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Forming perchlorates on Mars through plasma chemistry during dust events

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ABSTRACT

We report experimental evidences to support a new formation mechanism, multiphase redox plasma chemistry, for perchlorate on Mars observed during the Phoenix mission, whose high concentrations and high ClO_4/Cl ratio cannot be fully interpreted by photochemistry. This chemical reaction occurs between Cl-bearing minerals on the Mars surface and free radicals generated by electrostatic discharge (ESD) during Mars dust events (dust storms, dust devils, and grain saltation).

We conducted simulated ESD experiments in a Mars chamber with pure CO_2 , $CO_2 + H_2O(g)$, and Mars Simulate Gas Mixture at Martian atmospheric pressure. We directly observed (1) the instantaneous generation of atmospheric free radicals CO_2^+ , CO^+ , O_I , H_{III} , H_{II} , OH, Ar_I , N_2 , and N_2^+ in normal glow discharge (NGD), detected by *in situ* plasma emission spectroscopy, and O_3 by UV and Mid-IR spectroscopy; (2) the fast transformation of NaCl to NaClO₃ and NaClO₄ detected by laser Raman spectroscopy, with oxychlorine enrichment at the sample surfaces confirmed by ion chromatography. Through two sets of experimental comparison, we found that the oxidation power of ESD-electron is three orders of magnitude higher than that of UVC-photon. We scaled our experimental results to the modeled ESD in Mars dust events and Mars surface UV radiation level, and concluded that plasma chemistry occurred during Mars dust events can be an additional important formation mechanism for the large amounts of perchlorates observed during various missions to Mars.

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1. Introduction

High concentrations of perchlorate (ClO_4^-) were detected in polar regolith at the Phoenix landing site on Mars (Hecht et al., 2009; Kounaves et al., 2014b). The wide existence of perchlorate was also observed at Gale Crater (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2014; Sutter et al., 2017), Viking sites (Navarro-González et al., 2010), and four sites of Recurring Slope Lineae (Ojha et al., 2015) on Mars. Furthermore, chlorate and perchlorate were found in Martian meteorite EETA79001 (Kounaves et al., 2014a), Apollo lunar samples and carbonaceous chondrite meteorites (Jackson et al., 2015), revealing that they are widespread in our solar system. On Earth, perchlorate and chlorate are found in the upper regolith of hyperarid regions, but at much lower values. Specifically, the derived ClO_4^-/Cl^- ratio at the Phoenix site (~4.44, Hecht et al., 2009) is at least 1000 times the same ratio found on Earth: 2×10^{-3} in the Atacama Desert (Grossling and Ericksen, 1971), 1.8–6.3 × 10⁻⁴ in the ultraxerous zone in the Antarctica Dry Valleys (Kounaves et al., 2010), and ~0.5 × 10⁻⁶ at a dry playa on the Tibet Plateau (Wang et al., 2018a).

The global distribution of oxychlorines on Mars and the associated ClO_4^-/Cl^- ratios are two highly significant open scientific questions. They link directly to present and past Cl-cycles on Mars, and to the preservation of biosignatures in the modern Martian regolith (Kounaves et al., 2014a, 2014b; Nuding et al., 2017).

1.1. Perchlorate formation by photochemistry on Earth

The origin of terrestrial oxychlorines via atmospheric gas-gas reactions through *photochemistry* has been suggested and widely accepted, based on many sophisticated laboratory analyses including oxygen and chlorine isotope studies (Bao and Gu, 2004; Böhlke et al., 2005; Duncan et al., 2005). However, *photochem*-







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istry cannot fully explain the abundance of perchlorate on Mars, especially the high ClO_4/Cl ratio in Phoenix regolith. For example, a 1D-photochemical model successfully generated the correct quantity of perchlorate to explain the concentration of ClO_4^- found in Atacama (Catling et al., 2010). However, a study using the same model (Smith et al., 2014) generated a quantity of perchlorate seven orders of magnitude less (10^{-7}) than the perchlorate abundance found by Phoenix, requiring an additional *non-photochemical* process on Mars (Smith et al., 2014).

Furthermore, the Sample Analysis at Mars (SAM) team for the Curiosity rover reported a set of uniquely negative and highly variable δ^{37} Cl values (Farley et al., 2016) from seven drilled samples at Gale Crater. These δ^{37} Cl values can be separated into two groups with average δ^{37} Cl values of $-11 \pm 7\%$ and $-43 \pm 6\%$ and a minimum of $-51 \pm 5\%$. The last two values are much lower than the lowest δ^{37} Cl value found on Earth, i.e., -9.2 to -14.5% for Atacama perchlorates (Böhlke et al., 2005), whose photochemical origin has been well established. The Curiosity rover δ^{37} Cl data again imply that a mechanism *other than photochemistry* might have formed the large amounts of oxychlorines found on Mars.

1.2. Hypothesized perchlorate formation by multiphase redox plasma chemistry on Mars

We suggest that the *multiphase* (gas-to-solid) redox plasma chemistry process occurring between Cl-bearing minerals at the Martian surface and atmospheric free radicals generated by electrostatic discharge (ESD) in Martian dust events (dust storms, dust devils, and grain saltation) can be another mechanism driving oxychlorine formation on Mars.

