

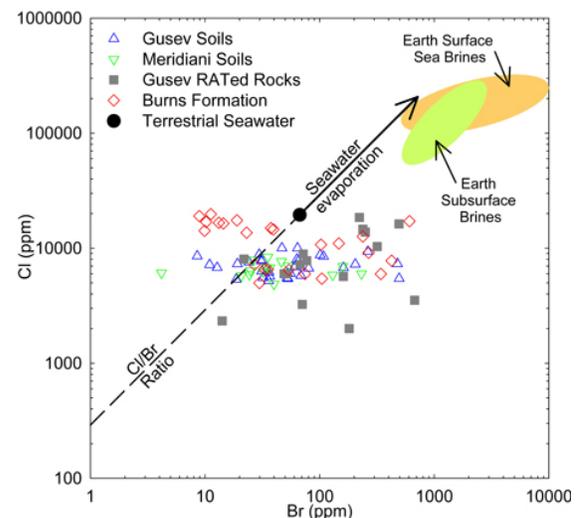
**EXPERIMENTAL CONSTRAINTS ON PARTITIONING BEHAVIOR OF THE HALOGEN ELEMENTS DURING SEDIMENTARY PROCESSES ON MARS: A PROGRESS REPORT.** Yuyan S. Zhao and Scott M. McLennan, Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100 (yuyan.zhao@stonybrook.edu; scott.mclennan@sunysb.edu).

**Introduction:** The Mars Exploration Rovers and orbital missions continue to deliver large volumes of high quality chemical and mineralogical data from the Martian surface. Particularly relevant to this study, a large number of measurements for the halogen elements chlorine and bromine are available. The Mars Exploration Rovers (MER) have returned more than 350 chemical analyses of rocks and soils by the alpha particle X-ray spectrometer (APXS) to date. The Mars Odyssey Gamma Ray Spectrometer (GRS) mapped the equatorial and mid-latitude distribution of elemental Cl abundances at the near-surface of Mars [1]. These datasets reveal that (1) Cl is ubiquitous on the Martian surface but not globally homogeneously distributed. It is significantly enriched within the upper few tens of centimeters of the surface relative to the Martian meteorites and estimates for the bulk composition of the planet [1]; (2) Br is highly variable. It is commonly low or undetectable in basaltic samples, but enriched in the samples that have undergone sedimentary processes (i.e. alteration, evaporation, diagenesis, etc.) [2,3]; (3) Cl/Br ratios are highly variable compared to comparable earth settings, and the Cl/Br variation is dominantly controlled by variable Br abundances, which contrasts with terrestrial sedimentary materials where Cl and Br broadly covary unless influenced by very late stage (i.e., chloride saturated) brines (Figure 1).

Cl and Br are well established as providing important constraints on surficial processes and indeed Br is the single most important trace element for evaluating evaporative processes on Earth [4]. Although some recent studies have obtained insights into the Br distribution on Mars by SNC meteorite investigations and geochemical modeling of APXS data [e.g., 5,6,7], the models and interpretations are all based on our understanding of chloride-dominated terrestrial fluids, in which both Br and Cl behave conservatively during evaporation through to chloride precipitation. However, this framework of understanding might not be suitable or sufficient for the conditions on Mars. During early evaporation of sulfate dominated fluids, Cl and Br may be both minor components and Cl may not act as a purely conservative element and so raises the question of whether the Cl/Br ratio may still remain unfractionated during such processes. Meanwhile, iron sulfates and iron oxides, such as jarosite and schwertmannite, have the potential to incorporate halogen

elements either by substitution (e.g., for OH<sup>-</sup>) or adsorption, near the Martian surface [8], however, how the Cl and Br will interact with iron oxide precipitates and how they will act during transformations of iron sulfates to oxides remain unknown. In addition, the recently recognized possibility of Br and Cl volatilization into the atmosphere from brines and salt pans further challenges traditional thoughts [9,10]. Therefore, it is of great interest to systemically investigate the possible controls on Cl and Br partitioning behaviors on the Martian surface.

In this study, we experimentally simulate evaporative, diagenetic and photochemical processes relevant to Martian conditions to evaluate controls on fractionation and partitioning of Cl and Br during these processes, and thus provide useful tests to the various models that have been proposed.



**Figure 1.** Plot of Cl (ppm) versus Br (ppm) for selected APXS analyses from Mars. Plotted for reference are the composition and Cl/Br mass ratio (dashed line) of terrestrial seawater, the evaporation trend of terrestrial seawater (solid arrow) and field for late stage terrestrial brines.

