

**HALOGEN GEOCHEMISTRY AT THE MARTIAN SURFACE.** Yu-Yan Sara Zhao and Scott M. McLennan, Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 ([yuyan.zhao@stonybrook.edu](mailto:yuyan.zhao@stonybrook.edu)).

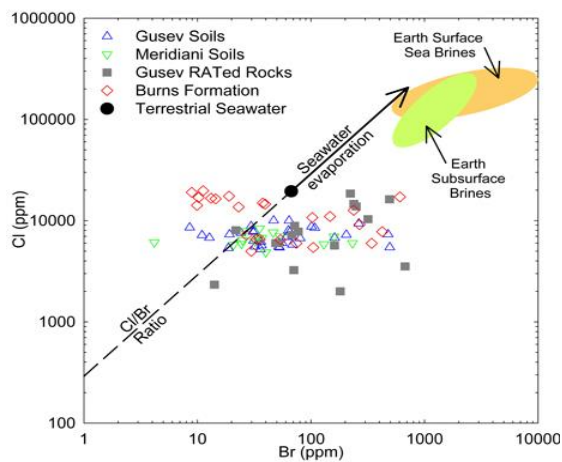
**Introduction:** Characterizing halogen (F, Cl, Br, I) geochemistry is essential for understanding a broad array of geological processes on Mars. Distribution, speciation, transformation, and geochemical cycles of halogens provide important constraints on aqueous history as well as past and current habitability. Here we focus only on Cl and Br for which abundant data have been accumulated by in situ and orbital missions. Fluorine and iodine, on the other hand, are not considered due to the lack of direct measurements by any Martian mission so far.

In magmatic systems, Cl and Br are moderately (Cl) to highly (Br) volatile, incompatible lithophile elements [1] and are central to models calling for Mars to be a volatile-rich planet [2-4]. Cl and Br also have a fundamental influence on melting conditions and phase relationships of Martian igneous rocks [5] as well as on late stage pyroclastic-hydrothermal systems [6-8].

Meteorite investigations provide an essential basis for constraining planetary elemental compositions. Average SNC meteorites (shergottites, nakhlites, and chassignites) have a Cl/Br ratio of 180 [9-11] which is close to the Cl chondrite ratio of 199 (Cl 698 ppm and Br 3.5 ppm; [12]). Based on SNCs, Wänke [13] estimated Cl and Br abundances of bulk Mars (mantle + crust) at 38 ppm (Cl) and 0.145 ppm (Br). However, one caveat is that most SNC meteorites are at best representative of young magmatism, and may not be fully representative of all the major geochemical reservoirs on Mars [14]. Taylor et al. [3] revisited this issue using Mars Odyssey GRS data and concluded an order of magnitude higher Cl (390 ppm) and Br (2.2 ppm) for bulk Mars compared to the Wänke model [13].

**Halogen Measurements on Mars:** Direct measurements of halogens have been made by four missions so far. (1) The Mars Odyssey GRS mapped elemental Cl in the top few decimeters and found a ubiquitous distribution [15,16]. Mean Cl content for low- to mid-latitudes is ~0.46% and assuming an average soil Cl/Br ratio, estimated average Br content is ~40 ppm [3]. (2) An unexpected result of the 2003 Mars Exploration Rovers was high abundances of Br on the Martian surface using onboard Alpha-Particle X-ray Spectrometers (APXS) [11,17-19]. In contrast to low abundances in meteorites, Br is enriched and varies by  $>10^3$ , which primarily controls the variations of Cl/Br ratios (Fig. 1). Although Br enrichment has been suggested to be related to aqueous processes on Mars, significant difference in Br concentrations in two samples close to each other with similar S contents [19] is difficult to explain

solely by aqueous chemistry of  $\text{Cl}^-$  and  $\text{Br}^-$  in evaporative systems. (3) The Phoenix lander identified substantial  $\text{ClO}_4^-$  (with 5-10 times less Cl) in the water-soluble fraction of soils in north polar area [20]. (4) The on-going Curiosity rover detected oxychlorine species (probably  $\text{ClO}_4^-$  and/or  $\text{ClO}_3^-$ ) at near equatorial Gale Crater [21,22]. Detection of oxychlorine species at two distinctive locations (Phoenix vs. Curiosity landing sites) and three different lithologies (surface soils, aeolian fines, ancient sedimentary rock) suggests that oxychlorine species may be important Cl components, widely distributed on the Martian surface and persistent through its history. The hypothesis of wide distribution of oxychlorine species on Mars has attracted increasing attention, since it has broad implications for the aqueous chemistry, brine stability, organics and habitability [23-25]. More importantly, it suggests that photochemical related oxidation processes, which have been underappreciated, may play an important role influencing the Cl behavior at the Martian surface. Such processes could also affect Br [26-28].



**Fig. 1.** Cl (ppm) vs. Br (ppm) for selected APXS analyses. Also shown are the Cl/Br path of evaporating terrestrial seawater and fields for terrestrial brines (low Cl/Br) from which halite (high Cl/Br) has precipitated. The Cl/Br ratio is highly variable and variation in Cl/Br ratios is mainly controlled by Br abundances.

