Mg in Gusev trench soil samples. Bivariate regression of Br with S (a) yields a slope, $m = 46 \pm 12$; and intercept, $C = -67 \pm 46$, at one standard error including a strong correlation coefficient of ~ 0.9 . Similarly, with a slope, $m = 160 \pm 23$, and intercept, $C = -800 \pm 100$, Br yields an ~ 1.0 correlation with Mg (b). Consequently, S and Mg alone model more than 90% of the variability in Br within trench soil, despite the statistical constraint of only six samples. Gray shading about each datum indicates 1 standard error uncertainty. Sample images by the MI shown in left-right top-bottom order (c): Bighole_RS2 (sol 114); Bighole_Trico (sol 115); Boroughs_Hellskitchen_side (141); Boroughs_Mills_bottom (140); Road cut_Floor3 (49); and Road Cut_WallMI (50). Each image has dimensions of $\sim 3 \times 3$ cm.

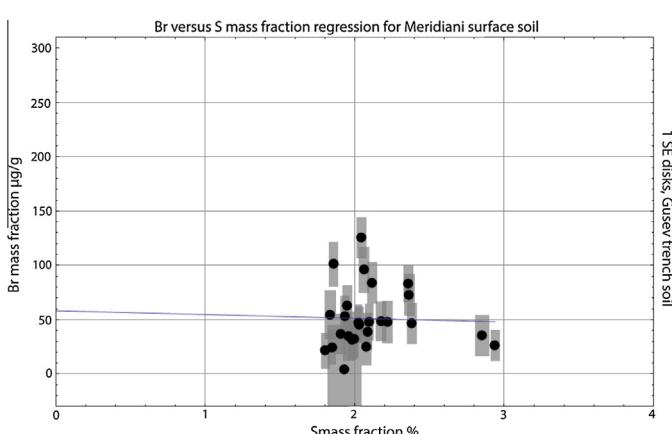


Fig. 4. Scatter plot of Br versus S revealing that Br (as $\mu\text{g/g}$) does not correlate with S within undisturbed surface soil at Meridiani. Provides contextual detail for the surficial soil type in the Br-S correlation and slope summary plot (Fig. 5). Regression results model $w(\text{Br})$ with slope, $m = -3 \pm 20$, and intercept, $C = 58 \pm 43$, at 1 standard error. The roughly factor of four higher uncertainty of the slope (corresponding to $23\times$ higher relative uncertainty) when compared with Gusev trench data (Figs. 2 and 3) reflects scatter overwhelming any correlation.

perhaps geologically old, and most representative of chemical processes over geologic time scales (Karunatillake et al., 2007). Furthermore, the Boroughs trench shows evidence for increasing Br depletion towards shallower 4–5 cm depths from 7 to 10 cm depths. Despite ambiguities, all three trenches show consistently lower Br mass fractions and correspondingly lower Br/Cl ratios at the surface (Fig. 6, surface samples highlighted as circles) relative to deeper wall and floor samples (Fig. 6, solid squares and disks, respectively).

Meridiani soil analyses suggest that Br varies at depth in a manner roughly similar to that at Gusev. For example, Br decreases towards the surface, thus acting as the primary control on elemental ratios (compare Fig. 6 with Fig. 7) as evident in consistently lower Br/Cl ratios and Br mass fractions at the surface (Fig. 7 open circles) relative to depth (Fig. 7 solid squares and circles) in trenches. Meridiani samples differ in some ways, including less clear variation in the correlation of Cl (Fig. 8) and Br (Fig. 5) with S across different soil types. Furthermore, Cl and Br correlate strongly at Meridiani in trench soil but not at Gusev (Fig. 9).

Do volatilized halogens – Br in particular – transported throughout the martian surface remain a viable model despite differences in the detailed trends of Br, Cl, and S at Gusev relative to those at Meridiani? Established differences in petrogenetic

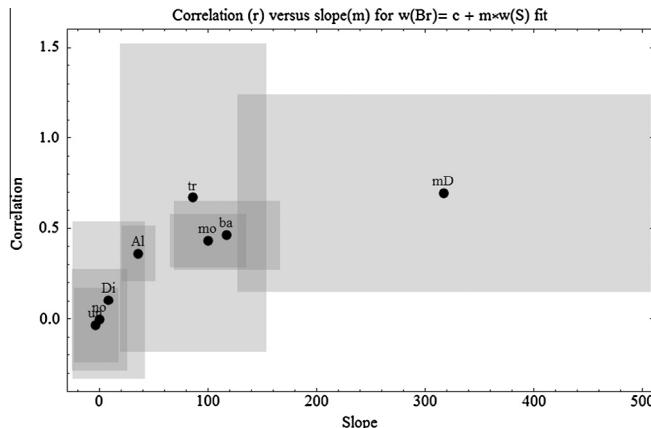


Fig. 5. Plot of correlation coefficient versus slope of linear regressions for Br-S in different soils classes. These mutually dependent regression parameters summarily illustrate Br-S association trends at Meridiani. Labels identify the seven soil types as described in detail in Section 2: moderate S content soils (mo), basaltic soils (ba), trench soils (tr), disturbed soils (Di), disturbed soils with moderate S content and low hematite content (mD), surficial soils (un), surficial soils without excessive hematite (no). The Supplementary Excel file “S1SoilCategories” identifies samples of each type. Shaded rectangles correspond to 1 standard error in each parameter.