Lofted sand and dust particles can frictionally electrify at planetary surfaces (Kok and Renno, 2008), which is commonly understood as the tendency of triboelectrical charge to result in negative charges on smaller grains and positive charges on larger grains of similar composition (Forward et al., 2009; Krauss et al., 2003). During convective aeolian processes (e.g., dust devils and dust storms on Mars), lighter, negatively charged grains lift upward while heavier, positively charged grains remain closer to the surface, thus generating large-scale charge separation, i.e., an active electric field (E-field). For example, E-fields of up to 60 kv/m and 166 kv/m were detected during the passage of terrestrial dust devils (Esposito et al., 2016; Farrell et al., 2004; Harrison et al., 2016; Jackson and Farrell, 2006) and grain saltation (Schmidt et al., 1998), 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 (Melnik and Parrot, 1998) and ~25–34 kv/m by measurements in Mars chambers (Farrell et al., 2015; Yan et al., 2017). The Mars' BEFT is \leq 1% of Earth's BEFT (~3000 kv/m, Winn et al., 1974; Zhai et al., 2006); i.e., ESD occurs much more easily on Mars than on Earth.

ESD can take different forms (Gallo, 1975), i.e., Townsend dark discharge (TDD), normal glow discharge (NGD), or lightning (Fig. S1). Because of the low BEFT on Mars, TDD and NGD are more likely than lightning. During ESD, an electron avalanche generates a flux of electrons with a relatively high drift speed. When these electrons collide with Martian atmospheric molecules, CO_2 , O_2 , N_2 , Ar, and H_2O , they easily cause molecular ionization or dissociation, resulting in positive and negative ions, plus new neutral species and chain electron avalanches (Atreya et al., 2006). These charged/neutral particles with high kinetic energy would stimulate redox plasma chemical reactions in the atmosphere and at the planetary surface, including the oxidation of chlorides to oxychlorines.

Lightning on Earth generates perchlorate. Laboratory lightning in Cl⁻ aerosols under terrestrial atmospheric conditions has been found to generate a wide range of ClO_4^-/Cl^- ratios (Dasgupta et al., 2005; Rao et al., 2012). Lightning (or ESD in a broad sense) has also been suggested as a potential mechanism for oxychlorine formation on Mars (Catling et al., 2010). Here, we experimentally validate this hypothesis.

2. Experiments

We conducted two sets of ESD experiments in a Mars chamber. The first set concentrated on identifying the atmospheric free radicals generated by ESD in simulated Martian atmospheric environments. *In situ* plasma emission spectroscopy, UV, and Mid-IR spectroscopy were used to identify the free radicals.

The second set of ESD experiments focused on the ESDstimulated transformation of chlorides to oxychlorines. NaCl powder was used as the starting phase. Laser Raman spectroscopy and ion chromatography were used to identify and quantify the oxychlorine species in ESD reaction products.

UVC-induced photochemistry is a well-accepted mechanism that driving the chloride to oxychlorines transformations, as demonstrated by experimental studies (Carrier and Kounaves, 2015; Zhao et al., 2018). In order to compare the oxidation power of ESD-electron with that of UVC-photon in photochemical process, we used UVC radiation from an Hg-lamp shining through a fused silica window of the Mars chamber, onto the sample cells that containing KI or NaCl powder. A standard iodometry procedure was used to quantify the I₂ generated from KI oxidations. A sequential ion chromatography – mass spectroscopy – mass spectroscopy (IC-MS/MS) was used to quantify ClO₃ and ClO₄ from NaCl oxidations. The yields from ESD-driving and UVC-driving oxidations were compared directly.

2.1. The Mars chamber

The ESD and UVC radiation experiments were conducted in the Planetary Environment and Analysis Chamber (PEACh, Sobron and Wang, 2012) (Fig. 1) at Washington University in St. Louis. PEACh can maintain an atmospheric pressure and a sample temperature in the ranges similar to those at the Martian surface. During an experiment, PEACh is first evacuated down to 3×10^{-2} mbar to remove the air and then filled with the desired atmospheric gases within a stable atmospheric pressure range (accuracy of 0.1 mbar). We used three atmospheric compositions: pure bone-dry CO₂, CO₂ + H₂O(g), and Mars Simulate Gas Mixture (MSGM) of 95% CO₂, 2% N₂, 2% Ar, and 1% O₂ to simulate the atmosphere of Mars. We also run the 1st set of ESD experiments in air and in air + H₂O in Mars atmospheric pressure range as control.

2.2. ESD apparatus in PEACh

We used two parallel copper electrodes in PEACh for ESD experiment (Fig. 1). The lower electrode was shaped like a sample cup, which was filled with powdered NaCl or KI in the 2nd set of ESD experiments. A sample cell made of fused silica that fits into the lower electrode was also used for a comparison experiment. The distance between the two electrodes was adjustable in the range of 3–12 mm using a motorized precision translation stage (Thorlab PTI-Z8). The lower electrode/sample cup was in good thermal contact with a cold plate, also copper, whose temperature was actively controlled through an OMEGA-CN7600 unit by a flow of evaporated N₂ gas at near LN₂ temperature. The temperature range of the electrode/sample cup can be controlled from room temperature to -100 °C (Sobron and Wang, 2012).