**Aqueous Geochemistry of  $\text{Cl}^-$  and  $\text{Br}^-$ :** Due to the 8% difference in ionic radius ( $\text{Br}^-$  1.96 Å vs.  $\text{Cl}^-$  1.81 Å),  $\text{Br}^-$  can substitute for  $\text{Cl}^-$  in most mineral lattices but preferentially remains in the brine while  $\text{Cl}^-$  forms halide minerals [29-31]. During evaporation of terrestrial waters, both  $\text{Br}^-$  and  $\text{Cl}^-$  act conservatively through to the point of  $\text{Cl}^-$  precipitation, beyond which Cl/Br ratios decrease in evaporating brines with Cl/Br ratios of precipitates being higher than ambient brines.

**Alteration.** Experiments have been used to investigate Mars-analog brines in equilibrium with Martian atmosphere after alteration of SNC compositions [32,33]. However, lack of Br data for starting material makes it difficult to evaluate variations in Cl/Br ratios.

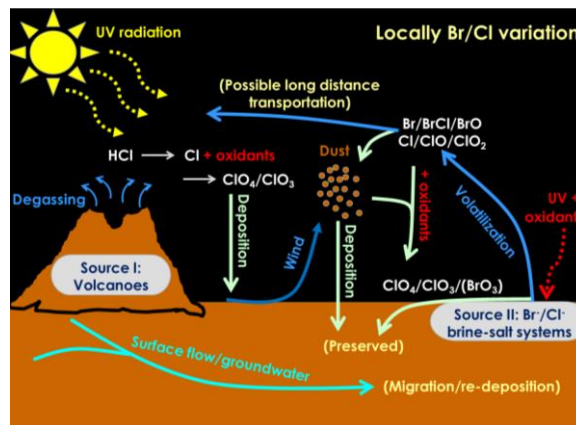
**Evaporation.** Cl<sup>-</sup> and Br<sup>-</sup> geochemistry during evaporative processes has been evaluated in meteorites, simulation experiments and thermodynamic models [34-38]. These studies all noted systematic Cl/Br variations in salt assemblages in Nakhilite meteorites and evaporite-bearing Burns formation at Meridiani Planum, consistent with differential partitioning associated with chloride precipitation (NaCl, MgCl<sub>2</sub>•H<sub>2</sub>O) and evaporative-forced diagenetic salt remobilization.

**Diagenetic oxidation.** It is now established that water-mediated diagenesis has taken place on Mars, perhaps over much of its geological history [39-41], and one likely mineralogical pathway is transformation of Fe<sup>II</sup> sulfates to Fe<sup>III</sup> oxides, involving jarosite, goethite and hematite. Zhao et al. [42] demonstrated that starting with diagenetic brines with molar Cl<sup>-</sup>/Br<sup>-</sup> > 1, precipitated jarosite preferentially incorporated at least 10X more Br<sup>-</sup> than Cl<sup>-</sup> and thus had a potential to fractionate Br<sup>-</sup> from Cl<sup>-</sup>. Accordingly, jarosite could be a candidate for hosting elevated Br at Meridiani Planum besides late-stage evaporative halide minerals.

**Atmospheric Influences on Halogen Geochemistry:** Due to limited understanding of formation mechanisms of natural perchlorate on Earth (e.g., [43-45]), key questions remain unclear for the origin of ClO<sub>4</sub><sup>-</sup> on Mars, such as most efficient pathways, roles of intermediate oxidizing Cl phases (e.g., ClO<sup>-</sup>, ClO<sub>2</sub><sup>-</sup>, and ClO<sub>3</sub><sup>-</sup>), types of oxidants, form of reactions (e.g., gas-gas, solid-gas or liquid-gas), etc. Pure gas-phases reaction in the atmosphere is likely [43], however, probably not quantitatively sufficient to form the majority of ClO<sub>4</sub><sup>-</sup> detected on Mars [46]. Heterogeneous reactions are able to convert Cl<sup>-</sup> to ClO<sub>4</sub><sup>-</sup> [27,45], of which gas-solid type reaction is most effective [27]. Chlorate (ClO<sub>3</sub><sup>-</sup>) formed in addition to perchlorate in simulation experiments of Zhao et al. [27], and ClO<sub>4</sub><sup>-</sup>, ClO<sub>3</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were recently reported in a sawdust fraction of a SNC meteorite [24].

Studies of terrestrial tropospheric Br suggest Br preferentially volatilizes over Cl in brines having Cl/Br ratios less than seawater [47-48] and this behavior could be important on Mars [26]. Zhao et al. [27] observed loss of Br<sup>-</sup> relative to Cl<sup>-</sup> in evaporating brines with initial molar Cl/Br ratios ~1. In some cases, bromate (BrO<sub>3</sub><sup>-</sup>) was also detected. Therefore, photochemical oxidation of Cl<sup>-</sup> and Br<sup>-</sup> fractionates Br from Cl in the original brine-salt system, and the presence of Br would affect Cl behavior by competing for available oxidants. A possible photochemical cycle of Cl and Br

on the Martian surface is illustrated in Fig. 2, which could explain some of the observed Br variation.



**Fig. 2.** Photochemical influences on Cl and Br at the Martian surface. Cl<sup>-</sup> and Br<sup>-</sup> can be oxidized photochemically, which greatly increases mobility and results in local variations. Arrows indicate three major pathways: transfer into atmosphere (blue), deposition from atmosphere (light yellow), migration via aqueous activity (light green). Br preferentially volatilizes into the atmosphere over Cl which is consistent with Br/Cl fractionation observed in Mars surface samples.

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