

**ELECTROCHEMICAL REACTION AT SURFACE INDUCED BY ELECTROSTATIC DISCHARGE DURING MARS DUST STORM AND DUST DEVILS.** Alian Wang<sup>1</sup>, Y. C. Yan<sup>1</sup>, Z. C. Wu<sup>2</sup>, <sup>1</sup>Dept. Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, 63130, USA; <sup>2</sup>Institute of Space Science, Shandong University, Weihai 264209, China; (alianw@levee.wustl.edu).

**Electrostatic Discharge (ESD) induced by near-surface atmospheric events:** Triboelectrical (frictional) charging of dust particles is expected to happen in volcanic eruptions, grain saltation, and especially, during martian dust storms (MDS) and martian dust devils (MDD). MDS occurs annually in regional scales and once per 2-3 years in global scales, which cover the majority of martian surface for months at a time [1]. MDD occurs frequently throughout the planet [2-4].

A general understanding is that the frictional electrification tends to result in negative charge on smaller grains (e.g., dust) and positive charge on larger grains (e.g., sand) [5]. During a convective Aeolian processes (MDD & MDS), the upward lifting of lighter and negatively charge grains with the heavier and positively charged grains remaining closer to the surface would generate a large scale charge separation, an active electric (E) field ( Fig.1)

This understanding was supported by many terrestrial E-fields measurements during the passage of small dust devils, some have measured strength > 100kV/m [6-8], depending on the size of DD, wind velocity, and the atmospheric conductivity. Once a local E-field reaches a saturation value (*breakdown electric field strength, BEFS*), the *electrostatic discharge (ESD)* would occur. The *BEFS* value on Mars (~20-25 kV/m) is estimated 1/100 - 1/150 times of that on Earth (~3 MV/m), because of its thin CO<sub>2</sub> atmosphere near the surface, i.e., **ESD is much easier to occur on Mars.**

ESD can happen in different forms [9], i.e. *Townsend dark discharge (TDD)*, or *normal glow discharge (NGD)*, or *lightning/arc* (Fig. 2). Regardless of the exact nature, *ESD* events would generate large quantity of high-speed-electrons (electron avalanche). When colliding with the molecules in Mars atmosphere, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, Ar, and H<sub>2</sub>O, they would cause the molecular ionization and/or dissociation, resulting positive and negative ions, plus neutral molecules of new species [10]. These charged particles with considerable

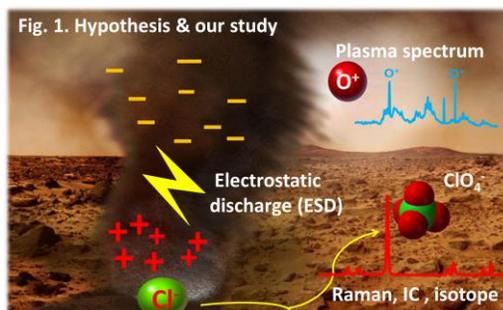
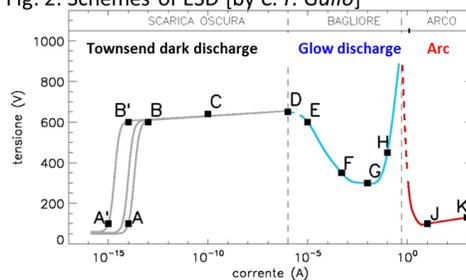


Fig. 2. Schemes of ESD [by C. F. Gallo]



kinetic energy would stimulate the *electrochemical reactions* in near-surface atmosphere and in martian surface/shallow subsurface.

**Electrochemical reactions might be a mechanism to drive Cl-phase transformations at Martian surface:** Large amount of materials from secondary processes were found at the surface and shallow subsurface on Mars. For obvious reasons, *aqueous chemistry processes* have been considered responsible for the majority of secondary phases, e.g., silica, phyllosilicates, and salts [11]. The finding of perchlorate by Phoenix mission [12, 13], with abnormally high ClO<sub>4</sub>/Cl ratio, brought up the

importance of *photochemistry processes* [14]. Through the efforts of modeling, experiments, and terrestrial analog studies, the role of *photochemistry* in the generation of chlorate/perchlorates was supported, its importance in Cl-cycle on Mars is also implied [14-17].