Fig. 1. Schematic diagram of our experimental setup. Inside and peripheral equipments of PEACh (Planetary Environmental and Analysis Chamber) for ESD and UVC experiments. Plasma probe was for *in situ* detection of free radicals in ESD-generated plasma. Raman probe was for *in situ* detection of oxychlorine salts. The insert is a photo of ESD generated plasma in CO_2 atmosphere. OFF = Optical Fiber Feedthrough; EF = Electronic Feedthrough. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

We generated ESD in the *NGD* regime (inset of Fig. 1, Fig. S1) using AC power (110 V, 50/60 Hz). The ESD-NGD was driven by a Contact Voltage Regulator (No. 2090 VR), which fed a triggering Neon Power Supply (CPI Advanced Inc. CPI-EZ12, max output 12 kV, 40 mA) that directly connected to the ESD electrodes in PEACh.

2.3. In situ plasma probe and plasma spectrometers

An *in situ* plasma probe was mounted near the gap between the two electrodes to collect photons from the ESD-stimulated normal glow (Fig. 1). It had a single optical fiber 600 µm in diameter. The collected plasma photons were sent through an optical fiber feedthrough (OFF) on the wall of the PEACh to a plasma emission spectrometer for spectral analysis. We used two spectrometers. The first was an Andor Mechelle5000 using an echelle grating; it covered a wide UV–Vis–IR spectral range (230–845 nm) with a spectral resolution range of 0.04–0.10 nm. The second was a set of three OceanOptics HR4000+ spectrometers with spectral resolutions of 0.2 nm in UV (239–339 nm), 0.3 nm in Vis (380–468 nm), and 0.8 nm in VNIR (461–910 nm). The trade-off of these lower spectral resolutions was a high optical throughput and thus higher S/N in the collected spectra than that of the Andor Mechelle5000 spectra.

2.4. UV and Mid-IR spectroscopy

We used UV and Mid-IR spectroscopy to detect O_3 . The exhaust gas from a similar ESD-apparatus in in CO_2 atmosphere or in air at Shandong University in China was filled into the UV or Mid-IR gas cells. A deuterium light source, a HR4000+ UV spectrometer (spectral range of 200–400 nm, spectral resolution of ~1 nm, Ocean optics), and a quartz gas cell (200 mm long) were used for recording UV transmission spectra. A Vertex70 FTIR spectrometer (spectral range of 2000–800 cm⁻¹, spectral resolution of ~4 cm⁻¹, Bruker Optics) and a transmission gas cell (100 mm long) with KBr windows were used for recording mid-IR transmission spectra.

2.5. In situ Raman probe and Raman spectrometers

A rotating sample-cup carrier (Fig. 1) could place the lower ESD electrode beneath the Raman probe inside of PEACh to analyze, *in situ*, the ESD products. This Raman optical fiber probe used a single-mode optical fiber to transfer a 532 nm laser beam onto the sample and a multimode optical fiber of 200 µm in diameter to collect the Raman photons scattered from the sample. This fiber probe passed through the wall of the PEACh through another optical fiber feedthrough (OFF) with its two fiber ends connected to a KOSI-NRXN-E Raman spectrometer and a CrystaLaser unit that emits a 532 nm beam. In addition, all ESD products were analyzed using a Renishaw-inVia Raman system (using 532 nm excitation, \sim 1 µm beam diameter at focus) after removing the sample cup from the PEACh. >100 Raman spectra were taken from each ESD product (Haskin et al., 1997).

2.6. Ion chromatography

The amount of NaClO₃ in the two ESD products (after 3 and 10 h of ESD) was quantified using ion chromatography. The samples in the electrode/sample cup (depth of 3.0 mm) were hand-sliced into four layers. The salt from each layer was dissolved in milliQ water and analyzed by ion chromatography. An A-Supp7-250 anion column (45 °C, 3 mM Na₂CO₃ eluent, 0.8 mL/min, with suppression) on a Metrohm 881 Compact IC pro with a conductivity detector was used. Standards were prepared from pure NaCl, NaClO (10–15% aqueous solution), NaClO₂, NaClO₃, and NaClO₄ from Sigma-Aldrich. The detection limit for ClO₃⁻ by IC analysis was 1 μ M. The concentration in solution (in μ M) is then converted to ppm (mg ClO₃/kg NaCl sample).

2.7. KI oxidation induced by ESD and by UVC and I₂ quantification

Equal amounts of KI powder, 240 mg, were used for both ESDdriving and UVC-driving oxidation experiments. A low-pressure Hg lamp (model 6047 & Hg(A)66019843 of Oriel Instruments) was used as the UV source, with 1.9 mW at the KI sample cup inside the PEACh. The UVC range (253.7 nm line) includes 85.5% of lamp power based on a deconvolution of its spectrum, from which we calculated the photon flux onto the KI sample (Table S1).

