

### Key Points:

- Br loss relative to Cl and S from soils at Gale, Gusev, and Meridiani suggests ubiquitous Br volatilization via soil-atmosphere processes
- Br and Cl vary in Mars soils from halide salts mixed with halogen -low or -free components and preferential volatilization of Br over Cl
- Soil-atmosphere multiphase reaction pathways are a key component missing from purely gas-phase photochemical models of the halogen cycle

### Supporting Information:

Supporting Information may be found in the online version of this article.

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## Multiphase Volatilization of Halogens at the Soil-Atmosphere Interface on Mars

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**Abstract** The Martian critical zone, especially its soil-atmosphere interface, may host an active halogen cycle affecting habitability, as inferred from halogen trends observed in situ at Gusev and Meridiani, along with oxychlorine species detected in situ. However, the sinks and sources of the Martian halogen cycle remain poorly constrained, especially for Br, including the broader geographic significance of halogen volatility in soils. Here, we statistically analyze Br, Cl, and S distribution and associated cations in the soils of Gale Crater and compare the results with soils of Gusev Crater and Meridiani Planum. We further place the overall in situ soil trends in the framework of terrestrial natural evaporative halides and Mars-analog evaporative experiments. We observe three lines of evidence that support preferential volatilization of Br versus Cl and S in Martian soils: (a) Unlike Cl and S, Br abundance decreases from subsurface to surface. (b) Br and Cl abundances correlate strongly at the relatively dust-free and freshly exposed surface of the active Bagnold dunes, but Br-Cl correlations weaken and Br concentrations decrease in less mobile surface soil. (c) Laboratory experiments show preferential Br loss over Cl and S under ultraviolet (UV) irradiation, consistent with the observed Br loss relative to Cl in Martian soil samples. Overall, these findings generally suggest that soil serves as a source for volatilized halogens. Specifically, soil-atmosphere multiphase reaction pathways constitute a crucial component missing from purely gas-phase photochemical models of the halogen cycle.

**Plain Language Summary** Soil records the complexity of processes at the Martian surface and is a key component of the critical zone that sustains interactions between the atmosphere and crust of Mars. Previous in situ explorations of the Mars landing site at Gusev Crater and Meridiani Planum showed that Br demonstrates a preferential loss into the atmosphere among volatile elements Br, Cl, and S in the topsoil samples. Here, we examine and demonstrate that Br volatilization observed at Gusev and Meridiani is also present in Gale Crater soils, indicating ubiquitous volatilization via soil-atmosphere processes on Mars. We further place the in situ soil trends of Martian Br and Cl in the framework of natural evaporative halides on Earth and Mars-analog evaporative experiments. The framework we construct shows that the Br and Cl variations in Mars soils are consistent with halide salts mixed with halogen -low or -free components (e.g., basaltic phases) and subsequent volatilization of Br over Cl. Our findings indicate a chemically active top layer on the Martian surface, challenging the preservation of any biological matter even in deeper soil horizons.

## 1. Introduction

As a byproduct of various weathering processes—aqueous, atmospheric, eolian, and impact gardening to name a few—soil records the complexity of processes at the Martian surface (Certini et al., 2020) and thus provides insight into near-surface environmental evolution. Soils are also a key component in the zone of sustained interactions between the atmosphere and crust (i.e., the Martian critical zone). Given the present cold and dry climate of Mars, briny fluids are one of the few ways by which chemical alteration can be sustained in the critical zone. Cl and Br are highly mobile in brine systems associated with soil processes, with Br commonly used to characterize terrestrial evaporation processes (e.g., Worden, 2018). Due to their possible shared provenance from volcanic outgassing and close relation in fluid systems and resultant secondary mineralogy, variations of Cl and Br in

Martian soils and rocks are frequently attributed to their behavior in water-rock systems, including evaporative sedimentation and post-deposition fluid migration (Clark et al., 2005; Gellert et al., 2006; Knoll et al., 2008; Marion et al., 2009; Rao et al., 2009; Yen et al., 2005).

The focus on fluid processes has generally overlooked the role of multiphase reaction pathways (e.g., solid-gas) in the distribution of reactive halogen phases in the Martian soil, such as oxychlorine species. However, in terrestrial hyper-arid evaporation environments, multiphase volatilization can also affect the halogen geochemistry in evaporites and sediments. Similar processes may also exist on the Martian surface (Bao & Gu, 2004; Honninger et al., 2004; Risacher et al., 2006; Smith et al., 2014), as suggested by laboratory experiments of brine-sand slurries under Mars-appropriate ultraviolet electromagnetic radiation exposure (Zhao et al., 2018). Such pathways may be a component missing from the 1-dimensional modeling of Martian atmospheric photochemistry (Smith et al., 2014). Common processes like electrostatic discharge from triboelectric charging of few to tens-of-micron size clast (i.e., dust) may also volatilize Cl from halides as determined from laboratory simulations (Wang et al., 2020).

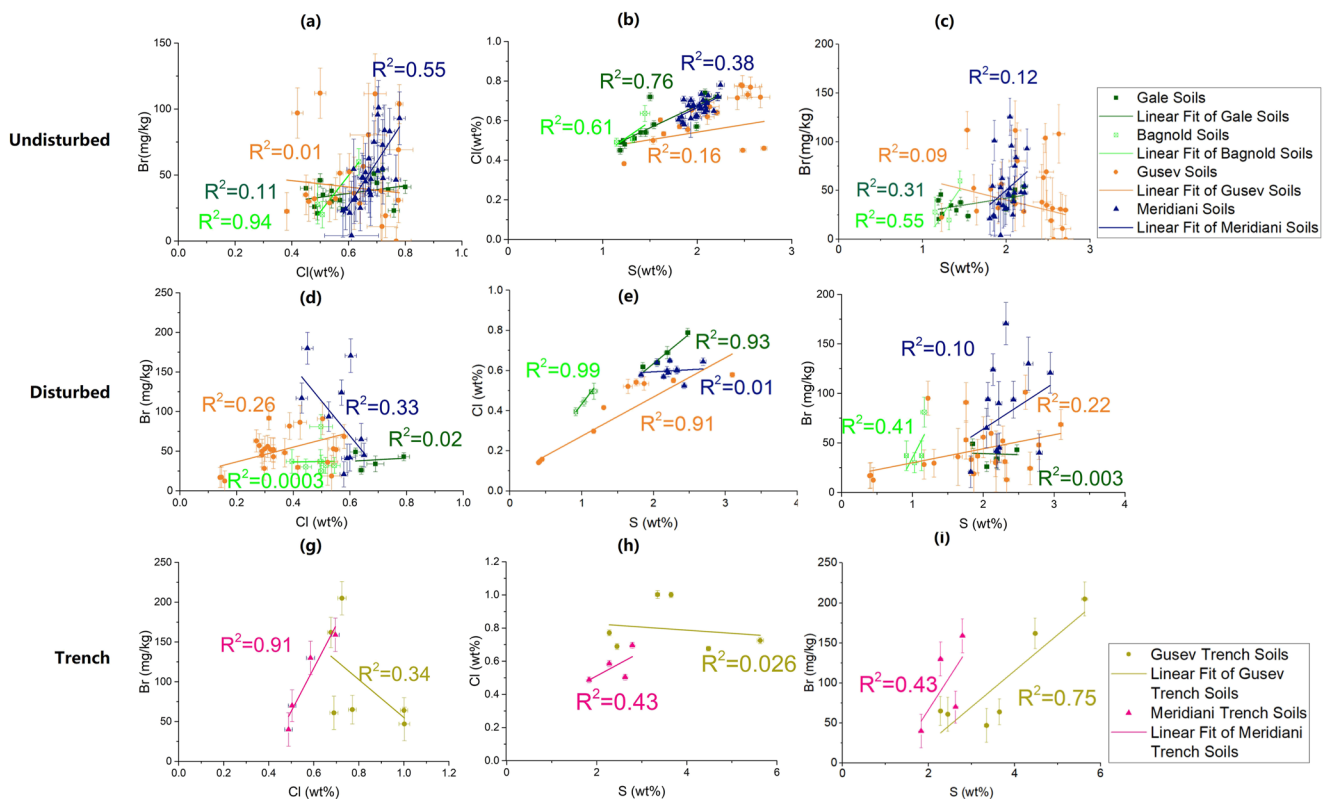
Terrestrial analog studies have exemplified the significance of reactive halogens for habitability and the associated risks of using Martian soil as an in situ resource (e.g., Kounaves et al., 2010; Kumarathilaka et al., 2016; Lynch et al., 2019; Vithanage et al., 2019). Detailed statistical analyses of Br, Cl, and S distributions at Gusev and Meridiani show that soil Br abundance decreases from subsurface to surface and the correlation between Br-S weakens. Br, Cl, and S decrease toward the surface in the order of  $Br > S > Cl$ . In some cases, soil Br variability appears decoupled from potential cations such as Mg (Karunatillake et al., 2013). Collectively, those observations support the relative loss of Br to the atmosphere compared to S and Cl, possibly caused by UV photolysis or chemical oxidants (Archer et al., 2019; Catling et al., 2010; Karunatillake et al., 2013; Smith et al., 2014), or as yet indeterminate electrostatic discharge effects on Br-phases (Wang et al., 2020). However, aside from observations at Gusev and Meridiani, the relative importance of aqueous mobility versus atmospheric volatility for halogen distributions remains unknown at other in situ sites on Mars, including Gale Crater, especially for Br-phases.