Nevertheless when going into the quantitative details, it was found that 1D photochemistry model was unable (by seven order of magnitudes less, 10<sup>-7</sup>) to account for the abnormally high ClO<sub>4</sub>/Cl ratio found by Phoenix [18]. In addition, a set of abnormally negative δ<sup>37</sup>Cl was recently found in all seven solid samples analyzed by MSL-SAM instrument at Gale Crater [19]. These Martian data are largely different from those observed in the samples from Atacama Desert, for which *photochemistry process* was accepted to be the major contributing mechanism [14, 17]. These discrepancies posted a call for a *NEW mechanism* that would potentially take the major responsibility for Cl-bearing phase transformations on Mars.

We proposed [20-22] that the *electrochemistry processes* induced by Mars Dust Storm (MDS) and Dusts Devil (MDD) can be an important & dominant mechanism responsible for the transformation of chlorides (Cl<sup>-1</sup>) to oxychlorine salts (Cl<sup>+1</sup>, Cl<sup>+3</sup>, Cl<sup>+5</sup>, Cl<sup>+7</sup>) by Mars atmosphere-surface interaction. A recent modeling paper [23] also suggests the role of *electro-*

chemistry process, induced by Galactic Cosmic Ray (GCR), Solar Cosmic Ray (SCR), and Solar Energetic Particles (SEPs).

**Simulated ESD experiments in PEACH:** We have designed and conducted a set of ESD experiments to study the generation of oxidants in simulated Mars atmosphere in a Mars chamber[21] and the phase transformation from Cl-1 to Cl+1, Cl+3, Cl+5, Cl+7 [24]. Our goal is to search for an important mechanism responsible for large amount of perchlorate found on Mars.

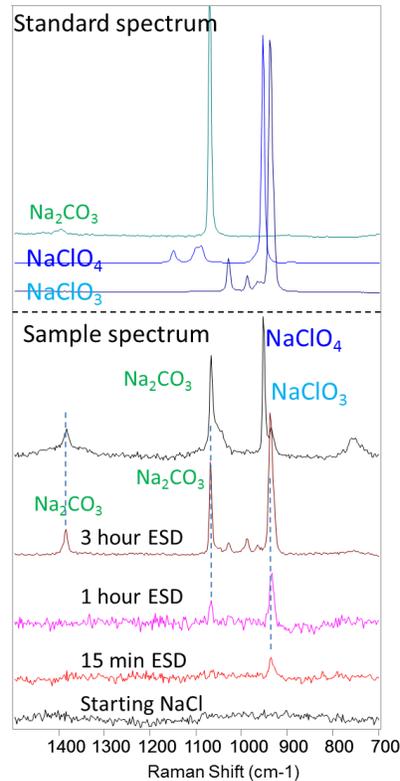
We have built an apparatus and realized stable ESD in our Planetary Environment and Analysis Chamber (PEACH[25]), which is capable to maintain Mars atmospheric pressure, composition (pure CO<sub>2</sub>, CO<sub>2</sub>+H<sub>2</sub>O, and Mars Simulating Gas Mixture, MSGM), and a well-controlled sample temperature (T) range relevant to Mars surface and shallow subsurface. Furthermore, PEACH is equipped with four *in situ* sensors for the characterization of molecular species, before, during, and after the ESD-experiments.

Our first set of ESD experiments concentrated on identifying the oxidant species generated from simulated Mars atmosphere. In pure CO<sub>2</sub>, CO<sub>2</sub>+H<sub>2</sub>O, and a MSGM of 95% CO<sub>2</sub>, 2% N<sub>2</sub>, 2% Ar and 1% O<sub>2</sub>, the major oxidants identified by *in situ* plasma optical spectroscopy are: CO<sub>2</sub><sup>+</sup>, O (I), Ar (I), N<sub>2</sub>, H $\alpha$ , and OH<sup>-</sup> [21]. Our second set of experiments concentrated in Cl-bearing phase transformation stimulated by ESD. A powdered NaCl sample was the starting phase.