**Evaporation of Martian Fluids:** Evaporation experiments are set up to determine the partitioning behavior of Cl<sup>-</sup> and Br<sup>-</sup> in sulfate-dominant fluids. We focus on a single fluid cation composition used by Tosca and McLennan [11] to construct a 'chemical

divide' model for evaporative processes on Mars. The composition was derived from acidic alteration of olivine-bearing Martian basalt [12]. Cations included (all in mmole/kg): 4.97 Mg; 3.56 Fe; 1.65 Ca; 0.25 Na; 0.10 K; 0.04 Al. Two evaporation pathways are formed by two different starting pH: A. ((Ca+Mg)>HCO<sub>3</sub>>>Fe; Mg>SO<sub>4</sub>>Ca; pH5) and B. (HCO<sub>3</sub><<Ca<SO<sub>4</sub>; SO<sub>4</sub>>Fe; pH3). The two evaporation pathways appear to give rise to the evaporite assemblages found in Nakhilites and on Meridiani Planum.

In brine A, HCO<sub>3</sub><sup>-</sup> saturation is maintained by bubbling Mars atmosphere (i.e., mainly CO<sub>2</sub>) directly into the solution. In brine B, low pH is reached by adding H<sub>2</sub>SO<sub>4</sub> in the initial fluids. To the brines, 100 ppm and 10 ppm Br will be added, which is equivalent to the Br abundances in the Martian mineral assemblages after 2-3 order of magnitude water loss in the experiments. The experimental apparatus is similar to Figure 1 of [11].

**Diagenetic Fe-oxidation Processes:** It is now well established that water-mediated diagenetic processes have taken place on Mars [e.g., 13, 14]. During such processes, a diagenetic transformation of ferrous sulfates to iron oxides may occur under Martian surface conditions [13, 14, 15, 16]. Tosca et al. [15] demonstrated that one likely mineralogical pathway involved ferric sulfates and oxides, including schwertmannite [Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>n</sub>•nH<sub>2</sub>O], jarosite [KFe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>], goethite [FeOOH] and hematite [Fe<sub>2</sub>O<sub>3</sub>]. Since Cl<sup>-</sup> readily substitutes for the hydroxyl ion in the jarosite structures [8], and the tunnel structure of schwertmannite is able to accommodate F<sup>-</sup> and Cl<sup>-</sup> [17] but likely not Br<sup>-</sup> due to the difference of ionic sizes, the diagenetic Fe-oxidation processes have the potential for incorporation and fractionation halogen elements near the Martian surface.

Similar to the work conducted by the authors [18], the open air oxidation experiment starts with a matrix fluid saturated with respect to epsomite. Two different loads of FeSO<sub>4</sub>•7H<sub>2</sub>O (melanterite) were then added to make initial Fe<sup>2+</sup> concentrations of 10 g/L (low Fe loading) and 200 g/L (high Fe loading). The Cl<sup>-</sup> and Br<sup>-</sup> are then added accordingly to make the overall SO<sub>4</sub> : Cl : Br mole ratio 4 : 2 : 1. All beakers are then covered but allowed to maintain contact with ambient atmosphere and regularly stirred at 25 °C. According to the results of our preliminary studies, the low Fe loadings yield a mixture of schwertmannite and goethite while the high Fe loadings yield pure jarosite. Therefore, Cl and Br behavior during precipitation of these oxides can be observed in the solution. In addition, halogen-free samples of jarosite, goethite and hematite

have been synthesized and used to evaluate adsorption in SO<sub>4</sub>-Cl-Br solutions. Batch experiments are also conducted by putting synthesized jarosite and schwertmannite into SO<sub>4</sub>-Cl-Br solutions, and allowed to age at 75 °C for at least 50 days to evaluate halogen behavior during the phase transformation of schwertmannite to goethite, and jarosite to hematite.

**Photochemical Influences:** As previously reported by the authors [19], two types of photochemical evaporation experiments are being carried out to evaluate the possible influences of photochemical volatilization of halogen elements. The first type is evaporation of Br<sup>-</sup> and Cl<sup>-</sup>-bearing sulfate brines under UV light. The second type is evaporation of brine-sediment mixtures under UV light. We evaporate the mixtures to dryness, and then re-dissolve and analyze evaporated solids for chloride and bromide concentration change. For these experiments, different pH and brine compositions, and sediment grain sizes are examined under Earth atmosphere and Mars-like atmosphere conditions as well as under vacuum conditions. The apparatus used in these photochemical evaporation experiments is illustrated in Figure 2 of [19].

At the time of writing, these experiments are at various stages of completion and we will report results of diagenetic Fe-oxidation experiment and photochemical experiment, as well as preliminary results of evaporation experiment at the meeting.

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