Here, we examine the extent to which the halogen volatility hypotheses originally developed from observations at Gusev and Meridiani are consistent with the compositional trends in Gale Crater soils. We statistically analyze the distributions of Br, Cl, and S and mass ratios of Br/Cl, Cl/S, and Br/S at Gale Crater and compare them with Gusev Crater and Meridiani Planum data. We further integrate in situ soil trends of Mars into the framework of terrestrial evaporative halides and Mars-analog evaporative experiments. Synthesis of Martian in situ data analysis, terrestrial natural analogs, and simulation experimental results (i.e., evaporation and volatilization) can advance our understanding of the halogen cycles on the Martian surface.

## 2. Materials and Methods

### 2.1. Data Sources of Mars In Situ Measurements

The Alpha Particle X-Ray Spectrometer (APXS) data are used for the chemistry of soils and rocks at Gale Crater, Gusev Crater, and Meridiani Planum. The Gale data in use are up to sols 2026 (Table S1 in Supporting Information S1; Gellert, 2013). The updated data sets of Gusev (up to sols 2073) and Meridiani (up to sol 3925) compared to the previous work (up to sols 1368) are used in this study (Gellert, 2004). As the APXS of MSL Curiosity rover has Mars Exploration Rovers (MER) heritage, derived geochemistry can be compared across the three sites without much risk of systematic errors (Gellert et al., 2016). Of the available data, we mainly focus on the concentrations of Br, Cl, S, Na, Mg, and K given immediate significance to soil halogen, halide, and oxyhalide processes. The sampling depth of APXS measurements varies as a function of element atomic number. The sampling depth of Br (180–240  $\mu\text{m}$ ) is about two orders of magnitude deeper compared to the S and Cl (6–7  $\mu\text{m}$ ) and Na and Mg (2–3  $\mu\text{m}$ ) (Schmidt et al., 2018). Such difference in sampling depth of different elements might disrupt correlations but mostly in the very surface micro-meter scale of topsoils and would not substantially interfere with the statistical analyses in our study. In addition, the Mars Hand Lens Imager (MAHLI) data are used for categorizing the Gale soils. MAHLI images offer a resolution of 14–15  $\mu\text{m}/\text{pixel}$ , which can resolve grains down to 45–60  $\mu\text{m}$  in diameter (Edgett et al., 2012).



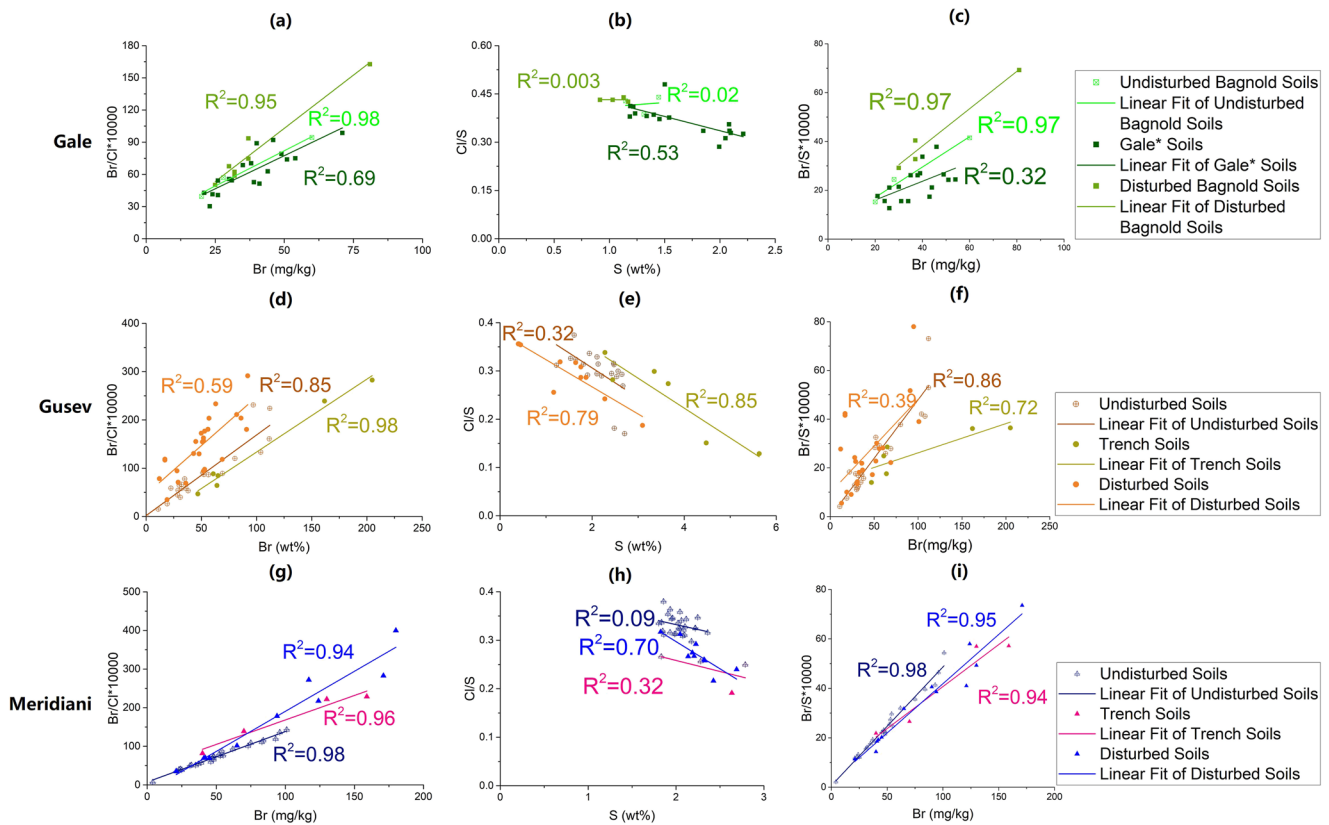
**Figure 1.** Correlations of Br-Cl, Cl-S, and Br-S at the landing sites of Gale, Gusev, and Meridiani. The dark green solid square represents Gale\* soils and the light green hollow square represents Bagnold dunes samples. (a–c) are of the “undisturbed” soil category, representing the topmost surficial soils. (d–f) are of the “disturbed” soil category, representing shallow subsurface soils. (g–i) are trench data at Gusev and Meridiani, representing cm-scale depth soils. Error bars are of the APXS data sets. Linear best fit lines and  $R^2$  values are shown in the same color as their corresponding data sets.

## 2.2. Categorization of Soil and Rock Samples at Three Landing Sites

Soil (defined following the pedological perspective by Certini et al., 2020) samples from each site are categorized as either “disturbed” or “undisturbed” following the precedence of prior work (Karunatilake et al., 2013). Based on Gellert et al. (2006), for Gusev and Meridiani samples, “undisturbed” soils are those mechanically untouched by the rover and “disturbed” soils have the topmost layer scuffed or removed by rover wheels. In general, “undisturbed” soils indicate surface soil trends while “disturbed” soils represent subsurface trends. Trench samples (~5–10 cm depth) by repetitive rover wheel motion are also available at Gusev and Meridiani (Gellert et al., 2016), representing subsurface bulk soil trends. However, such types of data are not available at Gale. Therefore, to include Gale for comparison, we evaluate trench chemistry only for reference purposes (Figures 1 and 2).

We apply similar “undisturbed” and “disturbed” categorizations to Gale soil samples. However, at Gale, the wheel marks of the Curiosity rover are shallow, making it difficult to determine whether a “disturbed” soil could represent a subsurface trend or not. Also, a few “scoop” samples excavated by the Sample Acquisition, Processing, and Handling (SA/SPaH) subsystem of the Curiosity rover, obtained unconsolidated sediments down to centimeter-depth (Anderson et al., 2012). The “scooped” samples are of a mixture of surface and subsurface soils, with the surface component (mm-thickness) constituting only a small portion of the mixture (O’Connell-Cooper et al., 2018). All “scooped” samples are included in the “disturbed” soil category of Gale.

Another peculiarity of Gale is that it includes the first active dune observed in situ on Mars—the Bagnold Dunes (Campaign Phase 1; sols 1162–1254). Constant eolian processing of the dune soil (62.5  $\mu\text{m}$ –2 mm, sand-size clasts on the Wentworth scales; ISO 14688-1, 2017; Wentworth, 1922) likely overprints provenance and alteration pathways. Thus, the compositions of the active Bagnold dune soil may be inconsistent with other more stagnant Gale soils (Bridges & Ehlmann, 2018; Ehlmann et al., 2017; O’Connell-Cooper et al., 2017, 2018).