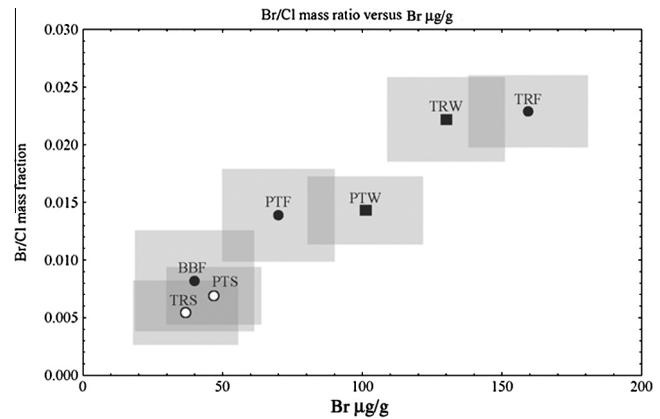


Fig. 7. Trench profile at Meridiani. Labels identify specific trenches, BB: Beagle Burrow; PT: Peanut Trench; TR: Trench. Suffixes identify location at trench site, S: Surface, W: Wall, and F: Floor. We propagated highly conservative numerical uncertainties from reported values for Br and Cl at 2 standard errors, shown as shaded rectangles. Consequently, the values may be more precise than they appear. Note the difference across floor, wall, and surface with highest ratios at the floor sampling the deepest. The ratio also varies roughly linearly with Br, indicating a relatively uniform Cl content.

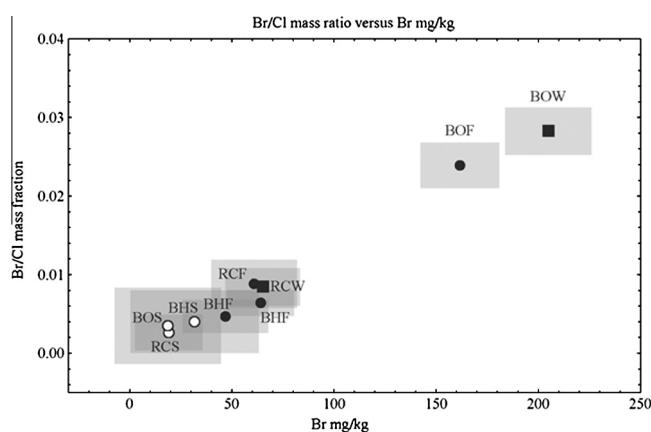


Fig. 6. Trench profile at Gusev for the mass fraction ratio Br/Cl. Labels identify specific trenches, BO: Boroughs; RC: Road Cut; BH: Big Hole. Suffixes and shapes identify location at trench site, S: surface as circle, W: wall as solid square, and F: floor as disk. We propagated highly conservative numerical uncertainties from reported values for Br and Cl at 2 standard errors, shown as shaded rectangles. Consequently, the values are more precise than they appear. Note the difference across floor, wall, and surface with highest ratios at the floor sampling the deepest. The ratio also varies roughly linearly with Br, indicating a relatively uniform Cl content.

processes at the two sites (McLennan et al., 2005; McSween et al., 2010, 2008) may drive some of the differences. For example, Meridiani outcrops likely originate from sedimentary processes sustained by temporally and spatially varying ground water tables analogous to terrestrial playas (McLennan et al., 2005). In contrast, most float rocks and outcrop at Gusev appear igneous, with those in the Columbia Hills suggesting limited aqueous alteration (McSween et al., 2010, 2008). Gusev sedimentary rocks seem coupled to volcanism – and in places impact related processes – such as Home Plate deposited in a pyroclastic surge (Lewis et al., 2008) and carbonate-bearing Comanche precipitating in hydrothermal environments (Morris et al., 2010). Local rocks at each site may contribute to soil via comminution and chemical weathering (Yen et al., 2005). For example, hematite lag deposits at Meridiani not only constitute a local component of soil (Fleischer et al., 2010)

