CHLORINE RELEASE FROM COMMON CHLORIDES DURING ATMOSPHERE-SURFACE INTERACTION ON MARS. Alian Wang1, Yuanchao Yan1, Bruce Fegley1, Bradley L. Jolliff1, Kun Wang1, Scott M. McLennan2, and William M. Farrell3, 1Dept. Earth and Planetary Sciences & McDonnell Center for Space Sciences, Washington University in St. Louis, MO, USA (awang@levee.wustl.edu), 2Department of Geosciences, Stony Brook University, NY, 3Solar System Exploration Division, Goddard Space Flight Center (GSFC), NASA.

Introduction: We have reported [1] a new atmosphere-surface interaction, the Electrostatic Discharge (ESD) during martian dust events (dust storms and dust devils), which, when comparing the oxidation power per electron with that per UV-photon, would be more likely responsible for the abundance of perchlorate observed during the Phoenix mission [2]. We also reported [3,4] that a similar mechanism may have induced the amorphization of Mg- and Fe-sulfates and the oxidation of Fe species in martian surface materials, as observed by several Mars surface exploration missions.

In this study, we report experimental evidence of Cl release from common chlorides during similar ESD processes induced by dust events. This study shows that the atmosphere-surface interaction can play an essential role in the circulation of martian volatile components, i.e., Cl, and possibly, S.

ESD and ESD products in martian atmosphere: Lofted sand and dust particles can fractionally electrify during martian dust events. It is commonly understood that a tendency of triboelectric charge would result in negative charges on smaller grains and positive charges on larger grains of similar composition [6,7]. The convective aeolian processes (dust storms and dust devils) would lift up the negatively charged lighter grains, while positively charged heavier grains remain closer to the surface. Therefore, a large-scale-charge-separation, i.e., an active electric field (E-field), can be generated. For example, E-fields of up to 60 kv/m and 166 kv/m were detected during the passage of terrestrial dust devils [8] and grain saltation [9], respectively.

Electrostatic discharge (ESD) is expected to occur when a local E-field accumulates beyond the breakdown electric field threshold (BEFT). Mars has a very low BEFT because of its thin atmosphere, i.e., ~ 20-25 kv/m by modeling [10] and ~ 25-34 kv/m by measurements in Mars chambers [11,12]. The Mars’ BEFT is ≤ 1% of Earth’s BEFT (~ 3000 kv/m); i.e., ESD occurs much more easily on Mars than on Earth. Among three types of ESD, Townsend dark discharge (TDD) and normal glow discharge (NGD) would more likely occur on Mars.

ESD generates an electron avalanche, i.e., a flux of electrons with a relatively high drift speed. When these electrons collide with martian atmospheric molecules, CO2, O2, N2, Ar, and H2O, they readily cause molecular ionization or dissociation, resulting in positive and negative ions, plus new neutral species and chain electron avalanches.

In the ESD experiments we conducted in a Mars Chamber [5] (Fig. 1), we used an in situ plasma emission spectroscopic probe to collect the plasma photons generated during a normal glow discharge (ESD-NGD) in simulated Mars atmosphere. The following free radicals were identified: CO2+, CO+, O2, H2O, H2, OH, Ar+, N2+, N22+, and O2 but not excluding O2, NO, and O3 because of plasma line overlapping [1].

Atmosphere-surface interactions: These charged or neutral particles with high kinetic energy would stimulate multiple redox plasma chemical reactions in the atmosphere and at the martian surface. The oxidation of chlorides to oxychlorines (chlorates and perchlorates) [1], the amorphization and dehydration of Mg- and Fe-sulfates, and the oxidation of Fe-species [3, 4] are among the phase transformations that we found hitherto.

Evidence of Cl-release from common chlorides during ESD: when using common chlorides as the starting phases (Fig. 2), we observed the release of Cl through two types of observations: (1) the in situ, direct detection of Cl-release during ESD, and (2) new mineral phases formed and coated at the UPPER electrode.

Using a plasma probe installed next to ESD electrodes inside of the Mars chamber (green colored probe in Fig.1), the emission line 837.8 nm of chlorine at the first excited state (ClI) was observed in the plasma spectra of MgCl2, FeCl2·4H2O, FeCl3·6H2O, and AICl3·6H2O during ESD processes. Figure 3 compares the plasma spectrum collected during an ESD when the lower electrode was empty (red spectrum) with that when the
The lower electrode was filled with FeCl₂·4H₂O (Fig. 2) (blue spectrum).

In our ESD experimental setup, the electron flux is 1.42×10²⁰ s⁻¹ m⁻², which is at a moderate level between the estimated (based on modeling [13]) electron flux of 9×10⁶ s⁻¹ m⁻² for TDD and of 1.5×10²⁴ s⁻¹ m⁻² for NGD on Mars [1]. Although we did not observe the ClInstalling line (837.8 nm) in the ESD-generated plasma from NaCl and CaCl₂, we cannot rule out the possibility of finding that line from those chlorides, if there was a higher electron flux during a stronger ESD process.

After an ESD process with FeCl₂·4H₂O filling the lower electrode (Fig. 2), a thin film of dark gray color formed on the UPPER electrode (Fig. 4). We would emphasize that the distance between the two electrodes was kept at 6 mm for all our ESD experiments, thus the released ClInstalling traveled 6 mm to reach the upper electrode.

Raman and XRD analyses were made on the gray-colored film after its removal from the upper electrode. Raman data suggest that the film does not contain H₂O, whose major Raman peaks (280, 329, 616, 1093 cm⁻¹) do not match with the known Raman spectra of Fe, ClInstalling-bearing species, nor with the known Fe-oxides/hydroxides.

The three intense narrow XRD lines of this phase (Fig. 5) match with the major lines of CuCl (pdf-04-007-2951), supporting a reaction product of:

\[ \text{ClInstalling (gas)} + \text{Cu (electrode)} \rightarrow \text{CuCl} \]

There are nine additional XRD lines with much wider line widths in three 20 ranges of 9-18°, 31-41°, and 48-54° (yellow highlights in Fig. 5). Candidates for contributing these lines are listed in Figure 5, akaganite (Fe₃O₈(33)OH₁₆₋₁₇,Cl₁₆₋₁₇) seems having a higher probability because of its two sets of doublets in 31-41°. The widened XRD lines, however, may indicate the formation of poorly crystalline phases, whose lines are generally difficult to match.

**Implications:** Considering the extremely large areal coverage and very long temporal coverage of martian dust events today, and possibly throughout the Amazonian period, the ClInstalling-release from common chlorides induced by a moderate strength ESD process as revealed by our experiments, may signify a large amount of ClInstalling “traveling” repeatedly from surface to atmosphere, and then back to the surface again; i.e., the atmosphere-surface interaction induced by martian dust events could play an important role in the ClInstalling cycle in Mars history.

A logical follow up question is in what form would the ClInstalling most likely travel? Experimental [14] and theoretical (based on experiments) [15] studies of moderately volatile elements (MVEs) suggest that besides K and Na, the next element with moderate volatility is Fe. With the available ClInstalling and atmospheric free radicals, CO²⁺, CO⁻, O⁻, O₂⁻, H⁻, H₂⁻, OH, the list of possible Fe-phases (many could be amorphous) can be quite long.

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