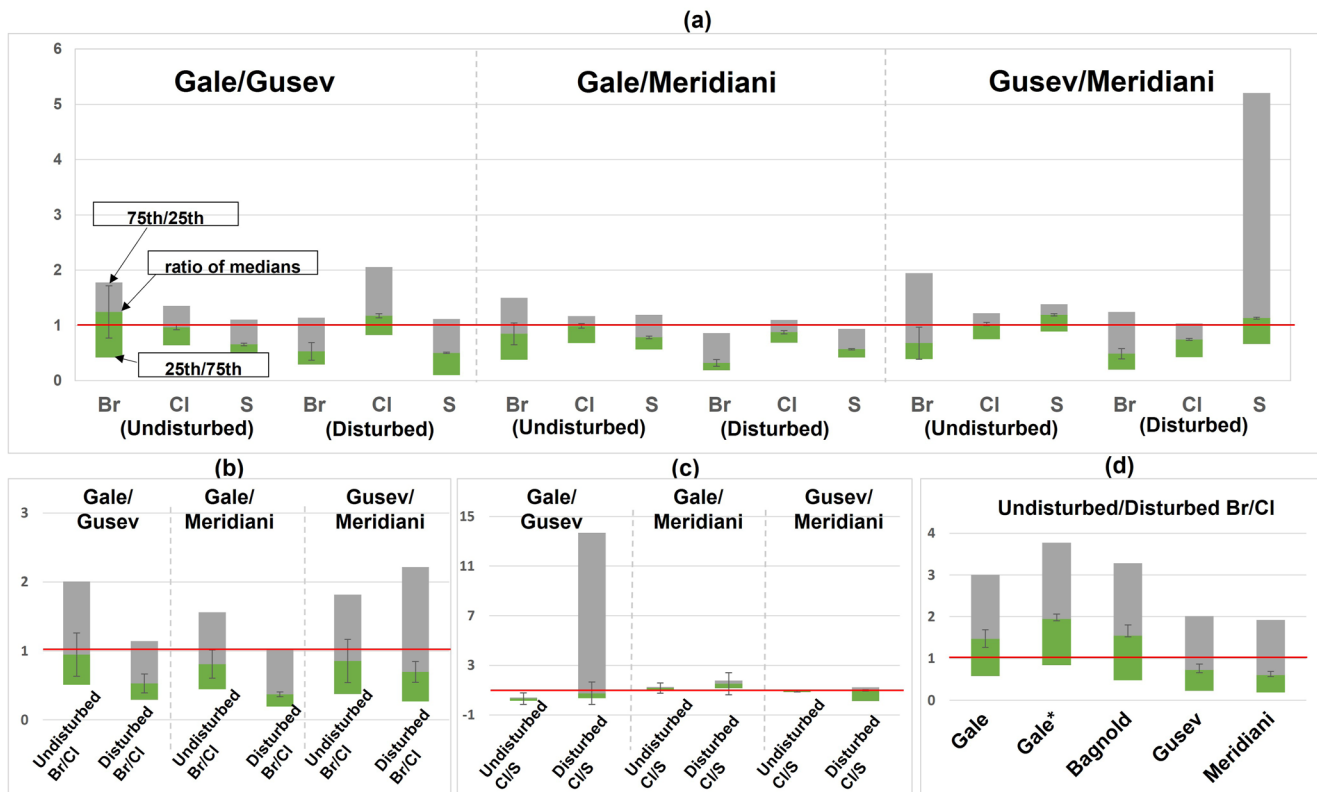
**Figure 2.** Correlations of Br/Cl ratios versus Br, S/Cl ratios versus S, and Br/S ratios versus Br at the three landing sites of Gale, Gusev, and Meridiani. Hollow symbols represent “undisturbed” samples and solid symbols represent “disturbed” (including trench) samples. (a–c) are of Gale Crater, with hollow turquoise squares represent undisturbed Bagnold dune samples and solid light green squares represent “disturbed” Bagnold samples. Solid dark green squares represent Gale\* samples. (d–f) are of Gusev Crater. The hollow orange dots represent undisturbed Gusev soils, the solid light orange dots represent “disturbed” Gusev soils, and the solid dark orange dots represent trench samples. (g–i) are of Meridiani Planum. Hollow blue triangles represent “undisturbed” soils and the solid blue triangles represent “disturbed” soils, and the solid navy triangles represent trench samples. Linear best fit lines and  $R^2$  values are shown in the same color as their corresponding data sets. Linearity in trends suggests that Br abundances control the variation of Br/Cl and Br/S, and the S abundances control the S/Cl variation.

Therefore, in the ensuing discussion, we separate Bagnold soils from the result of Gale samples (annotated as Gale\*). The Gale\* soils represent all Gale samples except for the Bagnold soils.

We also compare the Br and Cl abundances of soils versus local rocks at each landing site to provide insight on the element distribution and possible speciation. Rock targets analyzed by the rovers are generally grouped into three categories, from the soil mantled to the pristine interior. The “undisturbed” rock samples are not touched by the rover robotic arm, so the samples are not clear from dust or alteration layers. The “Brushed” and “DRT” rock samples are brushed by the “Rock Abrasion Tool” (RAT) of the MERs and the Dust Removal Tool (DRT) of the Curiosity rover, respectively. In these rock samples, the surface soil/dust is removed, but surface alteration rinds may be present. The “RAT” or “Drilled” rock samples are abraded or drilled using the RAT tool of MERs or the drill tool of the Curiosity rover, of which the freshly exposed interior may best represent the pristine rock composition.

### 2.3. Statistical Analysis of APXS Data

To quantify any soil depth-dependent variability in halogen abundances (i.e., Br and Cl) with other salt anions (represented broadly by S), we use their ratios and correlations across the landing sites. The linear correlation coefficients, slopes, and intercepts, along with their error bounds for Br–Cl, Br–S, Cl–S, Br–MgO, Br–Na<sub>2</sub>O, Br–K<sub>2</sub>O, Cl–MgO, Cl–Na<sub>2</sub>O, and Cl–K<sub>2</sub>O pairs are used as key statistical parameters for the Gale Crater, facilitating comparisons with Gusev and Meridiani data sets. The choice of compositional pairs is justified by bromide, chloride, and sulphate, all likely bound in soluble minerals. Their ratios would show correlative affinities if



**Figure 3.** Modified box-and-whisker plots qualitatively compare soil APXS data between Gale versus Gusev, Gale versus Meridiani, and Gusev versus Meridiani. (a) compares variations of elemental Br, Cl, and S. (b and c) compare variations of Br/Cl and Cl/S, respectively. (d) compares variations of Br/Cl of “undisturbed”/“disturbed” soils at the three landing sites. The Gale soils and two subgroups, Gale\* and Bagnold, are plotted respectively. The lower boundary, median value, and the upper boundary of the box designate the percentile ratios of the first quartile (25th/75th), median value (50th/50th), and the third quartile (75th/25th), respectively. The red line is the unity line, which denotes the 1-to-1 ratio. Boxes that lack overlap with the unity line suggest distinct concentration differences between the sample regions. The ratio of medians that falls below the unity line suggests a depletion at the former site of the two-site compared. In contrast, above the unity line suggests an enrichment at the former site. Error bars represent typical uncertainty on a root-mean-square basis (calculation methods are available in Text S1 of Supporting Information S1).

affected by similar brine interactions at the surface or subsurface. In contrast, divergent trends will arise if the three elements are not distributed by the same process. Statistical analyses are done separately for the subgroups Bagnold soils and Gale\* soils at Gale. Given our primary interest in elemental trends rather than specific values, and evidence showing high precision of Br measurements even for values lower than the nominal detection limit of 30 mg/kg (Rieder et al., 2004), we include data with Br concentrations lower than 30 mg/kg in our statistical analysis.

Besides aqueous alteration, Br and Cl phases can interact with the atmosphere, resulting in volatilization (from solids or brines to gas phases). If volatilization significantly influences Br and Cl distributions, decoupling from related cations such as Na, Mg or K is expected. Least squares trendlines, Pearson's bivariate correlation coefficient ( $r$ ), and the coefficient of determination ( $R^2$ ) are used to determine Br and Cl distribution and correlative relation between anions Br and Cl and cations Na, Mg, and K (Figure 4).

As a graphical nonparametric statistical method, we use the modified box-and-whisker (MBW) method to describe the general distribution of element concentrations and mass fraction ratios in surface and subsurface soils sampled across the three landing sites. The MBW is a robust graphical method for summarizing pairwise compositional variation among locations previously used in Mars geochemical data analysis (Hood et al., 2016; Karunatillake et al., 2011; Ojha et al., 2021; Susko et al., 2017). In a typical MBW plot (Figure 3), the lower boundary and upper boundary of a box are the low excursion (represented 25th/75th percentile ratio) and the high excursion (75th/25th percentile ratio), respectively relative to a reference set; the box bounds the range of relative variation (interquartile range; IQR) for the pair. Meanwhile, the alignment of the box about the median ratio (50th/50th)

**Table 1**

Elemental Abundances (Range and Average) of Br, Cl, and S in Soils at Gale Crater, Gusev Crater, and Meridiani Planum

	Br			Cl			S		
	Un-(mg/kg)	Dis-(mg/kg)	Un-Dis	Un-(wt.%)	Dis-(wt.%)	Un-Dis	Un-(wt.%)	Dis-(wt.%)	Un-Dis
Gale Crater	20–103 (43 ± 4)	25–97 (40 ± 7)	8%	0.45–1.05 (0.68 ± 0.04)	0.40–0.84 (0.58 ± 0.04)	17%	1.15–2.81 (1.87 ± 0.12)	0.92–2.47 (1.57 ± 0.15)	19%
Gale*	21–84 (42 ± 4)	26–49 (30 ± 9)	36%	0.45–1.05 (0.70 ± 0.04)	0.62–0.84 (0.72 ± 0.04)	–3%	1.19–2.81 (1.96 ± 1.14)	1.85–2.47 (2.19 ± 0.11)	–11%
Bagnold	20–103 (53 ± 19)	25–97 (46 ± 10)	14%	0.49–0.72 (0.59 ± 0.05)	0.40–0.62 (0.50 ± 0.02)	18%	1.15–1.63 (1.38 ± 0.10)	0.92–1.35 (1.18 ± 0.05)	17%
Gusev Crater	9–263 (53 ± 9)	12–494 (72 ± 0)	–27%	0.38–0.94 (0.68 ± 0.03)	0.14–1.88 (0.51 ± 0.05)	33%	1.23–11.89 (2.69 ± 0.32)	0.40–14.34 (6.21 ± 0.81)	–57%
Meridiani Planum	4–126 (55 ± 5)	21–434 (123 ± 0)	–56%	0.58–0.93 (0.71 ± 0.01)	0.43–0.87 (0.64 ± 0.03)	11%	1.80–3.23 (2.22 ± 0.06)	1.83–6.59 (2.92 ± 0.33)	–24%

Note. “Un-” represents “undisturbed” soil samples. “Dis-” represents “disturbed” soil samples. “Un-Dis” represents the percentage difference in mass. “Un-Dis” calculation formula = (“undisturbed” - disturbed)/disturbed × 100%, using the average values for calculation. Average values are given in parentheses. Errors represent typical uncertainty on a root-mean-square basis. Calculation methods are in Text S1 of Supporting Information S1. Numbers of soil samples in each subgroup: Gale Crater, “undisturbed”  $n = 24$ , “disturbed”  $n = 13$ ; Gale\*, “undisturbed”  $n = 20$ , “disturbed”  $n = 5$ ; Bagnold, “undisturbed”  $n = 4$ , “disturbed”  $n = 8$ ; Gusev Crater, “undisturbed”  $n = 31$ , “disturbed”  $n = 48$ ; Meridiani Planum, “undisturbed”  $n = 36$ , “disturbed”  $n = 22$ . The Gale\* represents all Gale soil samples (up to sols 2026) excluding Bagnold samples (sols 1187 to 1253).

indicates deviation from symmetric or Gaussian distributions. The unity line denotes the 1-to-1 ratio. Details on the statistical methodology are described in Text S1 of Supporting Information S1.

