

(PER)CHLORATE FORMATION THROUGH ELECTROCHEMISTRY IN MARTIAN ATMOSPHERE-SURFACE INTERACTION. Alian Wang¹, Andrew Jackson², Y. C. Yan¹, J. Houghton¹, ¹Dept. Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, 63130, USA; ² Civil and Environmental Engineering, Texas Tech University, 911 Boston, Lubbock, TX 79409-1023, (alianw@levee.wustl.edu);

Electrochemistry in Mars Atmosphere-Surface Interaction: We have reported in 2016 and 2017 [1-5] that the *electrochemistry processes*, through Mars atmosphere to surface interaction induced by Mars Dust Storm (MDS) and Dusts Devil (MDD), can be an important mechanism to form oxychlorine salts (Cl^{+1} , Cl^{+3} , Cl^{+5} , Cl^{+7}), which would be extremely important for Cl-cycle on Mars.

This abstract reports further in-depth electrostatic discharge (ESD) experimental studies on Cl-phase transformations, started from three chloride salts (Na, Mg, Ca), with or without structural H_2O , with an emphasis on the yields of (per)chlorates, their depth-dependence, and the potential intermediate Cl-O-species during Mars dust events.

Experiments in PEACH: we built an apparatus in our Planetary Environment and Analysis Chamber (PEACH) [6], and realized stable ElectroStatic Discharge (ESD) in the form of Normal Glow Discharge (NGD). The PEACH is capable of maintaining Mars atmospheric pressure, composition (pure CO_2 , $\text{CO}_2+\text{H}_2\text{O}$, and Mars Simulating Gas Mixture, *MSGM*), and a well-controlled sample temperature (T) range relevant to Mars surface and shallow subsurface. Furthermore, the PEACH is equipped with four *in situ* sensors for the characterization of molecular species as solid, liquid, and of atomic & ionic species in ESD-stimulated plasma.

The recent sets of ESD-NGD experiments were conducted in pure CO_2 atmosphere. All experiments were conducted under the same conditions, i.e., $P_{\text{CO}_2}=3 \pm 0.1$ mbar, $d_{\text{electrode}} = 6 \pm 0.5$ mm, $V_{\text{electrode}}= 300 \pm 10$ V, $I_{\text{electrode}}= 22 \pm 0.6$ mA, $31^\circ\text{C} < T_{\text{sample-cell}} < 61^\circ\text{C}$.

The chloride samples selected for this run of ESD-NGD experiments were NaCl, MgCl_2 , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , and $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$. The time durations of ESD-NGD were 60 minutes to 510 minutes..

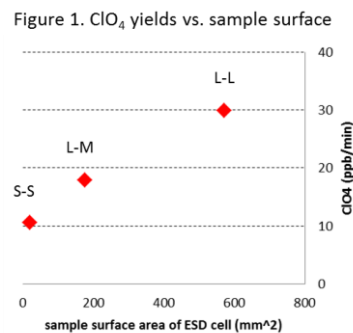
Identification of oxychlorine species: We use laser Raman spectroscopy to characterize the oxychlorine species generated by electrochemistry in ESD-NGD, between plasmatic oxidants and chlorides. Raman spectra of ESD products were taken immediately after ESD runs, on the surface of solid samples in the sample cups. In addition to typical Raman spectra of chlorate and perchlorate, few more Raman peaks were ob-

tained, suggesting some intermediate Cl-O-bearing species.

Quantification of oxychlorine species: we used Ion Chromatography (IC) only, or a sequential Ion Chromatography - Mass Spectroscopy - Mass Spectroscopy (IC-MS/MS) method to quantify the oxychlorine species.

The IC-only analysis uses an A-Supp7-250 anion column (45°C , 3mM Na_2CO_3 eluent, 0.8 mL/min, with suppression) on a Metrohm 881 Compact IC pro with a conductivity detector. Standards were prepared from pure chemicals of NaCl, NaClO (10-15% aqueous solution), NaClO_2 , NaClO_3 , and NaClO_4 from Sigma-Aldrich. The detection limit for ClO_3^- by IC only analysis is 1mM. The IC-MS/MS for ClO_4^- and ClO_3^- quantification uses an ion chromatography (Dionex LC 20) coupled to a triple quadrupole mass spectrometer (MDS SCIEX API 2000TM). The IC was equipped with an AS19 analytical and guard column. We used a 45 mM NaOH eluent for ClO_4^- and a gradient for ClO_3^- , at a rate of 0.2 mL/min. A 90% acetonitrile solution (0.3 mL/min) was used as a post-column solvent. All samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4^- or ClO_3^- internal standard.

Result #1: The sample surface area vs. yields. We found that with the same electron flux density and the same ESD time duration, the perchlorate yields from a set of different ESD sample cells are proportional to the effective electrode area ratio (100:31:3.4) (Figure 1), i.e., the highest yield from the sample with the largest surface. Suggesting that the electron avalanches generated in PEACH by ESD-NGD have a large number of electrons that is enough to react with the molecules at the surface of our largest sample cell with high productivity (as ClO_4 mg/kg per minutes of ESD). Oppositely, during the ESD-NGD using mid- or small sample cell, a considerable portion of electrons of the electron-avalanches flies directly to the bottom electrode, without reacting with



sample molecules, i.e., wasted (insert are the image of three cells).