We have generated ESD by using both DC and AC power supply, with most experiments conducted using AC power for the convenience of laboratory operations. In addition, we controlled our ESD experiment in form of *Normal Glow Discharge (NGD)*, in order to use plasma optical emission spectroscopy (Fig.1) to identify the generated oxidants.

**Breakdown Electric Field Strength (BEFS):** In our experiments, the ESD in form of *Normal Glow Discharge (ESD-NGD)* could only be seen when the pressure in PEACH (pure CO<sub>2</sub>, or CO<sub>2</sub> + H<sub>2</sub>O, or MSGM, or

Fig. 3. Identification of chlorate and perchlorate formed from chloride stimulated by ESD in a Mars chamber



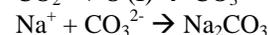
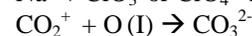
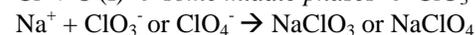
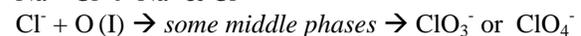
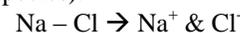
air) being reduced to < 9 mbar. The measured BEFS is a strong dependent of atmosphere pressure (P) that is consistent with the prediction. It is also a dependent of atmospheric compositions, a result of breakdown energy required by different types of molecule in atmosphere. We found the BEFS for ESD-NGD at 3mbar was ~ 34 kV/m in CO<sub>2</sub> or MSGM and ~ 28.5 kV/m in air. We thus demonstrated that **ESD would be much easier to occur on Mars than on Earth.**

**Raman characterization of Cl-phase transformations through ESD:** We first use laser Raman spectroscopy to characterize the molecular species generated in the electrochemistry reaction between plasmatic oxidants and NaCl. Fig. 3 shows the Raman spectra measured *in situ* on the solid samples in ESD sample cup.

Note the starting phase NaCl does not have a fingerprint Raman peak owing to the ionic nature of Na -- Cl bond (bottom spectrum in Fig. 3). A Raman peak at 936 cm<sup>-1</sup>

first appears in a sample after 15 min ESD experiment in PEACH at 3 mbar CO<sub>2</sub> (Fig. 3), suggesting the **instantaneous formation of an oxychlorine salt**. The intensity of this peak increases following the lengthening of the ESD duration (to 3 hours). At a few sampling spots, a Raman peak near 954 cm<sup>-1</sup> appears, suggesting the occurrence of NaClO<sub>4</sub>, which obviously is a minor component in the ESD products. Furthermore, a strong peak at 1068 cm<sup>-1</sup> and a weak peak at 1386 cm<sup>-1</sup> appear later in every Raman spot, whose positions suggest the occurrence of Na<sub>2</sub>CO<sub>3</sub>.

The identified new molecular species in ESD products would imply the following possible electrochemistry reactions (pending further study of some middle species):



IC (Ion Chromatography) to quantify the produced oxychlorine species: Fig. 4a shows the detected  $\text{ClO}_3^-$  (in ppm) from four layers of two ESD samples. The IC data first confirmed that the generated oxychlorine salt is dominantly  $\text{NaClO}_3$ , whose quantity increases with time exposed to ESD under Mars environmental conditions, and consistent with Raman detection. There is also an obvious surface enrichment (Fig.4a, 4b) of both oxychlorine species, implying a link to an atmosphere-surface interaction.