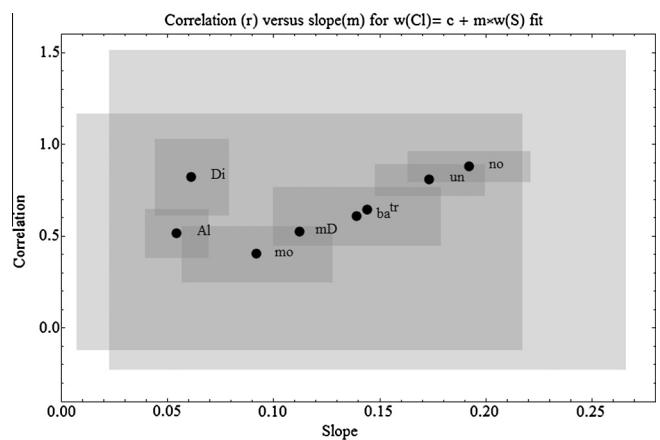


Fig. 8. Plot of correlation coefficient versus slope of linear regressions for Cl versus S mass fraction in different soils classes at Meridiani. These mutually dependent regression parameters summarily illustrate Cl-S association. Labels identify the seven soil types as described in detail in Section 2: moderate S content soils (mo), basaltic soils (ba), trench soils (tr), disturbed soils (Di), disturbed soils with moderate S content and low hematite content (mD), surficial soils (un), and surficial soils without excessive hematite (no). The Supplementary Excel file “S1SoilCategories” identifies samples of each type. Shaded rectangles correspond to 1 standard error in each parameter.

but also suggest mechanical weathering (Squyres et al., 2009) and sediment contribution from sedimentary S-rich host rock. If so, the high variability of Br in Meridiani rocks relative to other elements (Clark et al., 2005, p. 83) may obscure similarities with the halogen distributions in Gusev soil.

3.1. The variability of S/Cl across landing sites

Differences in labile element trends between Meridiani and Gusev motivated us to evaluate the common conclusion that martian soil remains quite uniform in elemental composition across the vast distances that separate different landing sites (Gellert et al., 2006; Yen et al., 2005). The ratio of S and Cl mass fractions in particular has been considered to be nearly constant at ~3.6 (Gellert et al., 2006, p. 73). Key models of Cl and S evolution on Mars also suggest a similarity of sources such as volcanic exhalations or

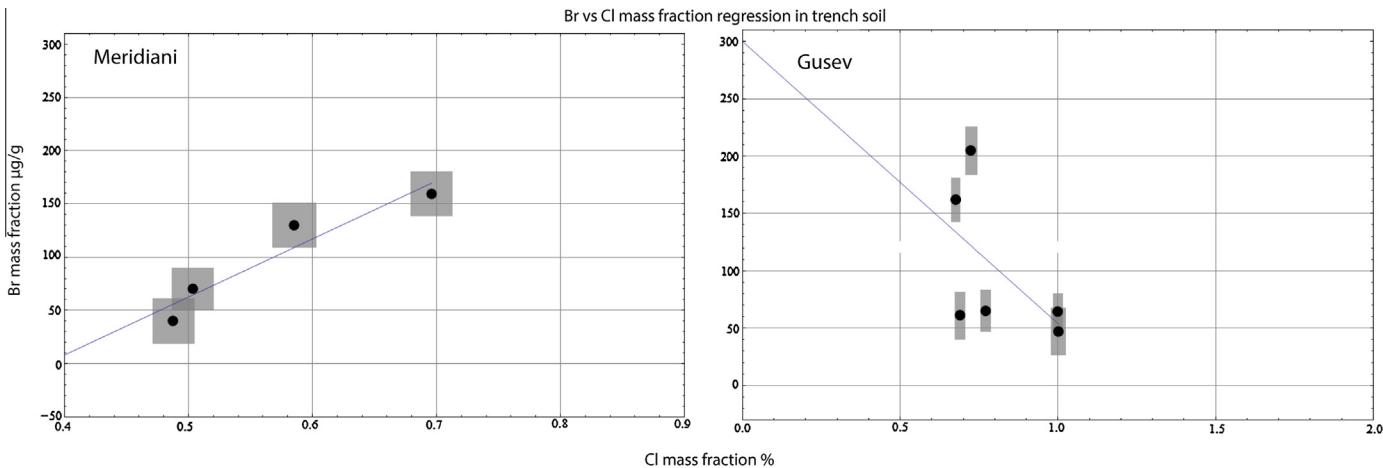


Fig. 9. Correlation of Br (mass fraction as $\mu\text{g/g}$) with Cl within trench soil compared between Meridiani (left) and Gusev (right). Despite the few samples, Br regression shows less uncertainty in slope (550 ± 120) at Meridiani, versus -250 ± 180 at Gusev, indicating less scatter. Accordingly, Cl models nearly $\sim 90\%$ of Br variability at Meridiani compared to only $\sim 15\%$ at Gusev. Unlike at Meridiani, Br also appears to anticorrelate with Cl at Gusev. Shaded rectangles signify one standard error uncertainty of each datum.