We used a standard iodometry procedure to quantify the I_2 generated by 0.5 h ESD and 176 h UVC radiation. Each KI powder sample was first dissolved into 4 mL of deionized water, which became faint yellow. Next, 1 mL of a starch solution (1% concentration) was dripped into the first solution, which became jet black. Finally, a sodium thiosulfate solution (0.0033 mol/L) was titrated into the target solution. The titration was stopped immediately after the jet-black color disappeared, i.e., when the solution became transparent and colorless. The amount of I_2 generated by the ESD or UVC radiation was calculated based on the concentration of sodium thiosulfate solution and titrated volumes.

2.8. Sequential ion chromatography – mass spectroscopy – mass spectroscopy (IC-MS/MS)

The amounts of ClO_3^- and ClO_4^- generated by 3 h ESD and 661 h UVC radiation in NaCl were quantified using an established IC-MS/MS procedure (Rao et al., 2010). This procedure 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 oxygenisotope (¹⁸O) labeled ClO_4^- or ClO_3^- internal standard. The detection limit of this IC-MS/MS procedure for these samples was 0.5 µg/l for ClO_3^- and ClO_4^- based on the lowest calibration standard.

3. Results

3.1. Breakdown electric filed threshold (BEFT), optimized ESD parameters, and plasma temperature

In our experiments, ESD-NGD could be seen only when the pressure in the PEACh (pure dry CO_2 , $CO_2 + H_2O(g)$, MSGM, air, or air + $H_2O(g)$) was reduced to <9 mbar. The measured *break-down electric field threshold (BEFT)* was strongly dependent on atmospheric compositions and atmospheric pressure (P), which reflects the breakdown energy required by different types of molecules in the atmosphere. We found the BEFT for ESD-NGD at 3 mbar was ~34 kV/m in CO₂ or MSGM and ~28.5 kV/m in air (Yan et al., 2017).

Fig. 2 shows the measured ESD voltage $V_{electrode}$ and ESD current $I_{electrode}$ as functions of the driving voltage provided by the voltage regulator (V-regulator) during the development of a stable NGD at 3 mbar CO₂ in the PEACh. A multimeter of KEYSIGHT-U1251B was used for these measurements.

Note that once the NGD stabilized, the ESD voltage remained almost constant (~340 V, Fig. 2a) within a large range of driving voltage, while the ESD current increased following the increase of driving voltage. Furthermore, the size of the electrode surface does not obviously affect V_{electrode} or I_{electrode}. When two pairs of electrodes were tested with outer diameters of 35 mm and 16 mm (100:21 area ratio, Fig. 2c), very similar values of V_{electrode} (343–355 V, $\Delta < 3.5\%$) and I_{electrode} (22.4–22.9 mA, $\Delta < 2.6\%$) were obtained at the same driving voltage of 120 V (V-regulator). However, a much brighter plasma glow was observed with the smaller pair of electrodes.

The ESD parameters were optimized in our first set of experiments against the intensity of the 777.5 nm plasma line of O_1 and that of the 289.6 nm plasma line of CO_2^+ , including atmospheric pressure ($P_{\text{atmosphere}}$, Fig. S2a, b), EDS driving voltage ($V_{\text{regulator}}$, Fig. S2c, d), and the distance between the electrodes ($D_{\text{electrode}}$, Fig.





Fig. 2. The measured (a) ESD voltage $V_{electrode}$ (V), and the measured (b) ESD current $I_{electrode}$ (A), during the development of a stable ESD-NGD, at 3 mbar CO₂ in PEACh. (c) The types of lower electrode, which also served as sample cell in 2nd set of ESD experiments. The last one in right shows a smaller sample cell (fused silica) being placed into the large electrode for an alternative ESD test.

S2e, f) in CO₂ and MSGM environments. Based on those results, we selected an optimum set of ESD parameters for the second set of ESD experiments, which was concentrated on Cl-bearing phase transformations. These parameters are, $P_{\text{atmosphere}} = 3.0$ mbar; $V_{\text{regulator}} = 120$ V, $D_{\text{electrode}} = 6.0$ mm. For example, using these optimized parameters, an average current of 22 mA was measured during the ESD-NGD experiment started from NaCl or KI powder, based on which we calculated the electron flux onto the sample (Table S1).

The temperature of the ESD-generated CO_2 plasma was measured using a thermocouple inserted in the center of the gap between the two electrodes. The thermocouple was isolated from the plasma using a thin quartz tube (wall thickness, 0.5 mm). We found that in our experimental setting, ESD-NGD generated a low-temperature plasma. Its temperature changed slowly with



Fig. 3. The plasma temperature (in CO₂ environment) as the function of the temperature of low electrode and the ESD driving voltage of adjustable $V_{regulator}$.

the environmental temperature (i.e., T of the lower electrode) and with the ESD driving voltage (Fig. 3). Nevertheless, we noticed that ESD-NGD was generated in the full tested T range of 294–197 K; i.e., its occurrence does not depend on environmental temperature when other conditions remained unchanged. This result suggests that *the generation of ESD during Martian dust events* would not be affected by local temperature at different latitude regions.