#### 2.4. Data Sources of Mars-Analog Experiments and Terrestrial Natural Halides

We also compare Br and Cl abundances and Br/Cl trends observed in situ in Martian soils to Br and Cl data from Mars-analog evaporation experiments and Mars-relevant terrestrial evaporative brines and halides (Tables S3–S6 in Supporting Information S1). Zhao et al. (2018) examined two brines (Brine #1: Mg-Fe-Ca-SO<sub>4</sub>-Cl-Br, pH = 2; Brine #2: Na-Mg-Ca-HCO<sub>3</sub>-SO<sub>4</sub>-Cl-Br, pH = 8), which represent aqueous conditions at Meridiani and Phoenix landing sites, respectively. The two brines were evaporated using ultraviolet (UV; wavelength 254 nm) irradiation under ambient atmosphere (Table S3 in Supporting Information S1). Rodríguez et al. (2018) evaporated the brine of the Kawah Ijen volcanic lake (Brine #3: Al-Fe-K-Na-Mg-Ca-Si-Sr-Ti-SO<sub>4</sub>-Cl-F-Br-B<sub>3</sub>, pH = 0.1) at 60°C under ambient atmosphere without UV irradiation (Table S4 in Supporting Information S1).

Besides terrestrial natural halide data, the experimental data of Br partitioning between brines and five marine halides (halite (NaCl), sylvite (KCl), kainite (KMgClSO<sub>4</sub> · 2.75H<sub>2</sub>O), carnallite (KMgCl<sub>3</sub> · 6H<sub>2</sub>O) and bischofite (MgCl<sub>2</sub> · 6H<sub>2</sub>O); Siemann & Schramm, 2002) are also included in Table S5 of Supporting Information S1. Initial Br<sup>–</sup> in the experimental brines ranged from 16 mg/kg to ~8.0 wt.%. The evaporative evolution sequences of terrestrial seawater and the Dead Sea brine are also included for reference (Tables S6 in Supporting Information S1). All the data are incorporated in the framework of Figure 5.

### 3. Results and Discussion

#### 3.1. Abundances and Ratios of Br, Cl, and S at Gale, Gusev, and Meridiani

The Br, Cl, and S abundance ranges and averages of soils (categories of “all”, “undisturbed”, and “disturbed”) for Gale, Gusev, and Meridiani sites are available in Table 1. The mass ratios of Br/Cl, Br/S, and Cl/S with the same categorization as used in Table 1 are present in Table 2. The Gale sample list and elemental abundances are available in Table S1 of Supporting Information S1.

Although Gale\* soils compose a larger fraction of all the Gale samples (25 samples of Gale\* vs. 12 samples of Bagnold), the geochemical trends of the Gale samples overall are primarily controlled by the Bagnold soils, not the Gale\* soils (Table 1). This is primarily due to the large variation of values present in the Bagnold samples,

**Table 2**  
Percentage Differences in Elemental Ratios Between “Undisturbed” and “Disturbed” Soil Categories of Br, Cl, and S at the Three Landing Sites on Mars

Sites	Br/Cl			Br/S			Cl/S		
	Un-	Dis-	Un-Dis	Un-	Dis-	Un-Dis	Un-	Dis-	Un-Dis
Gale Crater	6.44E-03	7.31E-03	−12%	2.46E-03	3.21E-03	−24%	0.37	0.39	−3%
Gale*	6.08E-03	4.47E-03	36%	2.24E-03	1.80E-03	24%	0.36	0.33	12%
Bagnold	8.35E-03	9.08E-03	−8%	3.61E-03	3.92E-03	−8%	0.42	0.42	0%
Gusev Crater	7.98E-03	1.52E-02	−47%	2.22E-03	2.07E-03	7%	0.29	0.23	24%
Meridiani Planum	7.58E-03	2.62E-03	−71%	2.49E-03	4.48E-03	−44%	0.32	0.25	29%

Note. “Un-” represents “undisturbed” soil samples. “Dis-” represents “disturbed” soil samples. “Un-Dis” represents percentage difference in mass, calculation formula = (“undisturbed” - “disturbed”)/“disturbed” × 100%.

as well as the relatively smaller number of Gale samples ( $n = 37$ ) compared to Gusev ( $n = 79$ ) and Meridiani ( $n = 58$ ) making it more susceptible to the outliers in any category. In Bagnold samples, surface soils contain higher Br, Cl, and S concentrations than subsurface samples (increase of 14% in Br, 18% in Cl, and 17% in S). Consequently, overall Gale samples exhibit higher Br, Cl, and S concentrations on the surface (increase of 8% in Br, 17% in Cl, and 19% in S) compared to the subsurface. Gale\* soils cannot provide an effective comparison between the surface and subsurface soils since “disturbed” in this subgroup contains a mix of surface and subsurface soil. In contrast, at Gusev and Meridiani, the surface soils show a significant loss of Br and S than the subsurface (this study and Karunatillake et al. [2013]). The loss of Br is 27% at Gusev and 56% at Meridiani, and the loss of S is 57% at Gusev and 24% at Meridiani, respectively. Note that the substantial decrease of S from the subsurface toward the surface at Gusev is due in part to the presence of sulphate-rich evaporites in the subsurface (Yen et al., 2008).

Table 2 shows percentage differences of Br/Cl, Br/S, and Cl/S ratios between “undisturbed” to the “disturbed” category at the Gale, Gusev, and Meridiani sites. The “undisturbed” Gale samples show a decrease compared to the “disturbed” category in Br/Cl ratios (−12%) due to the substantial increase of Cl over Br in the samples. In comparison, Gusev and Meridiani soils exhibit a substantial loss in Br/Cl ratios (−47% and −71%, respectively), but mainly due to the simultaneous decrease of Br and increase of Cl. The “undisturbed” Gale samples decrease by 24% than the “disturbed” category in Br/S ratios, primarily due to the greater increase of S over Br. In contrast, Gusev and Meridiani samples share consistent trends of decrease of both Br and S, and the consequent Br/S ratios increase by 7% at Gusev and decrease 44% at Meridiani. The Gale samples have the highest Cl/S ratios across the three landing sites, mainly due to the relatively low S abundances. Compared to the “disturbed” category, the Cl/S ratios in the “undisturbed” category are at a similar level (−3%) in Gale samples and higher in Gusev soils (23%) and Meridiani soils (29%).

### 3.2. Correlations of Br, Cl, and S at the Three Landing Sites

Statistically,  $R^2 < 0.3$  is considered no correlation,  $0.3 \leq R^2 < 0.5$  is considered weak correlation,  $0.5 \leq R^2 < 0.7$  is considered moderate correlation, and  $R^2 \geq 0.7$  is considered strong correlation (Moore et al., 2013). We adopt this basis but further define  $R^2 < 0.5$  as no correlation,  $0.50 \leq R^2 < 0.70$  as weak correlation,  $0.70 \leq R^2 < 0.90$  as moderate correlation, and  $R^2 \geq 0.90$  as strong correlation. This definition is mainly because of the low sample numbers in some of the subgroups, which requires the  $R^2$  close to 1 to be statistically meaningful. For the few cases, when the sample numbers are low (i.e.,  $n = 3-7$ ), we introduce two additional parameters  $R_{df}^2$  and  $R_0$  besides  $R^2$  to evaluate the correlations (Table S2 in Supporting Information S1; Karunatillake et al., 2012). The  $R_{df}^2$  represents adjusted  $R^2$  after the degrees of freedom regardless of data number and can be used instead of  $R^2$  in the data-number limited cases. The  $R_0$  is the predictor and a correlative analysis is statistically meaningful only when  $R^2$  (or  $R_{df}^2$ )  $> R_0$ . In the following texts and figures, we use  $R^2$  throughout for consistency and notify when exceptions occur (i.e., when  $R_{df}^2$  represents a different correlative significance than  $R^2$ ). The specific  $R^2$  values between the element contents and the element contents versus the element ratios are shown in Table 3.

**Table 3**  
The Coefficient of Determination ( $R^2$ ) Between Element Contents and Element Contents Versus the Element Ratios

$R^2$	Br-Cl	S-Cl	Br-S	Br-Br/Cl	S-Cl/S	Br-Br/S
Un-Gale						
Un-Gale*	0.11	0.76	0.31	0.69	0.53	0.32
Un-Bagnold	0.94	0.61	0.55	0.98	0.02	0.97
Un-Gusev	0.01	0.16	0.09	0.85	0.32	0.86
Un-Meridiani	0.55	0.38	0.12	0.98	0.09	0.98
Dis-Gale						
Dis-Gale*	0.02	0.93	0.003			
Dis-Bagnold	0.0003	0.99	0.41	0.95	0.003	0.97
Dis-Gusev	0.26	0.91	0.22	0.59	0.79	0.39
Dis-Meridiani	0.33	0.01	0.10	0.94	0.70	0.95
Trench Gusev	0.34	0.026	0.75	0.98	0.85	0.72
Trench Meridiani	0.91	0.43	0.43	0.96	0.32	0.94

Note. “Un-” represents “undisturbed” soil samples. “Dis-” represents “disturbed” soil samples. As Figure 2 defaults that all Gale\* samples are undisturbed samples, the Gale\* values are all grouped as the Un-Gale\*.