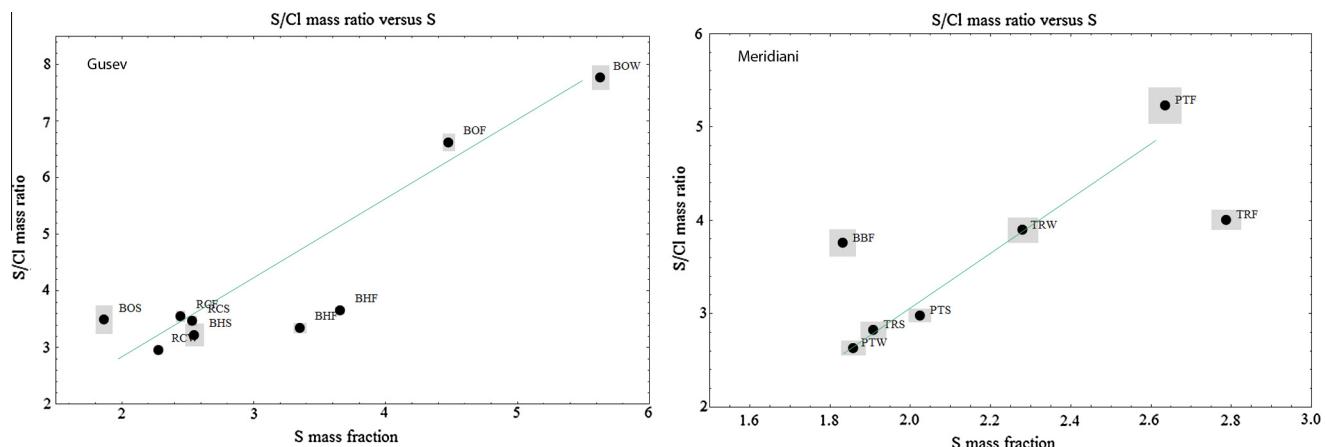


Fig. 10. Trench profile of S/Cl mass ratios versus S at Gusev (left) and Meridiani (right). Labels identify specific trenches at Gusev: BO: Boroughs; RC: Road Cut; and BH: Big Hole. Suffixes identify position within each trench, S: Surface, W: Wall, and F: Floor. Corresponding labeling at Meridiani indicate Beagle Burrow (BB), Peanut Trench (PT), and Trench (TR). We propagated highly conservative numerical uncertainties from reported values for Br and Cl at 2 standard errors, shown as shaded rectangles. Consequently, the values may be more precise than they appear. Note the difference across floor, wall, and surface with lowest ratios occurring at the surface. While less pronounced than with the Br/Cl ratio, linearity in trends (accentuated with the green lines) suggest S/Cl variations driven more by S than Cl.

secondary minerals from fluids (McSween et al., 2008, para. 19). Nevertheless, soils from different landing sites, despite broadly similar chemical composition, when examined in detail exhibit variations among landing sites, explained largely by differences in local geology; across each landing site, explained largely by variable geology and aqueous processes; and within vertical profiles. A variety of aqueous processes may explain the latter, perhaps extending to atmospheric processes for Br variability.

Some data across different landing sites suggest a variable S/Cl ratio. Analyses of trench soil samples at Gusev and Meridiani suggest a S/Cl ratio substantially higher than 3.6 at decimeter-scale depths of GRS sensitivity (Karunatillake et al., 2007). In contrast, Phoenix data indicate much lower S/Cl ratios approximating 1.8 (Kounaves et al., 2010), although this value only represents water-soluble salts in the soil. Collectively, such observations further suggest that the variability of the S/Cl ratio on Mars may have been underestimated. Our work also indicates a higher S/Cl ratio with depth at both Gusev (summarized in Table 1) and Meridiani, from ~ 3.6 at the surface to values of 4–5 in the subsurface (Fig. 10 shows trench profiles at both sites). While the S–Cl correlation weakens only at depth, positive Cl intercepts (Fig. 11), amounting

to $\sim 15\%$ of the typical 0.6–0.7% Cl mass fraction in basaltic soil, occur even in soil categories where S and Cl correlate strongly. Consequently, the two elements may fractionate significantly in bulk martian soil at depth scales on the order of decimeters or more.

Aqueous and photochemical processes on Earth and recent experiments suggest that Br may volatilize preferentially, imparting a stronger volatility signature relative to Cl (Vogt et al., 1996; Yang et al., 2008; Zhao et al., 2013). Once volatilized, gaseous inorganic Br may reside in the atmosphere almost three times longer than gaseous inorganic Cl, reflecting more efficient cycling of Br than Cl in the terrestrial atmosphere (Rancher and Kritz, 1980). However, perchlorates in the martian arctic zone, as observed by Phoenix (Hecht et al., 2009), support Cl volatility with soil acting as a sink over geologic time scales (Catling et al., 2010). S may also volatilize (Halevy and Schrag, 2009; Halevy et al., 2007) on Mars.