3.2. Free radicals generated by ESD-NGD

We purposely set our ESD conditions in the NGD regime to record the emission spectra from the glow using an *in situ* plasma probe. The collected plasma emission spectra exhibited emission lines of ionic and molecular species of CO_2^+ , CO^+ , O_1 , H_{III} , H_{II} , OH, Ar_I, N₂, and N₂⁺ (O₁ denotes the 1st excited state of oxygen atom, and so on) in the ESD-driven plasma in a pressure range of 3 to 9 mbar for CO_2 , $CO_2 + H_2O(g)$, and MSGM. Fig. 4 shows the plasma emission spectra, recorded using OceanOptics HR4000 + spectrometers. Table 1 lists the positions of the major emission lines and their assignment to specific atomic and molecular species, (Kramida et al., 2016; Endoh et al., 1982; Li et al., 2013; Pearse and Gaydon, 1963), recorded using Andor Mechelle5000 with high spectral resolution.

Not all ionic and molecular species generated by ESD-NGD have an emission line in the observed spectral range (230–910 nm). For that reason, we used Mid-IR and UV spectroscopy to make additional measurements, especially for one of the most important species, O₃. We filled an UV- and an IR-gas transmission cells with the exhaust gas from an ESD experiment in CO₂ (and in air for control), and measured their UV and Mid-IR transmission spectra (Fig. 5). The O₃ absorption peak centered at 253 nm in UV range and Mid-IR spectral branches (P, Q, R) of O₃ in 1000–1060 cm⁻¹ range were readily identified (Li et al., 2011), revealed the generation of O₃ in electrostatic discharge process.

3.3. NaClO₃ and NaClO₄ generated by ESD and the depth profile

The second set of ESD-NGD experiments in the PEACh was conducted in a pure, bone-dry CO_2 atmosphere at ${\sim}3$ mbar. We placed



Fig. 4. Emission spectra of plasma generated by ESD in PEACh within five different atmospheric environments at 3.0–7.2 mbar and room temperature, recorded using three Ocean Optics HR4000+ spectrometers with lower spectral resolution (0.2 nm for UV, 0.3 nm for Vis, 0.8 nm for NIR) but higher optical throughput, thus higher S/N than Andor Mechelle 5000 spectrometer that has a higher spectral resolution (from which the positions of plasma lines were obtained and listed in Table 1). The spectra lines in a spectrum were normalized with respect to the strongest line. The labeled molecular or atomic species were based on our line assignments listed in Table 1. (a) In dry CO₂ (3.0 mbar); (b) in CO₂ + H₂O(g) (6.2 mbar, 7.2% RH); (c) in Mars Simulate Gas Mixture (MSCM, CO₂ 95%, N₂ 2%, Ar 2%, O₂ 1%, 3.0 mbar); (d) in terrestrial air (3.0 mbar); (e) in Air + H₂O(g) (6.5 mbar, 6.0% RH). "In" marks the lines from the spectrometer. The N₂ and N₂⁺ lines in spectrum a & b came mainly from the residual air in PEACh. The OX + 410 CO₂ + H₂O environment means that line intensities were strengthened four times. OI and Arl donate the first excited state of O and Ar atoms. H α line is generated by transition from H_{III} to H_{II}.

Table 1

Major emission lines of ESD-generated free radicals in PEACh at 3.0-6.0 mbar and room temperature.

Atmospheric environment	Species	Positions (nm) of major emission liens	Assignment of transiti	on
			Lower level	Upper level
Dry CO ₂	C0 ₂ ⁺	288.20; 288.40; 289.54; 289.74; 289.82; 313.60; 315.88; 324.75; 325.44; 326.54; 326.70; 327.05; 337.06(O ₂)**; 337.79; 350.35; 351.13; 351.55; 351.78(O ₂); 354.57; 354.99; 355.22; 366.29; 366.90; 367.07(O ₂); 367.47; 369.24; 385.31; 385.64; 410.98; 412.18; 412.38; 413.70((CO ⁺); 415.98;	$B^{2} \sum_{u}^{+} (000) \\ B^{2} \sum_{u}^{+} (000) \\ A^{2} \Pi_{u}$	$\frac{\chi^2 \Pi_{\rm g} 3/2(000)}{\chi^2 \Pi_{\rm g} 1/2(000)}$ $\frac{\chi^2 \Pi_{\rm g}}{\chi^2 \Pi_{\rm g}}$
	CO ⁺ OI	418.53,419.77, 424.75 777.25; 777.49; 844.69;	${}^{B^2\sum\atop{2s^22p^3({}^4S^0)3s}}$	А ² П 2s ² 2p ³ (⁴ S ⁰)3p
$CO_2 + H_2O$ (RH ~7.2%) MSGM ^{****}	Hα OH Arı	656.30; 306.47; 306.82; 308.15; 309.06; 750.44; 751.51; 811.54;	$\begin{array}{c} 2p^2P^0 \\ A^2\sum^+ \\ 3s^23p^5(^2P^\circ_{1/2})4s \end{array}$	3d ² D Х ² П 3s ² 3p ⁵ (² P° _{1/2})4р
Air	N2	295.29(NO); 296.16; 297.63; 311.36; 313.54; 315.87; 326.72; 328.42;330.94; 331.50; 333.83; 337.10; 350.02; 353.60; 357.63; 358.20; 364.14; 367.11; 370.96; 375.46; 380.42(O ⁺); 394.20(O ⁺); 399.72; 405.84; 414 O4: 419 98; 427.81(O ⁺); 434.38(O ⁺);	$C^3 \Pi_{\rm u}$	$X^2 \Pi_g$
	N ⁺ ₂ O _{II} O _I Ar _I Ar _{II}	391.40(0 ₂); 465.20; 470.91; 522.81; 342.81; 423.65; 437.18; 448.89; 777.23; 777.47; 844.69; 750.44; 751.51; 811.58; 821.67;	$\begin{array}{l} B^2\sum_{u}^{+}\\ 2s^22p^2({}^3P)3d\\ 2s^22p^2({}^3P)3d\\ 2s^22p^3({}^4S^\circ)4p\\ 2s^22p^2({}^1D)3d\\ 2s^22p^3(4S^\circ)3s\\ 3s^23p^5({}^2P^_{3/2})4s\\ 3s^23p^4({}^3P)3d \end{array}$	$\begin{array}{c} X^2 \sum_{g}^{+} \\ 2s^2 2p^2 ({}^3P)5p \\ 2s^2 2p^2 ({}^3P)4fG \\ 2s^2 2p^3 ({}^2D^\circ_{3/2})3d \\ 2s^2 2p^2 ({}^1D)4fD \\ 2s^2 2p^3 (4S^\circ)3p \\ 3s^2 3p^5 ({}^2P^\circ_{3/2})4p \\ 3s^2 3p^4 ({}^3P)4p \end{array}$
$\begin{array}{l} \text{Air} + \text{H}_2\text{O}^{***} \\ (\text{RH} \sim 6.0\%) \end{array}$	Η _α ΟΗ	656.30; 306.47; 306.82; 308.15; 309.06;	$\begin{array}{c} 2p^2P^0 \\ A^2\sum^+ \end{array}$	3d ² D Х ² П