Examination of Br-Cl correlations shows that in the “undisturbed” category (Figure 1a), the Gale\* soils show no correlation while the Bagnold soils cannot be statistically evaluated due to the limited soil numbers ( $n = 3$ ;  $R_0 = 1$ ;  $R^2 = 0.94$ ). Gusev soils show no correlation and Meridiani soils show a weak correlation ( $R^2 = 0.55$ ). In the “disturbed” category (Figure 1d), no Br-Cl correlation is present in Gale (Bagnold or Gale\*), Gusev, or Meridiani. The trench soils show a moderate positive correlation of Br-Cl ( $n = 4$ ;  $R_{df}^2 = 0.73$ ;  $R^2 = 0.91$ ) at Meridiani but no correlation at Gusev (Figure 1g). The Br/Cl ratios show moderate to strong correlation to the Br abundances (Figures 2a, 2d, and 2g), indicating Br is the primary controlling factor of Br/Cl variations at all three landing sites.

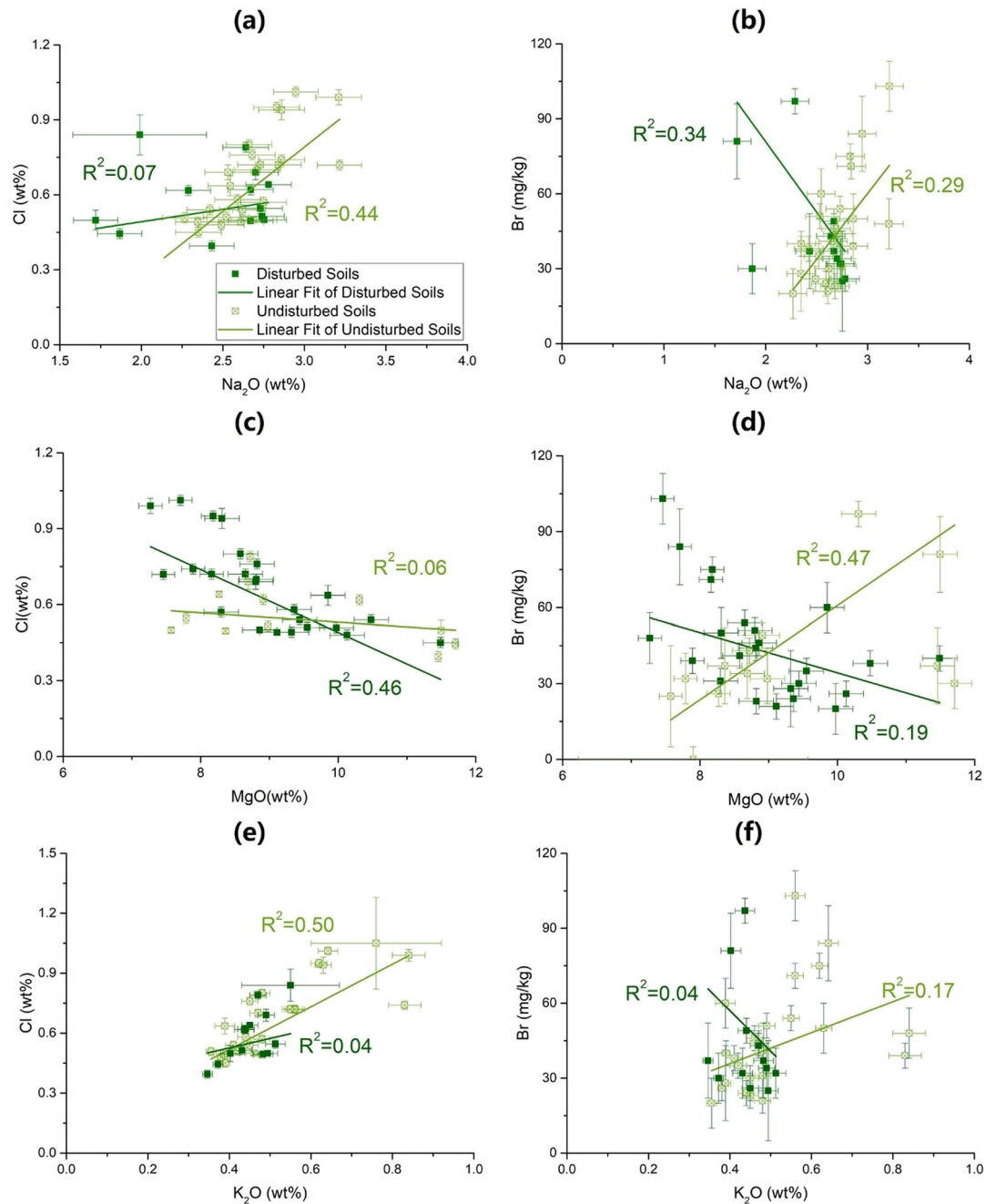
For the Cl-S correlations, in the “undisturbed” category (Figure 1b), the Gale\* soils show moderate ( $R^2 = 0.76$ ) correlation and Bagnold soils cannot be statistically evaluated ( $n = 3$ ;  $R_0 = 1$ ;  $R^2 = 0.61$ ). Gusev and Meridiani soils both have no Cl-S correlations ( $R^2 < 0.5$ ). In the “disturbed” category (Figure 1e), the Gale soils exhibit strong positive Cl-S correlations ( $R^2 \geq 0.93$ ). Gusev soils show strong positive Cl-S correlations ( $R^2 = 0.91$ ) after excluding the sulphate-rich Paso Robles soils (Text S2 in Supporting Information S1); otherwise, no Cl-S correlations can be found due to the presence of these substantially high S samples. The Meridiani soils show no Cl-S correlations. The “trench” soils of Gusev and Meridiani also have no Cl-S correlations (Figure 1h).

Plotting Cl/S versus S demonstrates that both Bagnold soils and Gale\* soils have negligible Cl/S and S correlation (Figure 2b). We also calculate Cl/S versus Cl for the Gale samples and find no correlations between the two parameters ( $R^2 = 0.15$ ; not shown in figures). Therefore, neither S nor Cl is the primary controlling factor of the Cl/S ratios at Gale. At Gusev, Cl/S versus S in “disturbed” and “trench” samples show moderate correlations, but the “undisturbed” soils show no correlations (Figure 2e). At Meridiani, only “disturbed” soils show moderate correlations (Figure 2h). Therefore, S may influence the Cl/S ratios in the subsurface samples at Gusev and Meridiani.

For the Br-S correlations, in the “undisturbed” category (Figure 1c), the Gale\* soils show no Br-S correlations and the Bagnold soils cannot be statistically evaluated ( $n = 3$ ;  $R_0 = 1$ ;  $R^2 = 0.55$ ). In the “disturbed” category (Figure 1f), the Bagnold soils and Gale\* soils have no Br-S correlations. The Gusev and Meridiani soils show no Br-S correlations either in the “undisturbed” or “disturbed” soils (Figures 1c and 1f). In trench soils, Meridiani shows no Br-S correlations and Gusev shows moderate correlations (Meridiani:  $R^2 = 0.43$ ,  $R_0 = 0.82$ ; Gusev:  $R^2 = 0.75$ ,  $R_0 = 0.63$ ) (Figure 1i; Table S2 in Supporting Information S1). In general, no moderate or strong correlations between the Br and S are observed either in “undisturbed” and “disturbed” soils at the three landing sites except for Gusev trench soils. The Br/S ratios are primarily controlled by Br variations in Gale, Gusev, and Meridiani soils (Figures 2c, 2f, and 2i). Exceptions are limited only to the “disturbed” category of Bagnold soils and Gusev soils ( $R^2 \leq 0.39$ ). Together, these results suggest that Br is the primary controlling factor of Br/Cl and Br/S ratios at the three sites.

At Gale Crater, the Br-Cl are strongly correlated at the relatively dust-free and fresh surface of the moving Bagnold dunes, suggesting that Br may share the same source as Cl in the coarse portion of soil locally (presumably as salts). In contrast, the Gale\* soils, which are relatively stagnant with more prolonged atmospheric exposure, are lower in Br abundances and lack of Br-Cl correlations. Such observations suggest that the prolonged exposure of the surface soil to the atmosphere-soil chemical interactions may account for the decrease of Br concentrations and the weakened Br-Cl correlation. The Gale samples appear to be intimate mixtures of both minerals and amorphous components (Bridges et al., 2015), and lithological differentiation is less pronounced, thus reducing the likelihood of differential mobility under aqueous conditions and surface processes within the Gale soils. The general lack of Br, S, and Cl correlations in Gale\* soils reinforces that Br may behave differently relative to Cl and S at Gale.





**Figure 4.** Correlations between Cl or Br versus  $\text{Na}_2\text{O}$ ,  $\text{MgO}$ , or  $\text{K}_2\text{O}$  in the “undisturbed” and “disturbed” soil categories at Gale Crater. Error bars are of the APXS data set. Linear best fit lines and  $R^2$  values are shown in the same color as their corresponding sample categories. Cations Na, Mg, and K are lack in correlations with Cl or Br in both “undisturbed” and “disturbed” soil categories.