Cl may volatilize, but the preferential decrease of Br towards the surface (Figs. 6 and 7 and Table 1) supports a more pronounced loss of Br to the atmosphere relative to Cl and S, at least at the Gusev landing site. Two pathways may contribute to this at unconstrained relative significance: (1) the soil surface may incorporate atmospherically sourced perchlorate preferentially, altering the S/

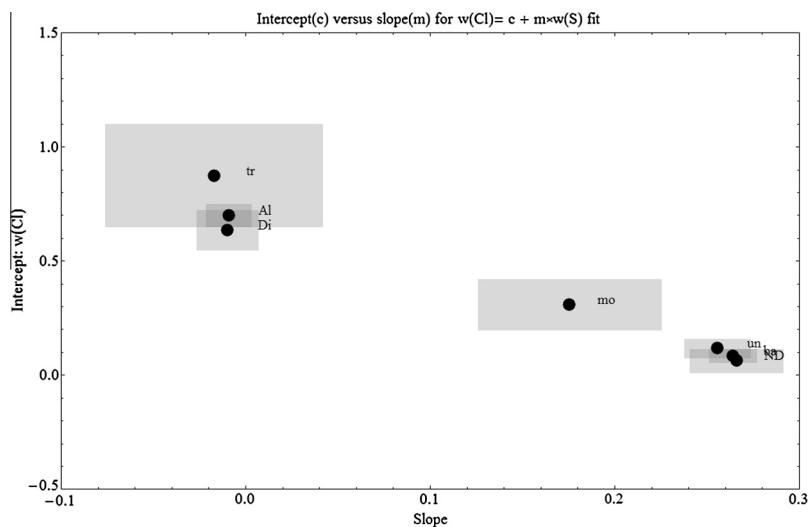


Fig. 11. Scatter plot showing the mutually dependent parameters of intercept versus slope in the regression of Cl with S at Gusev. Labels indicate soil type as described in detail in Section 2: trench (tr), disturbed (Di), all data (Al), moderate S (mo), undisturbed surface soil (un), basaltic soil (ba), normal disturbed soil (ND). The Supplementary Excel file “S1SoilCategories” identifies samples of each type. Shaded rectangles correspond to 1 standard error in each parameter. Cl and S dissociate in deeper soil, in turn disrupting the correlation within the set of all samples. Positive intercepts, even in surficial soil where Cl and S associate strongly, reveal the fractionation of Cl and S.

Cl ratio at the surface relative to the subsurface; (2) with halide phases less volatile and less soluble than bromide phases (Yang et al., 2008) as discussed in Section 1.1, Cl may redistribute in less concentrated brines while Br volatilizes from concentrated brine. This may impart a stronger aqueous signature to the Cl distribution than to that of Br.

Pathways to form perchlorate naturally remain unclear (e.g., Bao and Gu, 2004) both on Earth and Mars. Gaseous Cl species can oxidize to perchlorate in the atmosphere by photochemical processes (Catling et al., 2010). However, perchlorate can also form by aqueous Cl^- interacting with oxidants, such as ozone (Rao et al., 2010). In the latter case, photochemical processes may contribute indirectly as a provider of oxidants, while perchlorate forms via liquid-gas reactions *in situ* during evaporation. In such processes, dissolution of Cl species may dominate over the volatilization. More laboratory work remains essential to constrain the relative significance of aqueous mobility relative to volatility of halogens on Mars.

4. Conclusions and future work

Our soil analyses yield two key results. First, halogen variability in the soil profile is consistent with loss to the atmosphere. Accordingly, the more readily volatilized Br shows strong evidence of decreasing concentration and weakening correlation with S toward the surface. Consequently, analogs of some terrestrial processes that volatilize Br, such as frost flower facilitation (Zhao et al., 2008), low-temperature UV-photolysis oxidation (Saiz-Lopez et al., 2008), and salt pan UV-photolysis (Wood and Sanford, 2007), could be significant on Mars. Brine films on dust grains may also accelerate halogen volatilization (Sander et al., 2003).

We find our observations sufficiently compelling, necessitating additional work to distinguish volatility pathways from the alternative of evaporative processes and post-depositional fluid migration (e.g., Amundson et al., 2008; Clark et al., 2005; Yen et al., 2005). To this end, we have begun a laboratory program experimentally evaporating UV-exposed bromide-chloride and bromide-chloride-sulfate brines under conditions more representative of Mars (Zhao et al., 2013) than the single experiment

reported by Wood and Sanford (2007). Preliminary laboratory observations appear to strengthen the potential for halogen volatility to impart a discernible chemical signature (Zhao et al., 2013).

Second, the soil profile shows more variable S/Cl mass ratios than previously thought. The soil profile samples Mars at greater depth than the hundreds of microns by most remote sensing missions, in richer detail than at multi-meter resolution of compositional effects on dielectric properties by radar methods (Carter et al., 2009; Watters et al., 2007), and with greater fidelity of bulk soil than surface measurements. As a mix of surface material exposed to recent eolian processes with subsurface soil that may record varying climatic and aqueous conditions over geologic time scales, bulk soil presents the key to understanding martian surface evolution (McSween et al., 2010). Based on our observations, such soil – likely sampled globally by the GRS – bears a bi-modal S/Cl distribution with low values at the surface approximating 3.6, and higher subsurface values in the 4–5 range. Due to reasons discussed in Section 3.1, we posit further that aqueous processes may overprint S/Cl variability, unlike that of Br driven more by atmospheric release.

