

PHOTOCHEMICAL EFFECTS ON BROMINE AND CHLORINE DISTRIBUTIONS DURING BRINE EVAPORATION ON THE MARTIAN SURFACE. Yu-Yan Sara Zhao¹, Scott M. McLennan¹, Andrew W. Jackson², Suniti Karunatillake^{1,3}, ¹Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 (yuyan.zhao@stonybrook.edu), ²Department of Civil Engineering, Texas Tech University, Lubbock, TX 79409-1022, ³Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803.

Introduction: The relative distributions of halogen elements bromine (Br) and chlorine (Cl) on the Martian surface are poorly understood, despite implications for habitability, due to their reactivity, and for better understanding aqueous processes. Observations suggest that photochemical processes may volatilize Br and Cl from fluids and sediments into the atmosphere and subsequently influence their distributions on the Martian surface. These include: (1) Mars Exploration Rover (MER) Opportunity's APXS measurements revealed variable Br/Cl ratios of undisturbed surface soil and RATED rock samples controlled primarily by Br abundances [1]. Br concentrations in subsurface soils at both MER landing sites consistently exceed surface soils (Table 1) and may suggest atmospheric loss of Br in the topmost soil [2]. (2) Mars Odyssey gamma ray spectrometer (GRS) mapping of equatorial and mid-latitudinal distributions of near-surface Cl abundances [3] demonstrated that Cl is widely distributed, which could be consistent with an atmospheric influence. (3) The Phoenix mission detected substantial concentrations of perchlorate (0.4 - 0.6 wt%) in the water-soluble fraction of soils at the north polar landing site [4], which suggests that photochemical processes may influence the surface chemistry and distribution of Cl [5], processes that could also influence Br [6]. It is thus possible that photochemistry plays an important role in influencing halogen distributions on the surface of Mars.

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 composition, atmospheric composition (i.e., Earth vs. Mars), and sediment grain size were examined.

	Gusev Plains		Meridiani Planum	
	Surface	Subsurface	Surface	Subsurface
Br (ppm)	55 ± 37	65 ± 30	51 ± 11	148 ± 69
Cl/Br	28 ± 15	17 ± 7	21 ± 11	7.2 ± 4.5
n	15	15	26	12

Table 1. Comparison of Br and Cl/Br for surface and subsurface soils on Mars. Using averages and 95% confidence intervals (data from [1,7,8]).

Experiment Design and Analysis Methods: Fig. 1 illustrates the experimental apparatus. The reaction vessel has a quartz encased low-temperature UV light source (254 nm) inserted directly into the chamber. Starting materials were placed in quartz dishes in the chamber and the chamber was covered with heavy Al foil to avoid interference from other light sources.

Four types of brines were examined, including: (1) Mg-Cl⁻-Br⁻ (Cl⁻ and Br⁻ 2.8 M; pH 3); (2) Mg-SO₄-Cl⁻-Br⁻ (Cl⁻ and Br⁻ 0.025 M; pH 2); (3) Ca-Mg-Fe(III)-SO₄²⁻-Cl⁻-Br⁻ (Cl⁻ and Br⁻ 0.02 M; pH 1.7); and (4) K-SO₄-Cl⁻-Br⁻ (Cl⁻ and Br⁻ 0.1 M; pH 2). In each setting, the brine was mixed with quartz grains with initial sediment/brine mass ratio ~3-4. Possible influences of grain size were evaluated with the Type (1) brine and four different grain sizes (Fig. 2). Different atmospheric compositions were investigated using Earth and simulated Mars gas with Type (2), (3) and (4) brines. Simulated Mars gas had 95.35% CO₂, 1.62% Ar, 2.83% N₂, and 0.2% O₂.

Each mixture was evaporated to dryness at low pressure by continuously pumping. After 24 h the pump was stopped and the chamber was re-filled with simulated atmospheric gas and left undisturbed for another 24 h. After two such cycles, the pump was operated for an additional 24 h marking the end of the experiment. UV light was on continuously for a total of 120 h. Final mixtures were then re-dissolved, and the supernatants were collected, filtered with a 0.2 µm membrane and analyzed for anion concentrations.

Major anions (Cl⁻, NO₃⁻, and SO₄²⁻) were analyzed by ion chromatography following EPA Method 300.0. ClO₄⁻ and ClO₃⁻ concentrations were separately measured by sequential ion chromatography-mass spectroscopy-mass spectroscopy (IC-MS/MS) following the method detailed in [9,10]. ClO₄⁻ and ClO₃⁻ were quantified using a Dionex LC 20 ion chromatography system consisting of GP50 pump, CD25 conductivity detector, AS40 automated sampler and Dionex IonPac AS16 (250 X 2 mm) analytical column. The IC system was coupled with an Applied Biosystems-MDS SCIEX API 2000TM triple quadrupole mass spectrometer equipped with a Turbo-IonSprayTM source. A hydroxide (NaOH) eluent at 0.3 mL min⁻¹ was followed by 90% acetonitrile (0.3 mL min⁻¹) as a post-column solvent. To overcome matrix effects, all samples were

spiked with Cl^{18}O_3 (produced in house) or Cl^{18}O_4 (Dionex) internal standards.

