

**PHOTOCHEMICAL INFLUENCES ON BROMINE AND CHLORINE GEOCHEMISTRY ON THE MARTIAN SURFACE.** Yu-Yan Sara Zhao<sup>1</sup>, Scott M. McLennan<sup>1</sup>, Andrew W. Jackson<sup>2</sup>, Suniti Karunatillake<sup>3</sup>,  
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**Introduction:** The geochemistry of halogen elements bromine (Br) and chlorine (Cl) on the Martian surface, despite implications for habitability, is poorly understood. Several new lines of evidence from Mars suggest that besides Br<sup>-</sup> and Cl<sup>-</sup>, additional Br and Cl reactive species are also present and photochemical processes may be key in accounting for their presence.

Mars Exploration Rovers' (MERs) APXS detected highly variable Br abundances in surface soils and rock samples on Mars which in turn controls Br/Cl ratios [1]. Detailed statistical examination of soil profiles at both MER landing sites indicates decreasing Br abundance towards the surface and decoupled Br variability from potential related cations (e.g., Mg) at the surface relative to the subsurface, suggesting a loss of surficial Br into the atmosphere compared to S and Cl [2]. Volatilization of Br into the troposphere by photochemical related reactions has been identified in several terrestrial systems, some of which are quite relevant to Mars, including evaporative brines and salt pans in highly arid environments [3,4], brine films on suspended dust [5], and aerosol release from newly formed ice on brines [6,7]. Similar reactions to volatilize Br from the aqueous fluid-mineral systems may also occur on Mars.

On the other hand, Cl is widely distributed on the Martian surface [8-11], which could be consistent with an atmospheric influence. Perchlorate was identified in soils at the Phoenix landing site [12] and oxychlorine species (likely perchlorate and/or chlorate) were again detected at Gale Crater, in Rocknest aeolian deposits [13] and two drilled mudstone samples acquired by Curiosity at Yellowknife Bay [14]. The presence of oxychlorine phase(s) at two very different locations (Phoenix and MSL landing sites) suggest that oxychlorine species might be widely distributed on the Martian surface, and that some ubiquitous global processes, such as photochemical related reactions, might account for their formation.

Accordingly, we initiated a series of laboratory experiments, to evaluate the behavior of Br and Cl in brine-sediment mixtures during evaporation under UV exposure. Specifically, effects of brine compositions, sediment grain size, and atmospheric composition (i.e., Earth vs. Mars) were examined.

**Methods:** The experimental apparatus was described in detail in [15]. The UV source wavelength was 254 nm. Temperature was kept at 25 °C in all the experiments. Six types of brines were examined: Brine

#1 was Br<sup>-</sup> free (Mg-Cl<sup>-</sup>; pH 6); Brine #2 was a counterpart to Brine #1 with Br<sup>-</sup> (Mg-Cl<sup>-</sup>-Br<sup>-</sup>; pH 6); Brine #3 was a slightly alkaline bicarbonate brine without Fe (Ca-Mg-Na-HCO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-Br<sup>-</sup>; pH 8); Brine #4 was an acidic Fe<sup>(III)</sup> bearing brine (Ca-Mg-Fe<sup>III</sup>-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-Br<sup>-</sup>; pH 2); Brine #5 and #6 were single cation sulfate dominant brines, Mg-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-Br<sup>-</sup> (pH 6) and K-SO<sub>4</sub><sup>2-</sup>-Cl<sup>-</sup>-Br<sup>-</sup> (pH 6), respectively.

In a typical run (UV time = 120 h), the brine and quartz sand mixture was placed in the chamber and evaporated to dryness by continuously pumping. After 24 h, the pump was stopped and the chamber was refilled with simulated atmospheric gas and left undisturbed for 24 h. After two such cycles, the pump was operated for an additional 24 h marking the end of the experiment. Final mixtures were then collected, redissolved in water and the supernatants were filtered with a 0.2 µm membrane and analyzed for anions. This type of experiment was used to examine the effects of grain size (with Brine #2; Earth atmosphere) and atmospheric composition (with Brine #3, #5, #6; Earth and Mars). Simulated Mars gas had a composition of 95.35% CO<sub>2</sub>, 1.62% Ar, 2.83% N<sub>2</sub>, and 0.2% O<sub>2</sub>.

