**A SIMULATED ELECTRO-CHEMICAL REACTION FOR THE GENERATION OF OXIDANTS IN NEAR-SURFACE ATMOSPHERE AND THE $Cl^{-1}$ TO $Cl^{+x}$ PHASE TRANSFORMATION AT MARTIAN SURFACE.**

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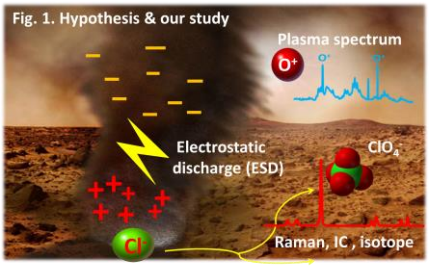
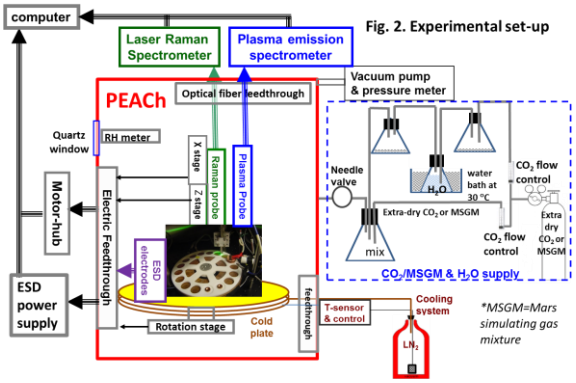
**Electrostatic Discharge (ESD) induced by near-surface atmospheric events:** Triboelectrical (frictional) charging of dust particles is expected to happen in volcanic eruptions, grain saltation, and especially, during martian dust storms (MDS) and martian dust devils (MDD). MDS occurs annually in regional scales and once per 2-3 yeas 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 > 150kV/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 $CO_2$ 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*, or *normal glow discharge*, or *lightning/arc* (Fig. 3). 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, $CO_2$, $O_2$, $N_2$, Ar, and $H_2O$, 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 kinetic energy would stimulate the ***electrochemical reactions*** in near-surface atmosphere and in martian surface/shallow-subsurface.




We have designed and conducted a set of ESD experiments to study the generation of oxidants in simulated Mars atmosphere in a Mars chamber[11] and the phase transformation from $Cl^{-1}$ to $Cl^{+1}$, $Cl^{+3}$, $Cl^{+5}$, $Cl^{+7}$ [12]. Our goal is to search for an important mechanism responsible for large amount of perchlorate found on Mars.

**Simulated ESD experiments in PEACh:** we have built an apparatus and realized stable ESD in our Planetary Environment and Analysis Chamber (PEACh, Fig. 2), which is capable to maintain Mars atmospheric pressure, composition (pure $CO_2$, $CO_2$+$H_2O$, 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.

During these experiments, we identified and quantified the oxidant species generated from Mars atmosphere[11]. In addition, using NaCl as starting phase, we identified and quantified the chlorate ($NaClO_3$), perchlorate ($NaClO_4$), and a carbonate ($Na_2CO_3$) as the products from an oxidants + chloride electrochemistry reaction[12]. The current abstract reports the properties of electron avalanche generated in our ESD experiments.

**Properties of electron avalanche in experiments:** 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, 2) 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 pres-

sure in PEACh (pure $CO_2$, or $CO_2$ + $H_2O$, or *MSGM*, or 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 $CO_2$ or *MSGM* and ~ 28.5 kV/m in air.

*Voltage & Current for ESD-NGD:* Fig. 4 shows the measured voltage across the two electrodes $V_{electrode}$ and the current $I_{electrode}$ sustained by the electron avalanche during the development of a stable *Normal Glow Discharge* (*NGD*) from none.