^{*} O_I, O_{II}, Ar_I, Ar_{II} donate the first or the second excited state of relevant atom.

** The symbol in () in column three is the free radical whose existence in the ESD-generated plasma cannot be excluded because of the heavily overlapped emission lines, based on the assignment of references (Li et al., 2013; Pearse and Gaydon, 1963).

For MSGM and CO₂ + H₂O environments, only additional lines (to dry CO₂) were listed. For Air + H₂O, only additional lines (to Air) were listed.

powdered dry NaCl in lower electrode/sample cup. The ESD experiments were conducted with time durations of 15 min to 10 h. Laser Raman spectroscopy was used to identify the new molecular species generated by ESD in NaCl samples.

Fig. 6a shows the Raman spectra measured on four NaCl samples, before ESD (spectrum 1), and after 15 min, 1 h, and 3 h ESD experiments (spectrum 2, 3, 4), compared with the spectra of pure chemicals (spectrum 6, 7, 8). Note that the initial NaCl does not have a fingerprint Raman peak owing to the ionic nature of the Na-Cl bond (spectrum 1). A Raman peak at 936 cm⁻¹ first appears in the product of 15 min ESD (spectrum 2), suggesting the onset of the transformation from NaCl to an oxychlorine due to the ESD-induced plasma chemical process. The overall intensity of this peak in the samples increases as the ESD experiment is prolonged to 1 h and 3 h (spectra 3, 4). The assignment of this peak to the v_1 symmetric vibration of NaClO₃ (compared with spectrum 6) is based on our previous study of the Raman spectral features of oxychlorine salts M[ClO_x]_y · zH_2O (M = Na, Mg, Ca; x = 1, 2, 3, 4; y = 1, 2; z = 0, 1, 2, 4, 6) at different pressures and temperatures in the PEACh (Wu et al., 2016). A Raman peak at 954 cm⁻¹ appears at a few sampling spots after 2 h of ESD (spectrum 5), suggesting the formation of NaClO₄ (compared with spectrum 7). The rare occurrence of NaClO₄ peak in observed Raman spectra implies its low concentration in our ESD products.

Furthermore, a strong peak at 1068 cm⁻¹ and a weak peak at 1386 cm⁻¹ appear in all sampling spots of the 2 h and 3 h ESD products (Fig. 6a, spectrum 3, 4, 5). These peak positions suggest the formation of Na_2CO_3 (spectra 3, 4, 5, com-

pared with spectrum 8). After long duration ESD experiments (>10 h), black soot appeared on the upper and lower electrode surfaces. Raman peaks of amorphous carbon were obtained at some spots.

Fig. 6b shows the variation of ClO_3 concentrations in four layers (from a 3.0 mm depth in a sample cup) of 3 hours and 10 hours ESD products started from NaCl, analyzed by ion chromatography. It reveals a clear surface enrichment of ClO_3 in the sample, implying the formation of ClO_3 through atmosphere–surface interaction.

The Raman detection of NaClO₃ and NaClO₄ in ESD products from NaCl (Fig. 6a, spectrum 5) was confirmed by IC-MS/MS analysis. Consistent with Raman findings, the NaClO₄ concentration by IC-MS/MS was much lower than that of NaClO₃ when using NaCl as the staring phase. However, when using NaClO₃ as the starting phase, the yield of NaClO₄ increased dramatically. It suggests a sequential generation of ClO_4^- is possible on Mars, once ClO_3^- is formed. The details of these processes are under further investigation (Wang et al., 2018b).