Acknowledgments

This work was supported by NASA Mars Data Analysis Program Grants (NNX07AN96G, NNX11AI94G, and NNX12AG89G) and by post-doctoral funding from Louisiana State University’s Geology & Geophysics program in the College of Science. We thank Dr. Johannes Brückner for discussions on APXS data. We thank Dr. Joel Hurowitz and an anonymous scientist for reviews that enhanced the science and clarity of our paper. Drs. Doug Archer, Brad Sutter, David Catling, Yuhang Wang, and Huiming Bao contributed illuminating discussions on the possibility and sources of reactive halogens on Mars.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.icarus.2013.07.018>.

References

- Amundson, R. et al., 2008. On the in situ aqueous alteration of soils on Mars. *Geochim. Cosmochim. Acta* 72, 3845–3864.
- Andrews-Hanna, J.C., Phillips, R.J., Zuber, M.T., 2007. Meridiani Planum and the global hydrology of Mars. *Nature* 446, 163–166.
- Archer Jr., P.D. et al., 2013. Possible detection of perchlorates by evolved gas analysis of Rocknest soils: Global implications. *Lunar Planet Sci.* 44, Abstract 2168.
- Bao, H., Gu, B., 2004. Natural perchlorate has a unique oxygen isotope signature. *Environ. Sci. Technol.* 38, 5073–5077.
- Broecker, W.S., Peng, T., Beng, Z., 1982. Tracers in the Sea. Columbia University.
- Buya, Z., Brough, N., Huey, G., Tanner, D., Von Glasow, R., Jones, A.E., 2012. Br₂, BrCl, BrO and surface ozone in coastal Antarctica: A meteorological and chemical analysis. *Atmos. Chem. Phys. Discuss.* 12, 11035–11077.
- Byrne, S. et al., 2009. Distribution of mid-latitude ground ice on Mars from new impact craters. *Science* 325, 1674–1676.
- Carr, M.H., 2008. The Surface of Mars. Cambridge University Press, New York.
- Carter, L.M., Campbell, B.A., Watters, T.R., Phillips, R.J., Putzig, N.E., Safaeinili, A., Plaut, J.J., Okubo, C.H., Egan, A.F., Seu, R., Biccari, D., Orosei, R., 2009. Shallow radar (SHARAD) sounding observations of the Medusae Fossae Formation, Mars. *Icarus* 199, 295–302.
- Catling, D.C. et al., 2010. Atmospheric origins of perchlorate on Mars and in the Atacama. *J. Geophys. Res.* 115, E00E11.
- Clark, B.C. et al., 2005. Chemistry and mineralogy of outcrops at Meridiani Planum. *Earth Planet. Sci. Lett.* 240, 73–94.
- Cockell, C.S., Catling, D.C., Davis, W.L., Snook, K., Kepner, R.L., Lee, P., McKay, Christopher P., 2000. The ultraviolet environment of Mars: Biological implications past, present, and future. *Icarus* 146, 343–359.
- Fairén, A.G., Davila, A.F., Gago-Duport, L., Amils, R., McKay, Christopher P., 2009. Stability against freezing of aqueous solutions on early Mars. *Nature* 459, 401–404.
- Finlayson-Pitts, B.J., 2010. Atmospheric chemistry. *Proc. Natl. Acad. Sci. USA* 107, 6566–6567.
- Fleischer, I., Agresti, D.G., Klingelhöfer, G., Morris, R.V., 2010. Distinct hematite populations from simultaneous fitting of Mössbauer spectra from Meridiani Planum, Mars. *J. Geophys. Res.* 115, E00F06.
- Gellert, R. et al., 2006. Alpha Particle X-ray Spectrometer (APXS): Results from Gusev Crater and calibration report. *J. Geophys. Res.* 111, E02S05.
- Grotzinger, J.P., Hayes, A.G., Lamb, M.P., McLennan, S.M., 2013. Sedimentary processes on Earth, Mars, Titan, and Venus. In: Mackwell, S.J. (Ed.), Comparative Climatology of Terrestrial Planets. University of Arizona.
- Halevy, I., Schrag, D.P., 2009. Sulfur dioxide inhibits calcium carbonate precipitation: Implications for early Mars and Earth. *Geophys. Res. Lett.* 36, L23201.
- Halevy, I., Zuber, M.T., Schrag, D.P., 2007. A sulfur dioxide climate feedback on early Mars. *Science* 318, 1903–1907.
- Hayes, A.G., Grotzinger, J.P., Edgar, L.A., Squyres, S.W., Watters, W.A., Sohl-Dickstein, J., 2011. Reconstruction of eolian bed forms and paleocurrents from cross-bedded strata at Victoria Crater, Meridiani Planum, Mars. *J. Geophys. Res.* 116, E00F21.