### 3.3. Comparison of Br, Cl, and S Across the Three Landing Sites

Distributions of Br, Cl, and S are compared pairwise in Figure 3. Gale/Gusev and Gale/Meridiani show similar patterns, with the most considerable and significant divergences occurring in the “disturbed” soil category (Figure 3a). The Gale samples demonstrate a uniform depletion of Br, Cl, S, and lower Br/Cl ratio compared to the Gusev and Meridiani sites (Figures 3b and 3c). The variations of Cl/S ratios across the three landing sites are small except for the Gale/Gusev case (Figure 3c). The MBW plots in Figures 3a–3c show that the three landing sites share similar trends of Br, Cl, and S abundances and Br/Cl and Cl/S ratios.

The contribution of Br/Cl in different subgroups and soil categories is further examined (Figure 3d). Gale samples show an almost identical trend of Br/Cl ratios in both “undisturbed” and “disturbed” categories. In contrast, Gusev and Meridiani both show a general trend of lower Br/Cl ratios in “undisturbed” soils compared to “disturbed” soils. The median lines and box ranges of Gusev and Meridiani are similar.

The abundances of Br, Cl, and S overlap respectively within the same general levels across the three landing sites, indicating that these volatile elements have uniform distribution characteristics. In a broad sense, the overlapping ranges in Br/Cl and Cl/S ratios at all three landing sites support the widely held notion of a homogenous Martian soil unit, likely resulting from a common source comparable to dust on Mars (Ojha et al., 2018) or a globally distributed provenance. The Cl/S ratios are more uniform across landing sites throughout “undisturbed” and “disturbed” soils. The Cl and S bearing phases (e.g., crystalline or amorphous compounds) are more stable in the soil or react similarly during alteration processes across the Martian surface. Br bearing phases are less stable and respond differently to surficial processes.

The variations of Br and Cl abundances across the three landing sites suggest local influences on the soil chemistry, either from surrounding geological contributions or by different weathering processes. Although trends of Gale samples are less consistent than the Gusev and Meridiani soils, due to the limited number of soil data and the general lack of lower soil horizons at the site (except for the Bagnold dunes), the halogen distributions in Gale samples mirror the other two landing sites. Also, the consistency between the Gusev and Meridiani sites indicates that similar surface-atmosphere processes (e.g., halogen volatilizations to the atmosphere) may alter soil chemistry at the landing sites and be widespread on the Martian surface.

### 3.4. Correlations Between Br and Cl Versus Cations Na, Mg, K at Gale Crater

Gale samples lack correlations between halogens (Br, Cl) and cations (Na, Mg, K) in either “undisturbed” or “disturbed” categories ( $R^2 \leq 0.50$ ; Figure 4), suggesting the cations play a relatively small role in controlling the halogen distributions at Gale. While most Gale soil samples represent a mainly surface geochemical trend, such a lack of correlation between halogens and cations at Gale is consistent with “undisturbed” samples at Gusev and Meridiani (Karunatillake et al., 2013).

### 3.5. Br and Cl in Soils Versus Local Rocks and Outcrops at Three Landing Sites

Since the local rocks provide an essential baseline to infer the subsequent Br concentration and Br/Cl ratios changes in the soils, comparing Br/Cl in the soils and local rocks or outcrops indicates processes that control halogen speciation and behavior on the Martian surface.

Abundance ranges of Br and Cl in soils and local rocks as well as outcrops at the three landing sites are listed in Table 4 for comparison. The “Bulk Mars” composition derived using Martian meteorites and the pristine basaltic rock analyzed in situ (i.e., “Adirondack” at Gusev Plain) are low in Br and Cl. Therefore, high Br and Cl concentrations in the Martian soils and sedimentary rocks are unlikely to result from mechanically weathered igneous rocks, but may be affected by aqueous-related processes on the Martian surface.

At the three landing sites, the “RAT” and “Drilled” rocks show the least variation in Br and Cl abundances and Br/Cl ratios compared to the “Brushed” or “Undisturbed” samples. Therefore, both enrichment and increased variations of Br and Cl are present on the rock surface rather than in the interior. Compared to the “undisturbed” samples, the Cl concentrations of the “drilled” rock samples are generally lower, suggesting that the dust substantially contributes elevated Cl to the sample surface. In contrast, the compositional range and variation of Br are similar between the “undisturbed” and “brushed” rock categories, indicating that dust is not the primary carrier of Br.

At Meridiani and Gusev, the RAT rocks and soils show a similar range of Br and Cl abundances and a similar level of variations. The sedimentary outcrops of Gale Crater that have been interacting with brines manifest at least one order of magnitude higher Br compared to the local soils, suggesting the addition of Br and Cl by fluid activity (e.g., Ehlmann et al., 2017; O’Connell-Cooper et al., 2017). If removing a few high outlier Br samples undergoing substantial aqueous processes (Rieder et al., 2004; Yen et al., 2008), the Br concentration in Martian soils ranges from 0 to 100 mg/kg. Chlorine is relatively constant at around 0.68 wt.%. The substantially narrow variation in Br abundances in general Martian soils suggests that Br enrichment may significantly relate to the local aqueous-related processes.

**Table 4**  
*Comparison of Br and Cl in the Soils Versus Rock Samples Locally at Three Landing Sites*

Categories	Cl/wt. %	Br/mg/kg	Notes
Bulk mars	0.0038	0.145	Estimated using SNC meteorite; Taylor and McLennan (2008)
Gusev-RAT-Primitive basaltic rock	0.2 ± 0.01	14 ± 15	Target “Adirondack” at Gusev Plain; Gellert et al. (2006)
Martian soil average	0.68	61	Taylor and McLennan (2008)
Gale-Rock “undisturbed”	0.37–3.36	5–1888	PDS data; sols up to 2026
Gale-Rock DRT <sup>a</sup>	0.41–2.68	29–1978	
Gale-Rock Drilled <sup>b</sup>	0.30–1.19	17–720	
Gale-Soil “undisturbed”	0.45–1.05	20–103	
Gale-Soil “disturbed”	0.40–0.84	25–97	
Gusev-Rock “undisturbed”	0.43–1.64	6–1543	PDS data; sols up to 2073
Gusev-Rock Brushed <sup>c</sup>	0.30–2.62	14–993	
Gusev-Rock RAT <sup>d</sup>	0.2–1.85	14–674	
Gusev-Soil “undisturbed”	0.38–0.94	9–263	
Gusev-Soil “disturbed”	0.14–1.88	12–494	
Meridiani Planum-Rock “undisturbed”	0.21–2.53	7–1470	PDS data; sols up to 3925
Meridiani Planum-Rock Brushed <sup>c</sup>	0.42–2.97	16–1004	
Meridiani Planum-Rock RAT <sup>d</sup>	0.1–2.8	9–471	
Meridiani Planum -Soil “undisturbed”	0.58–0.93	4–126	
Meridiani Planum -Soil “disturbed”	0.43–0.87	21–434	

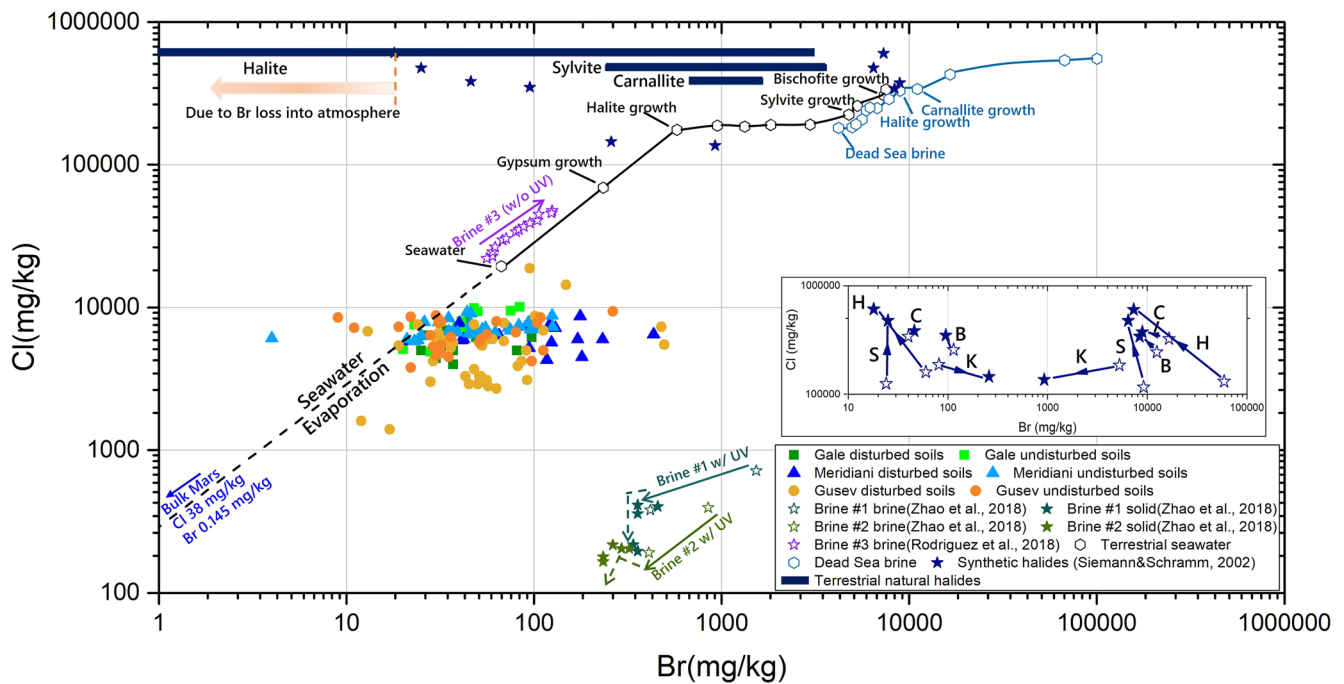
<sup>a</sup>Rock samples brushed by the Dust Removal Tool (DRT) of the Curiosity rover. The dusts/soils are removed but alteration rinds may be present. <sup>b</sup>Finely ground powders extracted from the rock using the drill tool of the Curiosity rover; sampling depth of up to several centimeters of the rock target. <sup>c</sup>Rock samples are brushed by the “Rock Abrasion Tool” (RAT) of the MERs. The dusts/soils are removed but alteration rinds may be present. <sup>d</sup>Rock samples are abraded by the MERs “Rock Abrasion Tool” (RAT) to remove the alteration rinds.