For comparison, we ran a similar ESD experiment but using NaCl filled fused silica cell (with a diameter of 15 mm, depth of 1.5 mm, Fig. 2C), that was inserted into the lower electrode. I.e., NaCl powder does not directly contact the lower electrode made of copper during ESD. A Raman peak of ClO₃ was easily detected in the 3 h products of this ESD test. The quantification of ClO₃ revealed by IC-MS/MS shows a reduced yield (about half of the yield of using copper electrode/sample cell, with diameter of 35 mm, depth of 3 mm, Fig. 2C). Catalytic effect of different Mars relevant materials (oxides, salts, phyllosilicates), on the transformation from



Fig. 5. The UV (a) and IR (b) absorption spectrum of \mbox{CO}_2 and air plasma dissociation reaction product.

chloride to oxychlorine will be the subject of next step investigation.

3.4. Oxidation power of ESD-electron over UVC-photon

In order to quantitatively compare the oxidation powers of ESDelectrons and UVC-photons, we first selected a fast oxidation reaction:

$$2KI + O_3 + H_2O \to I_2 + O_2 + 2KOH$$
(1)

UVC radiation in CO_2 is well known to generate O_3 (Eliasson and Kogelschatz, 1991). We also anticipated a three-step generation of O_3 by ESD in CO_2 (Skalny et al., 2007), evidenced by the detection of O_3 by UV and Mid-IR spectroscopy in our experiment (Fig. 5).

Fig. 7 shows the color changes (reflecting the I₂ concentration) from the starting KI powder (Fig. 7a), after 0.5 h of ESD (Fig. 7c), and after 176 h of UVC irradiation (Fig. 7b), both in 3 mbar CO₂. Iodometry revealed the I₂ concentration in the KI sample reacted by ESD (0.5 h) is 1.00×10^{-5} Mol, and that in the KI sample irradiated by UVC (176 h) is 6.05×10^{-7} Mol, respectively (top three rows in Table 2). The estimated uncertainties in I₂ quantification are also listed, which suggest that only the orders of magnitude can be meaningfully compared.

Converted to I₂ yield rates (number of I₂ molecule per second generated in KI oxidation) per ESD electron or per UVC photon, the values are 8.3×10^{-2} /electron and 7.7×10^{-5} /photon (the column before the last in Table 2). It indicates that the oxidation power of ESD electrons is approximately three orders of magnitude higher than that of UVC photons in our experimental setting (last column of Table 2) for KI oxidation.

We found a same ratio, 10^3 , through a much longer NaCl to NaClO₃ experimental comparison. First, a rough comparison showed that the 936 cm⁻¹ Raman peak for NaClO₃ was detectable



Fig. 6. (a) Raman spectral peaks obtained from the ESD reaction products (>100 spots per product). The Raman peak of NaClO₃ (936 cm⁻¹) appeared in 15 min ESD product (spectrum 2) with weak intensity. This peak was observed in almost all Raman spectra of ESD products, with increased peak intensity in the products of longer ESD duration (spectra 3, 4, 1 h and 3 h ESD). The Raman peak of NaClO₄ (954 cm⁻¹) was observed at a few Raman sampled spots in a 2 h ESD product (spectrum 5). Multiple Raman peaks of Na₂CO₃ were observed in all Raman sampled spots of the 2 h and 3 h ESD products (spectra 4, 5). The spectra 6, 7, 8 were measured on pure chemicals. (b) Concentrations of NaClO₃ in layers of 3 h and 10 h ESD products, quantified using ion chromatography.



Fig. 7. A color comparison of KI powder: (a) as starting phase, (b) the products from 176 h UV-radiation, and (c) the product of 0.5 h of ESD. Both (b) and (c) were generated in PEACh at 3 mbar and room T.

after 15 min of ESD (spectrum 2 in Fig. 6a) but was not detectable in NaCl after 661 h of UVC irradiation. Secondly, the quantifications made by IC-MS/MS revealed that the ClO₃ concentration was 309 mg/kg in NaCl after 3 hour-ESD, but only 12.3 mg/kg in NaCl irradiated 661 h by UVC (bottom three rows in Table 2, uncertainties also listed). After counting the electron flux and the UVC photon flux in our experimental settings (Table S1), we found that the oxidation power (the number of ClO₃ per second generated in NaCl oxidation) of each ESD-electron (the column before the last in Table 2) is approximately three orders of magnitude higher than that of UVC-photon (last column of Table 2), for NaCl oxidation as well.

4. Discussion

4.1. Energetic electrons, relevant processes, and free radicals

Different from the previous laboratory lightning tests (Dasgupta et al., 2005; Rao et al., 2012), our experiment presents the first direct observation and identification of ESD-generated atmospheric free radicals under Martian conditions (Fig. 4, Table 1). Most of the identified free radicals match those predicted by early modeling studies on ESD during Martian dust storms and dust devils (Atreya et al., 2006; Delory et al., 2006), and those predicted to be generated by energetic electrons from galactic cosmic rays (GCRs), solar cosmic rays (SCRs), and solar energetic particles (SEPs) (Wilson et al., 2016).