- Hecht, M.H. et al., 2009. Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. *Science* 325, 64–67.
- Hönninger, G., Bobrowski, N., Palenque, E.R., Torrez, R., Platt, U., 2004. Reactive bromine and sulfur emissions at Salar de Uyuni, Bolivia. *Geophys. Res. Lett.* 31, L04101.
- Hurowitz, J.A., McLennan, S.M., 2007. A ~3.5 Ga record of water-limited, acidic weathering conditions on Mars. *Earth Planet. Sci. Lett.* 260, 432–443.
- Hurowitz, J.A., Tosca, Nicholas J., McLennan, S.M., Schoonen, M.A.A., 2007. Production of hydrogen peroxide in martian and lunar soils. *Earth Planet. Sci. Lett.* 255, 41–52.
- Kaleschke, L., 2004. Frost flowers on sea ice as a source of sea salt and their influence on tropospheric halogen chemistry. *Geophys. Res. Lett.* 31, L16114.
- Karunatillake, S. et al., 2007. Chemical compositions at Mars landing sites subject to Mars Odyssey Gamma Ray Spectrometer constraints. *J. Geophys. Res.* 112, E08S90.
- Karunatillake, S. et al., 2012. Martian case study of multivariate correlation and regression with planetary datasets. *Earth, Moon, Planets* 108, 253–273.
- Knoll, A.H. et al., 2008. Veneers, rinds, and fracture fills: Relatively late alteration of sedimentary rocks at Meridiani Planum, Mars. *J. Geophys. Res.* 113, 1–27.
- Kounaves, S.P. et al., 2010. Soluble sulfate in the martian soil at the Phoenix landing site. *Geophys. Res. Lett.* 37, L09201.
- Lefèvre, F. et al., 2008. Heterogeneous chemistry in the atmosphere of Mars. *Nature* 454, 971–975.
- Lewis, K.W. et al., 2008. Structure and stratigraphy of Home Plate from the Spirit Mars Exploration Rover. *J. Geophys. Res.* 113, E12S36.
- Marion, G.M., Catling, D.C., Kargel, J.S., 2009. Br/Cl partitioning in chloride minerals in the Burns formation on Mars. *Icarus* 200, 436–445.
- Marion, G.M., Catling, D.C., Zahnle, K.J., Claire, M.W., 2010. Modeling aqueous perchlorate chemistries with applications to Mars. *Icarus* 207, 675–685.
- McLennan, S.M. et al., 2005. Provenance and diagenesis of the evaporite-bearing Burns formation, Meridiani Planum, Mars. *Earth Planet. Sci. Lett.* 240, 95–121.
- McSween, H.Y. et al., 2008. Mineralogy of volcanic rocks in Gusev Crater, Mars: Reconciling Mössbauer, Alpha Particle X-ray Spectrometer, and miniature thermal emission spectrometer spectra. *J. Geophys. Res.* 113, E06S04.
- McSween, H.Y., McGlynn, I.O., Rogers, A.D., 2010. Determining the modal mineralogy of martian soils. *J. Geophys. Res.* 115, E00F12.
- Ming, D.W. et al., 2008. Geochemical properties of rocks and soils in Gusev Crater, Mars: Results of the Alpha Particle X-ray Spectrometer from Cumberland ridge to home plate. *J. Geophys. Res.* 113, E12S39.
- Morris, R.V. et al., 2010. Identification of carbonate-rich outcrops on Mars by the Spirit Rover. *Science* 329, 421–424.
- Parker, M.V.K., Zegers, T., Kneissl, T., Ivanov, B., Foing, B., Neukum, G., 2010. 3D structure of the Gusev Crater region. *Earth Planet. Sci. Lett.* 294, 411–423.
- Rancher, J., Kritz, M.A., 1980. Diurnal fluctuations of Br and I in the tropical marine atmosphere. *J. Geophys. Res.* 85, 5581–5587.
- Rao, M.N., Nyquist, L.E., Sutton, S.R., Dreibus, G., Garrison, D.H., Herrin, J., 2009. Fluid-evaporation records preserved in salt assemblages in Meridiani rocks. *Earth Planet. Sci. Lett.* 286, 396–403.
- Rao, B., Anderson, T.A., Redder, A., Jackson, W.A., 2010. Perchlorate formation by ozone oxidation of aqueous chlorine/oxy-chlorine species: Role of Cl_xO_y radicals. *Environ. Sci. Technol.* 44, 2961–2967.
- Rieder, R. et al., 2004. Chemistry of rocks and soils at Meridiani Planum from the Alpha Particle X-ray Spectrometer. *Science* 306, 1746–1749.
- Risacher, F., Fritz, B., Alonso, H., 2006. Non-conservative behavior of bromide in surface waters and brines of Central Andes: A release into the atmosphere? *Geochim. Cosmochim. Acta* 70, 2143–2152.