## 4. Synthesis of Br and Cl Geochemistry at the Martian Surface

### 4.1. Bromide, Chloride, and Sulphate Variations in Mars-Analog Evaporation Experiments

Mars-analog evaporative experiments can provide important insights into the Br<sup>-</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> behavior during evaporation (e.g., Rodríguez et al., 2018; Zhao et al., 2018). Under UV irradiation and ambient atmosphere at 25°C, Br and Cl can volatilize into the atmosphere from the brine and salts containing Br<sup>-</sup> and Cl<sup>-</sup> via photo-oxidation processes (Zhao et al., 2018). Bromine preferentially volatilizes into the atmosphere under both acidic and circum-neutral conditions in the presence of UV. Chlorine loss is also observed at a similar level as Br under the acidic condition but to a lower degree than Br under circum-neutral conditions. Trace amounts of perchlorate (ClO<sub>4</sub><sup>-</sup>), chlorate (ClO<sub>3</sub><sup>-</sup>), and bromate (BrO<sub>3</sub><sup>-</sup>) are found in the final evaporites. The experiment also suggests that photo-oxidation processes would have orders of magnitude higher efficiency in a (hyper) arid environment when heterogeneous solid-atmosphere reactions can take place. These results are consistent with field observations of evaporating Sabkhas brine under UV, which show ~90% loss of Br (Wood & Sanford, 2007). Without UV irradiation, evaporation of acidic brine of Kawah Ijen volcanic lake (initial pH = 0.1) under ambient atmosphere at 60°C only found loss of Cl (~12%; presumably in the form of HCl) but no loss of Br (Rodríguez et al., 2018). It can be inferred that Br<sup>-</sup> is not likely volatilizing in the form of HBr. Consistently, in the terrestrial troposphere, sources of atmospheric bromine from condensed phases (e.g., liquid brines, ice surfaces, salt surfaces) involved speciation of Br<sub>2</sub>, Br, BrO, and HOBr, but no immediate release of HBr is suggested (e.g., Finlayson-Pitts, 2010; Simpson et al., 2007).

No volatilization of SO<sub>4</sub><sup>2-</sup> was found during brine evaporation, both with or without UV irradiation even with high acidity (Rodríguez et al., 2018; Zhao et al., 2018). Additional evaporation experiments of Fe<sup>2+</sup>-Fe<sup>3+</sup>-SO<sub>4</sub><sup>2-</sup> brines (initial pH ≤ 1.6) under both UV and UV-free conditions further reinforce this conclusion (Wang et al., 2019).



**Figure 5.** Cl and Br of Martian soils in the framework of terrestrial and simulated evaporation systems. The Cl- and Br-evolution along the evaporation trendline of terrestrial seawater (black line) and hollow hexagons represent the start growth of key precipitates (gypsum, halite, sylvite, carnallite, and bischofite). Evaporation of the Dead Sea brine (dross-blue line and hollow hexagons) follows a parallel trendline to the seawater evaporation. Horizontal navy bars represent Br-concentrations in terrestrial natural halides, varying by more than three orders of magnitude, and the low Br abundance (i.e., <20 mg/kg) is due to loss into the atmosphere. Solid navy stars present five key halides synthesized by evaporation. The inset emphasizes the different partitioning of Br and Cl between the halides (solid stars) and the co-existing brines (hollow stars). H = halite; S = sylvite; C = carnallite; B = bischofite; K = kainite. Hollow and solid stars in jade (Brine #1) and green (Brine #2) represent the UV-evaporation experiments which show a substantial decrease of Br and Cl both in brines and subsequent salts. The violet hollow stars (Brine #3) represent the evaporation without UV, of which Cl and Br concentrated proportionally following the seawater evaporation trendline. In situ Martian soil data (solid squares, triangles, and dots) show Cl varied within one order of magnitude and Br varied within two orders of magnitude. Such a distribution pattern can be obtained by the formation of halides (e.g., halite and sylvite) and dilution by mixing of non-halogen bearing phases. Subsequent oxidation of Br and Cl (e.g., via UV irradiation) may volatilize Br and Cl into the atmosphere.

Therefore, sulphate is mainly associated with aqueous-related processes and precipitated as evaporite minerals regardless of the UV irradiation condition or the acidity of the evaporative system.

Long-term aridity on modern Mars may provide additional mechanisms for halogen volatilization from the evaporative salts on the surface. Electrochemistry experiments simulating multiphase redox plasma chemistry induced by Martian dust activity (e.g., dust storms) demonstrated the instantaneous chlorine release from common chloride salts, likely in the primary form at first excited state (Wang et al., 2020). Bromide salts have not been investigated yet, but we speculate that Br can be readily oxidized and volatilized via this pathway, making it more susceptible to redox processes than chloride.

#### 4.2. In Situ Halogen Trends of Martian Soils in the Framework of Terrestrial Natural Halides and Mars-Analog Experiments

Geochemical trends of Br and Cl in Martian soils are incorporated into the framework of terrestrial natural evaporative halides and Mars-analog simulation experiments to provide insights on halogen behavior on the Martian surface (Figure 5).

Most terrestrial evaporative brine systems relate to seawater ( $\text{Cl}^-$  1.88 wt.% and  $\text{Br}^-$  67 mg/kg;  $\text{Br}/\text{Cl}_{\text{mass}} = 0.0036$ ; Hanley & Koga, 2018). The  $\text{Br}^-$  and  $\text{Cl}^-$  in the brine evolve proportionally along the seawater evaporation trendline until the precipitation of halide minerals, which preferentially take  $\text{Cl}^-$  and leave  $\text{Br}^-$  concentrated in the residual brines. The saturation of halides starts with halite ( $\text{NaCl}$ ) and subsequently sylvite ( $\text{KCl}$ ), carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ), and bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). The Dead Sea brine, which contains the highest Br concentration on Earth (5,899 mg/kg of  $\text{Br}^-$  and 24.0 wt.% of  $\text{Cl}^-$ ; Steinhorn, 1983), also follows a similar trendline

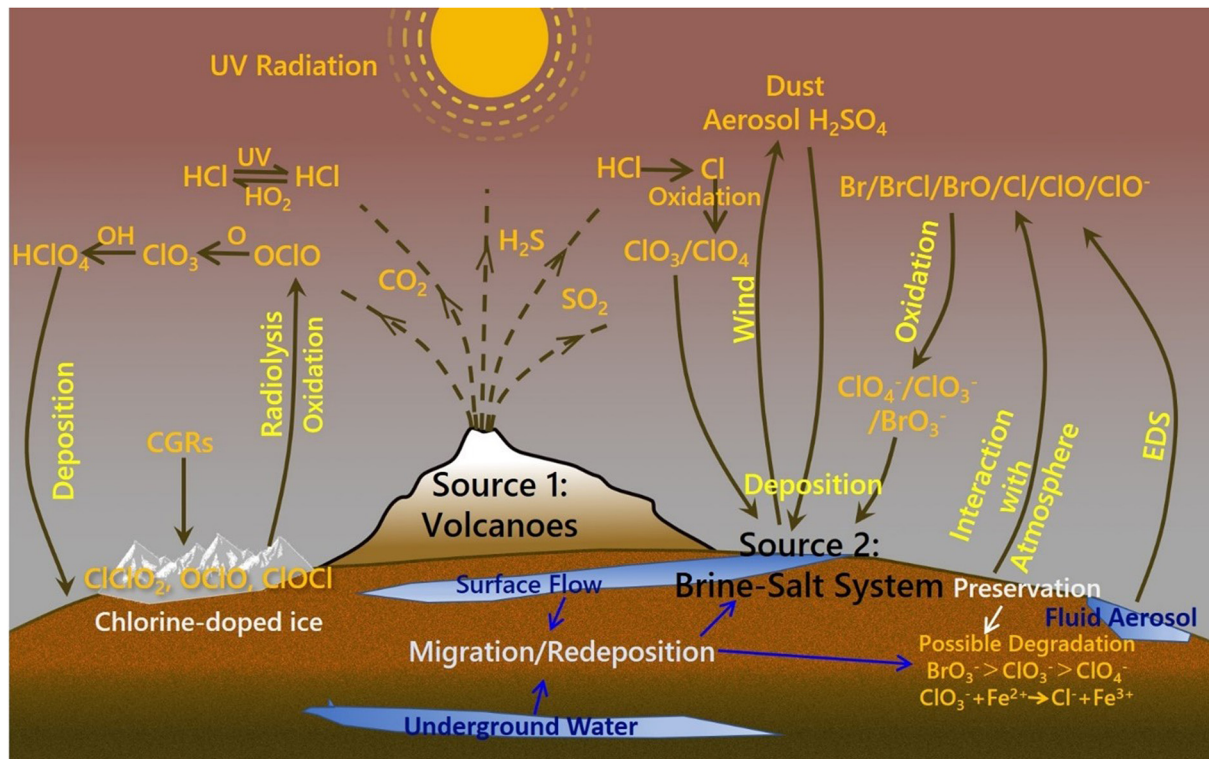
parallel to the seawater evaporation line, and the  $\text{Br}^-$  can concentrate up to about 10 wt.% in the residual brine. Mars-analog experimental results plotted in Figure 5 demonstrate two pathways for possible Br and Cl evolution. Without UV irradiation, Cl and Br concentrated proportionally following the seawater evaporation trendline, although partial Cl loss was observed due to the hyperacidity in the evaporative system (Brine #3). Under UV irradiation, a substantial decrease of Br and Cl was evident both in the brine and the subsequent salts (Brines #1 and #2) (Rodríguez et al., 2018; Zhao et al., 2018).