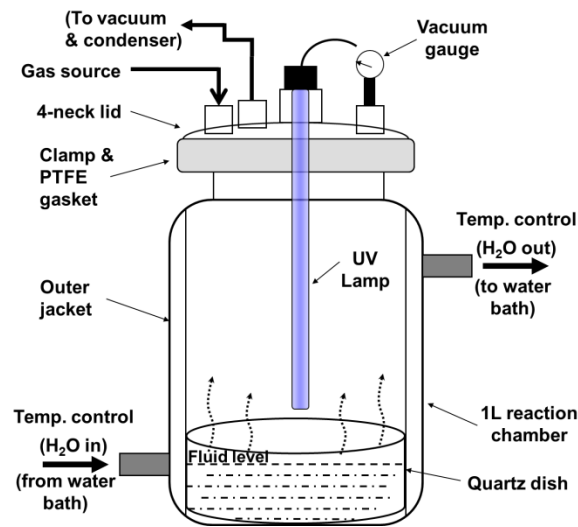


Figure 1. Experimental apparatus used in this study.

Preliminary Results: Br/Cl fractionations and production of perchlorate were observed in all UV experiments under both Earth and Mars atmospheric conditions. Based on our initial experiments for Type (1) and (2) brines (Table 2), initial brines had Br/Cl molar ratios ~1 without detectable perchlorate. Evaporites produced in the absence of UV had similar Br/Cl ratios as initial brines, and no detectable perchlorate. Under UV conditions, Br/Cl decreased significantly and perchlorate was present in all samples. Presence of molecular oxygen in the atmosphere may play a crucial role in these experiments, in which the decrease of Br/Cl and production of perchlorate were more pronounced under Earth conditions than Mars (Table 2; Type (2) brine).

A correlation of Br/Cl ratios with sediment grain size was observed using Type (1) brine with four different grain size sediments (Fig. 2). Br/Cl ratios decreased compared to initial conditions of all four grain sizes, and the decrease positively correlated with the increase of grain size. Contrary to expectations that

smaller grain sizes, with higher specific surface area, would facilitate volatilizing halogens, large grain sizes may in fact provide more exposed surface area to the environment due to higher porosity, thus facilitating the gas-brine-salt interaction under UV light.

We are currently carrying out duplicate experiments under those conditions that indicated significant Br/Cl fractionation and a complete anion dataset is being evaluated. We will report these results at the meeting.

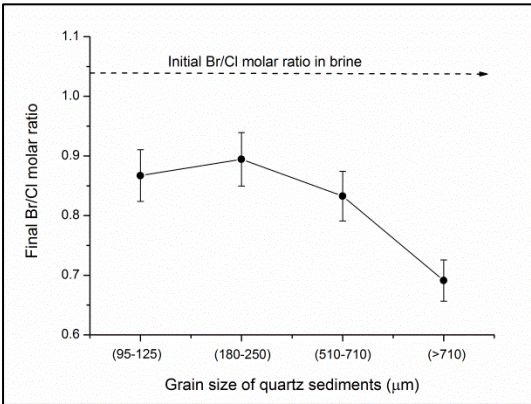


Figure 2. Br/Cl molar ratios of evaporite from Type (1) brine mixed with different grain size sediment. Dash arrow indicates initial Br/Cl molar ratio in brine. Final Br/Cl ratios decrease as grain size coarsens. Error bar represents $\pm 5\%$ analytical uncertainties.

References: [1] Brückner, J., et al. (2008) In: *The Martian Surface: Composition, Mineralogy and Physical Properties* (Cambridge), pp 628. [2] Karunatillake et al. (2013) *Icarus*, submitted. [3] Keller, J. M., et al. (2007) *JGR*, 111, E03S08. [4] Hecht, M. H., (2009) *Sci.*, 325, 64-67. [5] Catling, D. C., et al. (2010) *JGR*, 115, E00E11. [6] Finlayson-Pitts, B. J. (2010) *Anal. Chem.*, 82(3), 770-776. [7] Gellert, R., et al. (2006) *JGR*, 111, E02S05. [8] Ming, D. W., et al. (2008) *JGR*, 113, E12S39. [9] Rao, B., et al. (2007) *Environ. Sci. Technol.*, 41: 4487-4832. [10] Rao, B., et al. (2010) *Environ. Sci. Technol.*, 44: 8429-8434.

Type of brines	Initial solution		Final evaporites (Earth atm. No UV) ^a		Final evaporites (Earth atm. UV) ^a		Final evaporites (simulated Mars atm. UV) ^a	
	Br/Cl	ClO ₄	Br/Cl	ClO ₄	Br/Cl	ClO ₄ /Cl _{total}	Br/Cl	ClO ₄ /Cl _{total}
Mg-Cl ⁻ -Br ⁻ (pH = 3)	1.04	< DL	1.12	< DL	0.86	n.a. ^b	n.a. ^b	n.a. ^b
Mg-SO ₄ -Cl ⁻ -Br ⁻ (pH = 2)	1.00	< DL	0.96	< DL	0.18	0.02%	0.51	0.01%

Table 2. Molar ratios of Br/Cl and ClO₄/Cl_{total} measured in UV experiments. Detection limit for perchlorate is 0.05 ppb. Footnotes: (a) Heterogeneous grain size sediment. (b) Pending data.