

Laboratory and in situ characterization of halogen volatility in martian soil. X. Wang¹, D. Lacznak², Y. S. Zhao³, S. Karunatilake⁴, ¹Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803, ²Center for Lunar and Planetary Sciences, Institute of Geochemistry, Chinese Academy of Science, Guiyang, China (wangxiyu@mail.gyig.ac.cn)

Introduction: In previous work, the method of analyzing the soil grain sizes of the surface of Mars has been established[13]. Soil grain sizes can be related to mineralogy and chemical composition, and the distribution of elements on the Martian surface[14].

Specifically, the study of the distribution of halogens in Martian soils, especially the highly mobile elements of bromine and chlorine, provides insight into the weathering process that affects not only the local and global soil components of the planet, but also atmospheric chemistry. Previous studies of Martian soils have shown that changes in the abundance of Br and Cl are mostly related to the near-surface processes of water [1-5]. However, other studies have shown that in arid, evaporative environments surface-to-atmosphere interactions alter soil chemistry through the volatilization of halogens [6-9]. By studying the changes in halogens in soil samples from different landing sites, comparing with laboratory evaporation simulation study of the formation of perchlorate under Martian atmosphere, we can understand the history of halogen behavior on the Martian surface and subsurface, and explain the possibility and the volatilization mechanism of Br and Cl. On this basis, the global halogen cycle can be examined.

Methods:

To conduct this geochemical and spatial analysis, we collocated Alpha Particle X-Ray Spectroscopy (APXS) element and oxide compositions for Gale Crater soils from the Planetary Data System Geosciences Node (PDS). Additionally, we added APXS compositions to Gusev and Meridiani soil datasets previously compiled by [6]. Soil samples from each rover landing site were categorized by their nature (i.e. undisturbed or disturbed). Undisturbed samples consist of soils that had no contact with rover wheels. Disturbed samples consist of soils whose upper-most layers (mm-scale) were mixed or removed by rover wheels [10]. Gale scoop samples—which excavate a cm-scale portion of loose sediment using Curiosity's Sample Acquisition, Processing, and Handling (SA/SPaH) subsystem were in-

cluded in the undisturbed category [11]. We only show the general comparison of data in Figure 1.

The experimental apparatus used for the UV experiments is illustrated in Fig. 1. The 1-liter borosilicate reaction chamber was built to withstand high-vacuum conditions (10–6 mbar), with a 254-nm ultraviolet (UV) light source inserted directly into the chamber (UVP Pen-ray PCQ Lamp, part number 90-0049-06). The lamp emits 8.5 mW/cm² at 2 cm distance from the light source with 90% of the emission at $\lambda = 254$ nm and 10% of the emission at $\lambda > 254$ nm (up to 436 nm). Circulating water in the outer jacket of the chamber was maintained at 25 °C for all experiments. Temperature conditions lower than 25 °C were not pursued due to expected similar reaction mechanisms in general but sluggish kinetics. The starting materials were placed in a quartz dish at the bottom of the chamber. The brines of interest were slurried with pure silica beads (ACROS Organics™). During the experiments, the chamber was fully covered with heavy duty aluminum foil to eliminate UV leaks and prevent interference by other wavelength light sources.

Seven brines (Table 1) were examined in this study, which can be divided into three major categories.

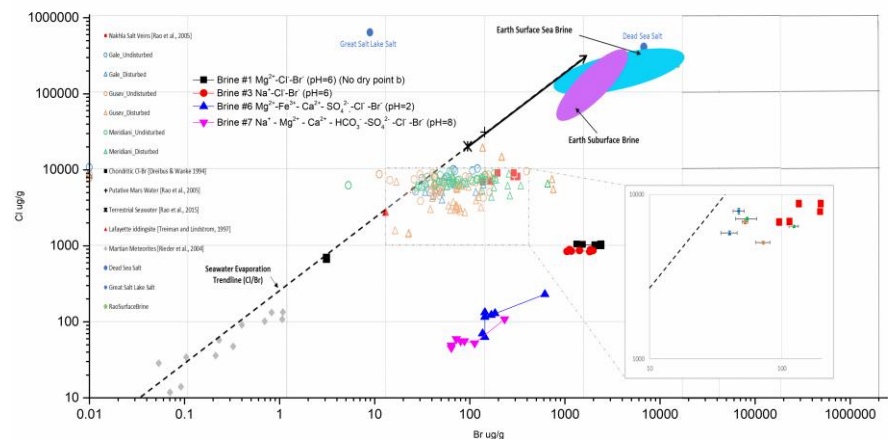


Figure 1: APXS soil compare with changes in laboratory evaporation simulation Cl (ug/g) and Br (ug/g) concentrations plotted relative to the terrestrial seawater Cl/Br evaporation trendline. The call-out box (lower right) displays the root-mean-square-error for each data category. These error bars are centered on the mean of the corresponding dataset.

Brines #1, #3 were simple halide brines, and brines #6 and #7 were designed to simulate aspects of the Meridiani Planum and Phoenix landing site geo-logical environments, respectively. In this study, we chose 4 origin brines to compare with the Martian Natural status.