Experimental investigations of  $\text{Br}^-$  partitioning into five halides (halite, sylvite, kainite, carnallite, and bischofite) show that  $\text{Br}^-$  can end up in the halides ranging from 18 mg/kg to 8,907 mg/kg, with the initial  $\text{Br}^-$  in the brine ranging from 16 mg/kg to ~8 wt.% (Siemann & Schramm, 2002). Usually, the  $\text{Br}^-$  concentrations in the halide minerals are at the same or lower level than the co-existing saturation brines. Kainite is unique in that it may enrich higher Br in the salts than in the brine at the low Br fraction brine but reversed at the high Br fraction brine (the inset of Figure 5).

The terrestrial natural evaporative halides demonstrate a large variation of  $\text{Br}^-$  concentrations for more than three orders of magnitude. The  $\text{Br}^-$  concentrations vary from 0 to 3,000 mg/kg in halite and from 20 to 3,500 mg/kg in sylvite and carnallite (Figure 5; Table S5 in Supporting Information S1). In comparison, the  $\text{Cl}^-$  concentrations vary more systematically from 38.3 wt.% to 60.7 wt.% depending on the specific halides that precipitate (Figure 5; Table S5 in Supporting Information S1). The low concentration of Br in halite samples (i.e., 5–20 mg/kg Br in halite at Andean area) are suggestive of Br loss into the atmosphere via photo-oxidation, which might be a general characteristic of evaporative systems on Earth (e.g., Platt & Honninger, 2003; Risacher et al., 2006). The reason for that is that fluid-related processes alone would not form natural halite containing very low Br abundance. Initial Br/Cl ratios of seawater (from which most brine on Earth originates) and partition coefficient of  $\text{Br}^-$  between seawater and halite are well known, that both initial precipitations of halite and subsequent dissolution-precipitation of precipitated halite would not result in a Br as low as 5–20 mg/kg (Worden, 2018). In addition, as the brine continuously concentrates after halite precipitation, the fluid would contain higher  $\text{Br}^-$  content since Br prefers to remain in the brine when halite precipitates. Therefore, other halides form after halite would contain much higher Br concentrations than that in halite. Bromide is also reported to concentrate in the finest diameter fraction of marine aerosols preferentially (Winchester & Duce, 1967). At the same time,  $\text{Cl}^-$  displays no such preference, and thus the  $\text{Br}^-$  containing aerosols can remain longer in the atmosphere compared to the larger aerosol particle with relatively high  $\text{Cl}^-$  concentrations. It is also worth noting that natural or synthesized halide minerals show no Br-Cl correlation ( $R^2$  ranges 0.05–0.54) but a strong correlation between Br/Cl ratios and Br abundances ( $R^2 > 0.91$ ) (Figure S1 in Supporting Information S1), similar to what has been observed in the Martian soils.

In Figure 5, most Gale, Gusev, and Meridiani sand and soil data are plotted on or to the right of the seawater evaporation trendline, suggesting an enrichment of Br relative to the Cl. A few samples show depletion of Br relative to Cl (to the left of evaporation trendline), which are primarily the “undisturbed” soils in nature. Gale soils show the least variation in Br. Gusev samples have the largest variation in Br and Cl, possibly due to substantial aqueous alteration related to volcanic and hydrothermal activities (Schmidt et al., 2008; Yen et al., 2005) in addition to surface-atmosphere volatilization. Meridiani soils show consistently lower Br abundances in the “undisturbed” soils than the “disturbed” soils.

The distribution pattern of Br and Cl in Martian soils can result from mixing halide or bromide minerals with components containing low to negligible halogen concentrations (equivalent to the proportional dissolution of halides). Like Martian soils, terrestrial halides generally lack Br-Cl correlations and their Br/Cl ratios are controlled by Br abundances (Figure S1 in Supporting Information S1), suggesting that halide or bromide salts are the primary Br-bearing phase in Martian soils. Subsequent alteration of these Br-bearing salts by surface-atmosphere processes can result in the Br and Br/Cl distribution observed in this study. This inference is reinforced by the observation that the Br is enriched in the coarse grain proportion (150  $\mu\text{m}$ –1 mm) in the Bagnold soils (Ehlmann et al., 2017), eliminating the contribution from finer-grain components such as dust, clay, or nano-particle oxides. In most cases of Martian soils across the three landing sites, depletion of Br in the surface soils relative to the subsurface soils and decoupled Br with potential cations Na, Mg, and K in the surface soils reinforce the volatilization of Br from the surface soil. As demonstrated by the Mars-analog evaporation experiments, the higher fluxes of short-wavelength UV and (hyper) arid and oxidizing nature of the present Martian surface may greatly facilitate the Br volatilization into the atmosphere.



**Figure 6.** The updated conceptual model of the Cl and Br geochemical cycles on the surface of Mars, incorporating new insights from this work and other relevant studies. Volcanic degassing (dashed arrows) and halide brine-salt systems are the two primary sources of Cl<sup>-</sup> and Br<sup>-</sup>. Preferential release of Br from the surface to the atmosphere and faster degradation of oxyanions of Br may cause a faster geochemical cycle of Br compared to Cl on the surface of Mars.

### 4.3. The Conceptual Model of Multiphase Br and Cl Geochemical Cycles in Martian Soils

The aqueous and surface-atmosphere processes are the two driving forces for the Br and Cl geochemical cycles on the Martian surface. Figure 6 updates conceptual models of the Br and Cl geochemical cycles using our results at Gale Crater in comparison to other sites, terrestrial analogs and experimental results. This model involves S in related volcanoes and aerosol dust and liquid aerosol as a source of Cl in the atmosphere (Knoll et al., 2008). Proposed radiolysis pathways to account for chloride oxidation in chlorine-doped ice (Wilson et al., 2016) are also included in the conceptual model.

Volcanic degassing and halide brine-salt systems are the two primary sources of Br<sup>-</sup> and Cl<sup>-</sup>. The geochemical cycle of Br and Cl consists of three major pathways (Zhao et al., 2018): (a) volatilization or mobilization into the atmosphere via volcanic degassing or surface fluids, colloids, soils, and salt deposits; (b) removal from the atmosphere by direct deposition, dust, or aerosol (where the halogen species can be further oxidized on the surface as the suspensions in the atmosphere); and (c) movement with brines (i.e., migration and redeposition) and subsequent preservation or degradation. Among the three pathways, the volatilization of halogens, particularly the Br from the soils and salt deposits, is greatly supported by Figure 3d in this work. Br is expected to follow a similar but faster redox cycle as Cl species since the Br<sup>-</sup> is more susceptible to oxidation. The BrO<sub>3</sub> is more susceptible to reduction compared to their Cl counterparts (Zhao et al., 2018).

An active Br and Cl cycles operating on the Martian surface may have persisted over Ga time scales as the climate became semi-arid to hyper-arid and in the presence of other oxidants (e.g., peroxides and superoxides), not only to form a reactive surface layer of Mars but also to present challenges for the survival of organics and microbes potentially in the subsurface.

## 5. Conclusions

In this study, we statistically analyze the distributions of Br, Cl, and S in the soils of Gale Crater, to examine the extent to which the halogen volatility hypothesis developed based on Gusev and Meridiani and supported by laboratory simulations is applicable across Mars. We also integrate in situ soil trends of Mars into the framework of terrestrial evaporative halides and Mars-analog evaporative experiments. Lastly, we use the insights obtained from the analyses to advance the emerging model of possible halogen cycles on the Martian surface. Four major findings follow:

1. Br, Cl, and S variations in the Martian soils are influenced not only by the local sedimentology but also by soil-atmosphere interactions. Generally, Br abundances fluctuate by one order of magnitude less in soil compared to local bedrock. Elevated Cl and S abundances in the surface soils are substantially contributed by the dust, as described by Yen et al. (2005)
2. Surface soils consistently show loss of Br relative to the subsurface samples. Br decouples with possible anions Cl and S and cations Na, Mg, and K, particularly in the surface soils. In contrast, Cl and S correlate with each other and show less variance compared to Br
3. In Martian soils and terrestrial natural halides Br and Cl are disassociated and Br controls the variations of the Br/Cl ratios. The general Br and Cl variations in Martian soils can result from mixing (i.e., proportional dilution) the halide salts (containing Br) with components low or free of halogens. However, substantial loss of Br relative to Cl in the surface soils suggests preferential volatilization of Br over Cl by soil-atmosphere multiphase reaction pathways as a component missing from purely gas-phase photochemical models (cf., Smith et al., 2014)
4. The redox cycles of Br and Cl may operate more efficiently on Mars than Earth, with the aid of various oxidation agents and semi-arid to hyper-arid climate conditions. The presence of active radicals and oxyanions of halogens in the halogen redox cycles may increase the chemical reactivity of Martian soils and might also challenge the preservation of organics and potential microbes in deeper soil horizons

## Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

## Data Availability Statement

The APXS data are available from the PDS (Gale, Gellert, 2013; Gusev and Meridiani, Gellert, 2004). All data generated and analyzed during this study are included in this published article and Supporting Information. A complete source data set supporting the paper has also been uploaded to Science Data Bank, <http://www.doi.org/10.11922/sciencedb.00063> (Wang et al., 2021).

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