Notice that once the *NGD* becoming stable, the voltage crossing electrodes would remain almost constant (~ 340 V in our case, Fig. 4) within a large range of driving voltage (V-regulator =75-140V, Fig.4). The increase of V-regulator would only increase the current $I_{electrode}$. Another important phenomenon is that neither $V_{electrode}$ nor $I_{electrode}$ show changes with the size of electrode. The effective electrode area ratio is 100:71:21 among the three pairs of electrodes used in our experiments (insert of Fig. 4). While at same driving V-regulator (120V), very similar values of $V_{electrode}$ (335-355V, $\Delta$<3.2%) and $I_{electrode}$ (22.4-22.9mA, $\Delta$<1.7%) were observed from the three electrodes. However, a much brighter plasma emission was observed when using the smallest electrode.

*Plasma temperature:* We have found that *the generation of ESD-NGD* is not a strong dependent of environmental temperature (T). I.e., it occurs in the full tested T range, from 0°C to -80°C that is relevant to Mars surface/shallow subsurface, when other conditions remaining unchanged. A thermocouple inserted in the gap between the two electrodes shows a corresponding plasma temperature range of 110°C to 30°C.

**Implications:** (1) The occurrence of ESD in MDS and MDD seems not depending on T or gran size. (2) *ESD-NGD* is self-sustainable, i.e., the fluctuation of external E-field has little effect. (3) A 22 mA $I_{electrode}$ (at 120V V-regulator) corresponds an electron flux of 1.43 x$10^{14}$ $s^{-1}mm^{-2}$ for the large electrode pair and of 6.84 x$10^{14}$ $s^{-1}mm^{-2}$ for the small electrode pair. When comparing the yields from a same type of oxidation reaction induced by our ESD and by UV radiation, we found that the oxidizing capability per electron of this *ESD-NGD* is $10^3$-$10^4$ times of that per UV photon. (4) By calculating the kinetic energy ($E_k$=$V_{electrode}$ * $Q_{electron}$) carried by each electron in the electron avalanche generated by *ESD-NGD*, we found that each electron would have a speed of 1.1x$10^4$ km/s when traveling through the space between the two electrodes. Such high-speed-electron would certainly have a high potential to disassociate or to ionize atmospheric molecules ($CO_2$, $H_2O$, $O_2$, $N_2$, Ar), as reported by [11].

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 electron flux but lower kinetic energy per electron than TDD (Fig. 3). 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[11], but it would take a longer time in forming chlorate/perchlorate than our experiments[12]. For both cases, the results from our simulation experiments are valid in a conservative way.

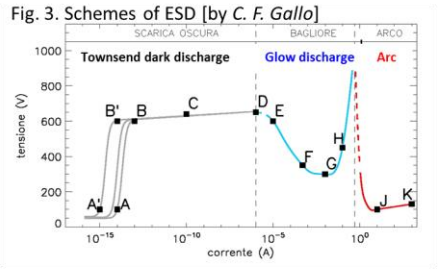
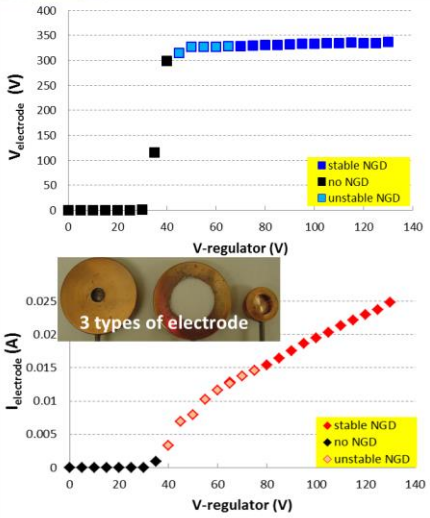


Fig. 3. Schemes of ESD [by *C. F. Gallo*]


Fig. 4. ESD-Normal Glow in 3mb $CO_2$, the measured voltage and current vs. stability of NGD.

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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;* [10] Atreya et al., (2006), *Astrobiology, 6;* [11] Wu et al., (2016), *#2227, LPSC;* [12] Wang et al., (2017), *this volume;* [13] Farrell et al., (2015), *Icarus, 254*, 333-337.