Brine #1 Mg^{2+} - Cl^- - Br^- (pH 6) (No dry point^b)

Brine #3 Na^+ - Cl^- - Br^- (pH 6)

Brine #6 Mg^{2+} - Fe^{3+} - Ca^{2+} - SO_4^{2-} - Cl^- - Br^- (pH 2)

Brine #7 Na^+ - Mg^{2+} - Ca^{2+} - HCO_3^- - SO_4^{2-} - Cl^- - Br^- (pH 8)

Results and Discussion: The formation of a weathered layer on the surface of Mars is a complex process, and previous data suggest that it is difficult to deconvolve the effects of fluid and surface atmospheric processes. The Br-enrichment found in many soils at different landing sites may interact with brine formed by evaporation. The observed geochemical relationship, significant fluctuations in Br/Cl, and a reduction in Br/Cl to the surface support the hypothesis that Br mobility is enhanced at the surface.

In our laboratory work (e.g., Fig. 1 [7]), for neutral-alkaline solutions, Br^- has a tendency to volatilize over time, Br/Cl gradually decreases with time after precipitation, and almost no Br is observed in sediments in acidic environments. In the laboratory environment, Cl of Brine#1 and #3 did not change much from the origin composition after evaporation, while #6 and #7 both lost nearly half of Cl. It may be evaporated in the forming of HCl or photo-oxidized into a gaseous substance, which are modeled after the Meridiani and the Phoenix landing sites. Moreover, it was proved to be more prone to generate Cl-oxide in a dry environment. This reflects, to some extent, the role of halogens and the atmosphere in the region.

Laboratory simulations have shown that atmospheric and photochemical processes also alter the geochemical behavior of halogens in highly arid evaporation environments. There is a very different perchlorate/chlorate ratio on Mars and Earth, and photochemistry in arid environments is likely to oxidize chlorate to perchlorate. Furthermore, brine #6 that may approximate martian surface conditions, produced extreme ClO_4^- that can explain the high content of perchlorate on Mars. Moreover, there are shared pathways to Br and Cl on oxidation, although the natural Br on Mars is very limited so this control can be difficult to observe. Past work has confirmed that the Martian subsurface soil has a higher Br content than the surface soil [8], and Br is more volatile than Cl [7], which may also indicate that the surface halogen interacts with the atmosphere. Therefore, we can combine a previous study to create a halogen cycle model (e.g., Fig. 2), discharge and galactic cosmic ray (GCR) oxidation on the surface of Mars. (Figure 2). Degradation of BrO_3^- , ClO_3^- and ClO_4^- may

occur after storage or redeposition, with BrO_3^- most likely reduced to Br^- . The active redox cycle of Br relative to Cl on the surface of Mars can result in changes in Br abundance and Br/Cl fractionation on a local scale, consistent with Br and Cl measurements in situ on Mars.

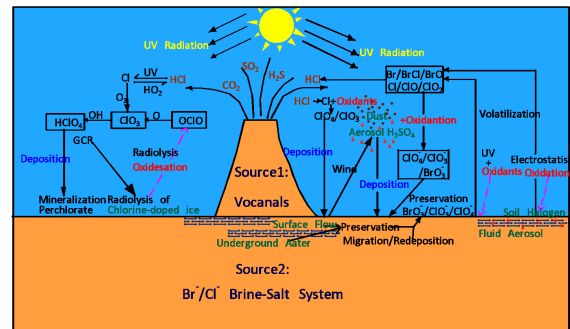


Figure 2: The conceptual model of the Cl and Br circles of Martian surface and atmosphere. Volcanic degassing and halide brine-salt systems are the two main sources of Cl- and Br-. The cycle consists of three major pathways: [1] volatilization from the ground or underground fluids, soils and colloids or into the atmosphere. Mobilization; [2] removal from the atmosphere or dust and aerosols in the atmosphere; [3] through active migration and redeposition of water. The main means of oxidation are: : photo-chemistry [7], electrostatic [10] and Radiolysis [11].

References: [1] Clark, B.C. et al. (2005) Earth Planet. Sci. Lett., 240, 73-94. [2] Yen, S.A., et al. (2005) Nature, 436, 49-54. [3] Knoll, A.H. et al. (2008) JGR, 113 (E6), E06S16. [4] Marion, G.M. et al. (2009) Icarus, 200(2), 436-445. [5] Rao et al. (2009) Earth Planet. Sci. Lett., 286(3), 396-403. [6] Karunatillake, S., et al. (2013) Icarus, 226, 1438-1446. [7] Zhao et al. (2018) Earth Planet. Sci. Lett., 497, 102-112. [8] D. Lacznik et al., (2017) LPSC. [9] Wilson, E.H. et al. (2016) J. Geophys. Res. Planets, 121, 1472-1487. [10] M.L. Smith et al. (2014) Icarus 231, 51-64. [11] Anderson R.C. et al. (2012) Space Sci. Rev., 170, 57-75. [12] Karunatillake, S. et al. (2011) J. Sci. Comput., 46(3), 439-451. [13] Karunatillake, S., et al. (2010) JGR, 115, E00F04. [14] McGlynn, I. O. et al. (2011). JGR, 116(January), E00F22.