An extended time UV exposure experiment (UV time = 384 h) was carried out using larger initial samples, to demonstrate how halogen species change as a function of UV exposure time. The evaporating mixture was sampled after each pumping-reaction cycle.

Major anions Cl<sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and oxyanions including ClO, ClO<sub>2</sub>, ClO<sub>3</sub>, ClO<sub>4</sub> and BrO<sub>3</sub> were analyzed (methods described in [15]). Final results were reported as the absolute abundances of the initial evaporating mass before evaporation and sampling, to provide a base for comparison from sample to sample.

### Results:

*Br<sup>-</sup>/Cl<sup>-</sup> fractionation in evaporating mixture.* Br<sup>-</sup> and Cl<sup>-</sup> continuously decreased in evaporating mixtures, and Br<sup>-</sup>/Cl<sup>-</sup> molar ratios varied, following a similar trend as Br<sup>-</sup> variation (Fig. 1). By the end of the experiment, 69% of initial total Br<sup>-</sup> and 16% of initial total Cl<sup>-</sup> were lost from Brine #3, and 73% of total Br<sup>-</sup> and 48% of Cl<sup>-</sup> were lost from Brine #4.

*Production of oxychlorine phases.* Production of ClO<sub>4</sub> and ClO<sub>3</sub> occurred in all UV experiments under both Earth and Mars atmosphere (detection limit 4 ppb). ClO and ClO<sub>2</sub> were undetected in all the samples (detection limit 8 ppm). Control samples undergoing the same process without UV were oxychlorine free.

Abundances of  $\text{ClO}_4$  and  $\text{ClO}_3$  (in the case of Brine #1 and #3) increased as a function of prolonged UV exposure (Fig. 2). Moreover, significantly higher amounts of  $\text{ClO}_4$  and  $\text{ClO}_3$  were present in samples without further water vapor loss than the ones containing excess water, suggesting that dry conditions better served oxychlorine formation. In addition,  $\text{ClO}_3$  was dominant over  $\text{ClO}_4$  in all brines, except Brine #4 in which orders of magnitude higher  $\text{ClO}_4$  than  $\text{ClO}_3$  was persistent throughout the experiment. Since Brine #4 was the only Fe-bearing brine with low pH, the extreme  $\text{ClO}_4/\text{ClO}_3$  ratios might be due to decomposition of  $\text{ClO}_3$  which occurs at low pH condition, and the by-product  $\text{ClO}_2$  can lead to additional  $\text{ClO}_4$  formation [16]. Depending on the phases, the precipitated Fe-minerals might facilitate  $\text{ClO}_4$  production as well [17].

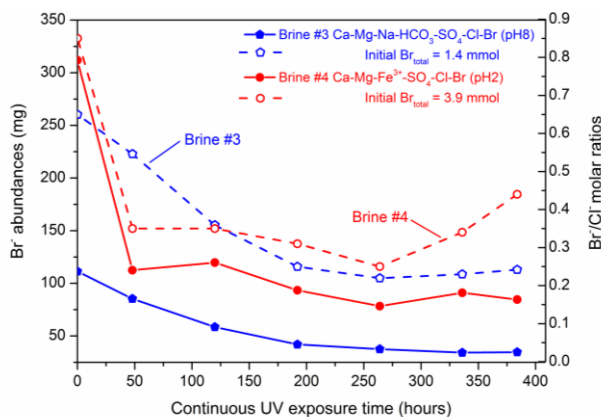


Fig. 1.  $\text{Br}^-$  abundances (solid symbols and lines) and  $\text{Br}^-/\text{Cl}^-$  molar ratios (open symbols and dash lines) of the evaporating mixture during extended time UV exposure experiment with Brines #3 and #4.  $\text{Br}^-$  and  $\text{Br}^-/\text{Cl}^-$  ratios continuously decreased suggesting that  $\text{Br}^-$  abundances controlled the  $\text{Br}^-/\text{Cl}^-$  variations.