- Rontó, G. et al., 2003. Solar UV irradiation conditions on the surface of Mars. *Photochem. Photobiol.* 77, 34–40.
- Ruff, Steven W. et al., 2011. Characteristics, distribution, origin, and significance of opaline silica observed by the Spirit Rover in Gusev Crater, Mars. *J. Geophys. Res.* 116, E00F23.
- Saiz-Lopez, A. et al., 2008. On the vertical distribution of boundary layer halogens over coastal Antarctica: Implications for O₃, HO_x, NO_x and the Hg lifetime. *Atmos. Chem. Phys. Discuss.* 8, 887–900.
- Sander, R. et al., 2003. Inorganic bromine in the marine boundary layer: A critical review. *Atmos. Chem. Phys.* 3, 1301–1336.
- Simpson, W.R. et al., 2007. Halogens and their role in polar boundary-layer ozone depletion. *Atmos. Chem. Phys. Discuss.* 7, 4285–4403.
- Smith, M.D., 2008. Spacecraft observations of the martian atmosphere. *Annu. Rev. Earth Planet. Sci.* 36, 191–219.
- Smith, P.H. et al., 2009. H₂O at the Phoenix landing site. *Science* 325, 58–61.
- Smoydzin, L., Von Glasow, R., 2009. Modelling chemistry over the Dead Sea: Bromine and ozone chemistry. *Atmos. Chem. Phys. Discuss.* 9, 4525–4565.
- Squyres, S.W., 2004. The Spirit Rover's Athena science investigation at Gusev Crater, Mars. *Science* 305, 794–799.
- Squyres, S.W. et al., 2006. Two years at Meridiani Planum: Results from the Opportunity Rover. *Science* 313, 1403–1407.
- Squyres, S.W. et al., 2009. Exploration of Victoria crater by the Mars rover opportunity. *Science* 324, 1058–1061.
- Sutter, B. et al., 2013. The detection of evolved oxygen from the Rocknest eolian bedform material by the Sample Analysis at Mars (SAM) instrument at the Mars Curiosity landing site. *Lunar Planet. Sci.* 44, 2046.
- Urbansky, E.T., 1998. Perchlorate chemistry: Implications for analysis and remediation. *Bioremed. J.* 2, 81–95.
- Vogt, R., Crutzen, P.J., Sander, R., 1996. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature* 383, 327–329.
- Von Glasow, R., Crutzen, P.J., 2007. Tropospheric halogen chemistry. In: Heinrich, D.H., Turekian, K.K. (Eds.), Treatise on Geochemistry. Pergamon, Oxford, pp. 1–67.
- Wang, A. et al., 2006. Sulfate deposition in subsurface regolith in Gusev Crater, Mars. *J. Geophys. Res.* 111, E02S17.
- Wang, A. et al., 2008. Light-toned salty soils and coexisting Si-rich species discovered by the Mars Exploration Rover Spirit in Columbia Hills. *J. Geophys. Res.* 113, E12S40.
- Warren, J.K., 2006. Evaporites: Sediments, Resources, and Hydrocarbons. Springer, Berlin, New York.
- Watters, T.R. et al., 2007. Radar sounding of the Medusae Fossae Formation Mars: Equatorial ice or dry, low-density deposits? *Science* 318, 1125–1128.
- Wayne, R.P. et al., 1995. Halogen oxides: Radicals, sources and reservoirs in the laboratory and in the atmosphere. *Atmos. Environ.* 29, 2677–2881.
- Wood, W.W., Sanford, W.E., 2007. Atmospheric bromine flux from the coastal Abu Dhabi sabkhat: A ground-water mass-balance investigation. *Geophys. Res. Lett.* 34, L14405.
- Yang, X., Pyle, J.A., Cox, R.A., 2008. Sea salt aerosol production and bromine release: Role of snow on sea ice. *Geophys. Res. Lett.* 35, L16815.
- Yen, A.S. et al., 2005. An integrated view of the chemistry and mineralogy of martian soils. *Nature* 436, 49–54.
- Yen, A.S. et al., 2008. Hydrothermal processes at Gusev Crater: An evaluation of Paso Robles class soils. *J. Geophys. Res.* 113, E06S10.
- Zhao, T.L. et al., 2008. A three-dimensional model study on the production of BrO and Arctic boundary layer ozone depletion. *J. Geophys. Res.* 113, D24304.
- Zhao, Y.-Y.S., McLennan, S.M., Jackson, A.W., Karunatillake, S., 2013. Photochemical effects on bromine and chlorine distributions during brine evaporation on the martian surface. *Lunar Planet. Sci.* 44, 3002.
- Zorzan, M.-P., Mateo-Martí, E., Prieto-Ballesteros, O., Osuna, S., Renno, N., 2009. Stability of liquid saline water on present day Mars. *Geophys. Res. Lett.* 36, L20201.