Results #2, cations in chlorides vs. the yields: We found that the types of cation in starting chloride salts does have an effect on the yield of (per)chlorates (Figure 2). Basically, $MgCl_2$ transfers to $Mg(ClO_3)_2$ and $Mg(ClO_4)_2$ more readily than the similar transformation from $NaCl$ and $CaCl_2$ to relevant (per)chlorates. The reason for the difference in yields may reside in the chemical bonding structures of starting chlorides.

Results #3, Surface enrichment of chlorates: we have reported an obvious surface enrichment of ClO_3^- for the 3 hr and 10 hr ESD products ($NaCl$ starting material) [4], indicating an atmosphere-surface interaction during these ESD experiments. Figure 3 shows a similar surface enrichment of ClO_3^- in seven ESD products with different starting chlorides and different ESD duration. Because the physical separations of the three layers of each product can only be done very coarsely, we combined the data from the upper two layers and compared with that of the bottom layer. The ClO_3^- production rate with respect to the mass percentage of each layer decreases with depth reflecting a surface enrichment, which again confirms the surface enrichment of chlorates in these ESD products.

Results #4, the effect of structural H_2O vs. yields: We also found that the existence of structural H_2O in the starting species influenced the yield of (per)chlorates. Figure 4 shows the yields (ClO_3^- and ClO_4^- mg/kg per ESD minute) for each starting material ($NaCl$, $MgCl_2$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and

Figure 2. ClO_3^- & ClO_4^- yields vs. types of chlorides

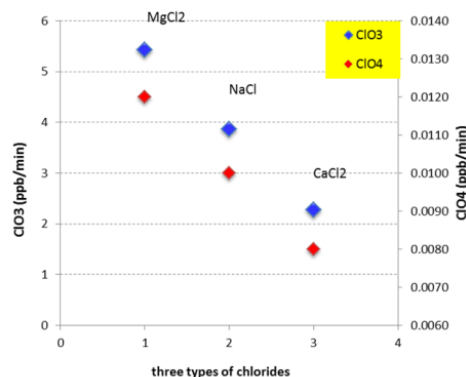


Figure 3. ClO_3^- enrichment in upper two layers of sample

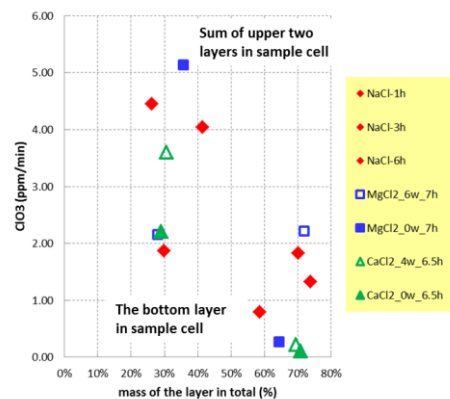
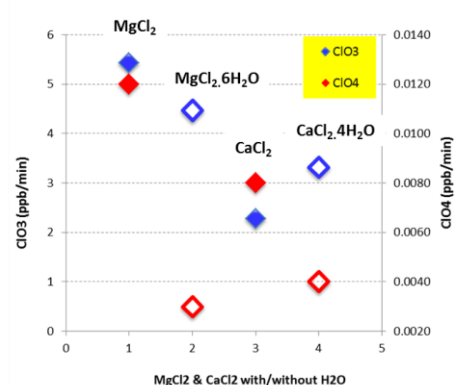


Figure 4. Effect of structural H_2O on (per)chlorate yields



$CaCl_2 \cdot 4H_2O$). Notice for ClO_4^- generation, the starting chlorides with structural H_2O ($MgCl_2 \cdot 6H_2O$ & $CaCl_2 \cdot 4H_2O$) have lower yields. While for ClO_3^- generation, $MgCl_2 \cdot 6H_2O$ has a lower yield than $MgCl_2$, but $CaCl_2 \cdot 4H_2O$ has a higher yield than $CaCl_2$ (data to be confirmed again by repeating ESD experiments). There are two competing factors that may influence the (per)chlorates yields, which will be discussed at the conference.

Results #5, Sequential generation of ClO_4^- : The yield of ClO_3^- is much higher than that of ClO_4^- , for all types initial chloride salts. However, the production rate of ClO_4^- is much higher when the starting phase of an ESD experiment is $NaClO_3$. This observation implies a sequential generation of ClO_4^- is possible on Mars.

Conclusion: Our new experimental data confirmed the generation of (per)chlorates by electrochemistry through atmosphere-surface interaction, and further revealed the yields dependence on the starting types of chlorides. In addition to the observation of extra Raman peaks different from chlorate and perchlorate in ESD products, we also observed additional Cl-peaks in IC-only analysis. Both suggest the intermediate Cl-O phases that need further study. The next step of study is ongoing in two aspects: (1) catalysis effect of co-existing species and (2) Cl-isotopic differentiation.

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References:

[1] Wu & Wang, (2015), AGU, #70053; [2] Wu & Wang (2016), LPSC, abs#2227; [3] Wu & Wang; (2016), EPSL, 452, 123; [4]; Wang et al. (2017), LPSC, abs#2685; [5] Yan et al., (2017), LPSC, abs#2413; [6] Sobron and Wang (2011), J. Raman Spectroscopy, DOI 10.1002/jrs.3017