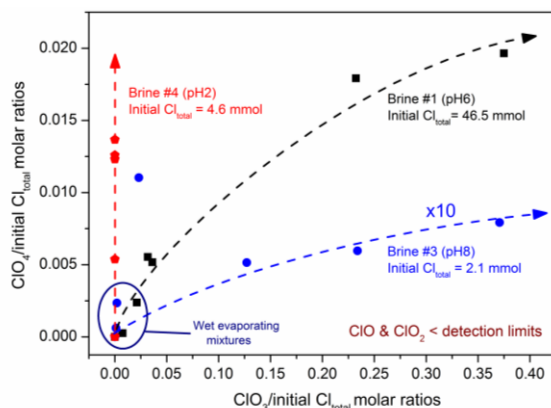


Fig. 2. Molar ratios of  $\text{ClO}_4/\text{initial Cl}_{\text{total}}$  versus  $\text{ClO}_3/\text{initial Cl}_{\text{total}}$  in evaporating mixtures during extended time UV exposure experiment with Brines #1, #3 and #4. Solid symbols represent samples collected

every 48-72 h, and arrows show direction of increasing UV exposure time. Brine #3 (blue) ratios were multiplied by 10 to allow plotting on the same scale as others. Samples within oval were at “wet” conditions, as excess water was continuously lost via evaporation.

*Effects of sediment grain size.* Amounts of  $\text{ClO}_4$  and  $\text{ClO}_3$  in evaporating mixtures were correlated with quartz grain size (Fig. 3). The finer the grain size, the higher the abundances of  $\text{ClO}_4$  and  $\text{ClO}_3$  produced, and the higher the  $\text{ClO}_4/\text{ClO}_3$  ratios. The sediment may provide a surface for the heterogeneous reactions to occur on even before the evaporating mixture dried out. Thus, the finer grain size facilitates such process by providing larger surface area.

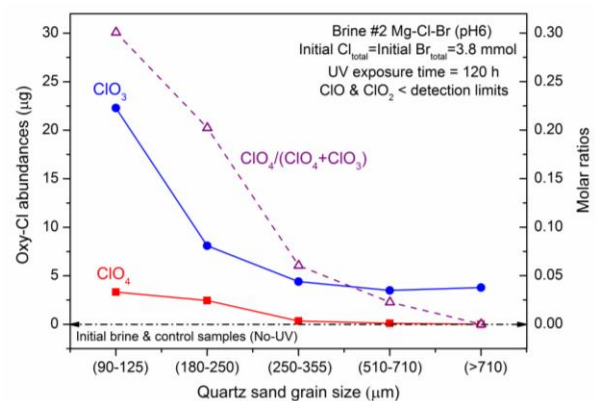


Fig. 3. Change in  $\text{ClO}_4$  and  $\text{ClO}_3$  abundances (solid symbols and lines) and  $\text{ClO}_4/(\text{ClO}_4+\text{ClO}_3)$  molar ratios (open symbols and dash lines) with quartz grain size. Dash arrow indicates initial brine and control samples produced without UV were free of oxychlorine.

We are currently finalizing anion and isotopic analyses. We will report the complete dataset at the meeting, including a discussion of Earth vs. Mars atmospheric conditions, and isotopic signature of our synthetic samples compared to terrestrial perchlorate samples.

**References:** [1] Brückner, J., et al. (2008) In: *The Martian Surface: Composition, Mineralogy and Physical Properties* (Cambridge). [2] Karunatillake, S. et al. (2013) *Icarus*, 226, 1438. [3] Risacher, F., et al., (2006) *Geochim. Cosmochim. Acta*, 70, 2143. [4] Hänninger, G., et al. (2004) *Geophys. Res. Lett.*, 31, L04101. [5] Sander, R. et al., (2003) *Atmos. Chem. Phys.* 3, 1301. [6] Kaleschke, L., (2004) *Geophys. Res. Lett.* 31, L16114. [7] Yang, X., et al., (2008) *Geophys. Res. Lett.* 35, L16815. [8] Clark, B. C. et al., (1982) *JGR*, 87, 10059. [9] Gellert, R. et al., (2004) *Sci.*, 305, 829. [10] Rieder, R., (2004) *Sci.*, 306, 1746. [11] Keller, J. M., et al. (2007) *JGR*, 111, E03S08. [12] Hecht, M. H., (2009) *Sci.*, 325, 64. [13] Leshin, L. A., et al., (2013) *Sci.*, DOI: 10.1126/science.1238937. [14] Ming, D.W., et al., (2013) *Sci.*, DOI: 10.1126/science.1245267. [15] Zhao, Y.-Y. S., et al., (2013) *LPS XLIV*, Abst. #3002. [16] Masschelein, W. J. (1979) *Ann Arbor Sci. Publ.*, pp 190. [17] Schuttlefield, J. D., et al., (2011) *J. Am. Chem. Soc.*, 133, 17521.