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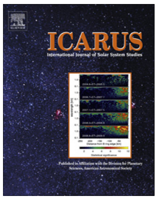

Does martian soil release reactive halogens to the atmosphere?

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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.

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), H_2O_2 (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, Br_2, BrO,

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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 (Hurowitz 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 10^8 times longer at concentrations about 10^6 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 10^9 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 H_2O 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 $BrONO_2$ 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 (ClO_4^-) 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 $Mg(ClO_4)_2{\cdot}nH_2O$. 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