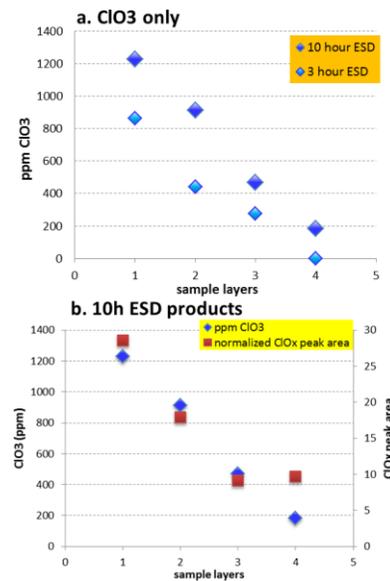
Although at this moment, we cannot fully identify and quantify the  $\text{ClO}_x^-$  in ESD products, its IC peak area should be a linear function of its concentration. There is a close agreement in relative abundance of both products can be found. It is likely a reflection of a fixed relative probability for two reactions (of forming  $\text{ClO}_3^-$  or forming  $\text{ClO}_x^-$ ) to occur in our specific plasma-solid electrochemical reaction, which needs further investigation.

This study demonstrated the formation of oxychlorine salts from chloride stimulated by electrostatic discharge in an environment simulating the ESD that might occur in MDS and MDD. The data imply (1) the formation of oxychlorine salts is instantaneous; (2) the formation is through an atmosphere-surface interaction; (3) there might exist a fixed pattern between the forming reactions of two types of oxychlorine salts in this specific electrochemical reaction that is worthy further study.

**Implication --Electrostatic Discharge on Mars:** Two E-field sensors were planned for two missions to Mars, ECHOS/MATADOR for the Mars Surveyor 2003 mission [6] (Mars mission line was restructured in 2000-2001 and Mars03 was then replaced with MER) and MicroARES [8] for ExoMars entry, descent and landing demonstration module (EDM, crashed in 2016 during landing). In addition, the dust devils observations made by MER rovers have not provided convincing evidence for ESD occurrence during MDD.

Hitherto, without an actual E-field measurement on Mars, it is hard to guess which type of ESD, *Townsend Dark Discharge* (TDD) or *Normal Glow Discharge* (NGD), might occur during Mars atmospheric events. In order to detect oxidants, we controlled our simulation experiment in NGD regime, which has a larger

Fig. 4. quantification of  $\text{ClO}_3$  and  $\text{ClO}_x$  by IC



electron flux but lower kinetic energy per electron than TDD (Fig. 2). If in some cases, ESD on Mars takes the form of TDD[13], it would have a slightly higher capability in generating oxidants than our experiment[21], but it would take a longer time in forming chlorate/perchlorate than our experiments [24]. For both cases, the results from our simulation experiments are valid in a conservative way.

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**References:** [1,2] Cantor et al., (2001, 2002), *JGR*, 106 & 107; [3] Fisher et al., (2005), *JGR*, 110; [4] Greely et al., (2006), *JGR*, 111; [5] Delory et al., (2006), *Astrobiology*, 6; [6] Farrell et al., (2004), *JGR*, JE002088; [7] Jackson & Farrell (2004), *IEEE Trans. Geosci. Rem. Sens.* 44; [8] Harrison et al., (2016), *Space Sci. Rev.*; [9] Gallo C. F., *Coronas and Gas Discharges in Electrophotography: A Review* (1975); [10] Atreya et al., (2006), *Astrobiology*, 6; [11] McLennan (2012), *SEPM No. 102*, p. 119; [12] Hecht et al., (2009), *Science*, 325, 64; [13] Kounaves et al., (2014), *Icarus*, 232, 226; [14] Catling et al., (2010), *JGR*, 115, E00E11; [15] Carrier & Kounaves, (2015), *GRL*, 42, 3739; [16] Zhao et al., (2014), 44<sup>th</sup> LPSC, abs 3002; [17] Bao & Gu (2004), *Environ. Sci. Technol.*, 38, 5073; [18] Smith et al., (2014), *Icarus*, 231, 51; [19] Farley et al., (2016), *EPSL*, 438, 14; [20] Wu & Wang, (2015), *AGU*, #70053; [21] Wu & Wang (2016), *LPSC*, abs#2227; [22] Wu & Wang; (2016), *EPSL*, 452, 123; [23] Wilson et al., (2016), *JGR*, 10.1002/2016JE005078; [24] Wang et al., (2017), abs #2685, LPSC; [25] Sobron & Wang (2011), *JRS*, DOI 10.1002/jrs.3017