The characters of the ionization processes caused by initial ESD electron avalanche were revealed by the observed free radicals in our experiments (Table 1). For example, CO_2^+ was the dominant species generated by ESD in CO_2 , $CO_2 + H_2O(g)$, and MSGM. CO_2^+ is a product of electron impact ionization (EII) of CO_2 (Jackson et al., 2010):

$$e^{-} + CO_2 = 2e^{-} + CO_2^{+}$$
⁽²⁾

which requires the initial electron to have a minimum kinetic energy > 14 eV. This reaction generates two more energetic electrons, thus creating a further electron avalanche and facilitating subsequent chain reactions.

Furthermore, the occurrence of EII of CO_2 suggests that other processes requiring less electron kinetic energy (<14 eV) can occur, such as electron/ CO_2 dissociation attachment (ED of CO_2) at 4.4 eV (Delory et al., 2006):

$$e^{-} + CO_2 = CO + O^{-} \tag{3}$$

We do not anticipate to detect the negative O^- from reaction (3) by our plasma emission spectroscopy, because of the inevitable mutual neutralization between positive and negative oxygen ions in the following reaction (Ishikawa et al., 1998):

$$0^+ + 0^- \to 0_{\rm I} + 0$$
 (4)

In contrast, the oxygen in the first excited state, $O_{I_{i}}$ as the product of the reaction (4) was detected by plasma emission spectroscopy (Fig. 4, Table 1), as well as CO⁺. These phenomena imply interactions among the ionic and molecular species in ESD products.

For the same reason, electron/ H_2O dissociation attachment (ED of H_2O) at 6.5 eV (Delory et al., 2006; Jackson et al., 2010) may also occur:

$$e^{-} + H_2 O = OH + H^{-}$$
 (5)

as observed emission lines of OH (Fig. 4, Table 1). Furthermore, the very strong H α line at 656.3 nm (Fig. 4, Table 1, in CO₂ + H₂O(g) atmosphere, generated by a transition from H_{III} to H_{II}) indicates the existence of an even higher electron kinetic energy, >17.19 eV (Delory et al., 2006; Itikawa and Mason, 2005), in the ED of H₂O process.

A general understanding of O_3 formation in ESD was summarized (Hokazono et al., 1991; Skalny et al., 2007) as the following three steps:

$$e^- + CO_2 \rightarrow CO + O + e^- \tag{3} mod$$

$$0 + 0 + CO_2 \rightarrow O_2 + CO_2$$
 (6)

$$0 + 0_2 + C0_2 \to 0_3 + C0_2$$
 (7)

Due to the plasma line overlap, free radicals other than the major types listed in Table 1 cannot be excluded, such as O_2 , CO^+ , NO, and O^+ , which are listed in parentheses after some major lines in column 3 of Table 1.

We noted that CO_2 splitting (or dissociation) by dielectric barrier discharge at atmospheric pressure (or in gas flow) has been studied in the past. The products, in addition to those from EII (2) and O_3 (7), are highly variable (e.g., CO_3^- , $C_2O_2^+$, $C_2O_3^+$), and can form complicated cluster ions (e.g., $CO(CO_2)_n)^+$). Some of them were detected by ion mobility spectrometry or time-resolved atmospheric pressure ionization mass spectrometer (Rokushika et al., 1986). The relevant reactions were modeled (Aerts et al., 2015) or listed (Wilson et al., 2016) to understand the experimental observations.

The types of atmospheric free radicals in CO_2 plasma observed in our experiments are limited by the sensing technologies we used. Nevertheless, the detected CO_2^+ , CO^+ , N_2^+ , O_3 , N_2 , OH, O_I , H_{III} , H_{II} , Ar_I at excited states are known to be extremely reactive (Atreya et al., 2006; Delory et al., 2006). They readily interact among themselves and with immediately surrounding materials, i.e., atmospheric molecules and surface mineral molecules if they occur in ESD process on Mars. Free radicals with high kinetic energy could play a key role in transforming chlorides to oxychlorines.

4.2. Formation paths and rates for oxychlorines

The molecular species in ESD products identified by Raman spectroscopy and ion chromatography imply that the following electrochemical reactions should have occurred in a CO_2 or CO_2 + $H_2O(g)$ environment (where M is a third body in collision).

$$e^{-} + CO_2 + M \rightarrow CO_2^{+}, O_I, CO^{+}, C$$
 (8)

$$e^{-} + H_2O + M \rightarrow OH, H_{III}, H_{II}, O_I$$
(9)

$$e^{-} + \text{NaCl} + \text{M} \rightarrow \text{Na}^{+}, \text{Cl}^{-}$$
(10)

 $Cl^{-} + O_{I} + M \rightarrow \text{intermediate species} \rightarrow ClO_{3}^{-}, ClO_{4}^{-}$ (11)

$$Na^{+} + ClO_{3}^{-} + ClO_{4}^{-} + M \rightarrow NaClO_{3} + NaClO_{4}$$
(12)

Table 2														
Quantitative	comparison	of I ₂ yields ir	ו KI oxidation and Cl	lO ₃ yields in N	VaCI oxidation	ı, per ESD-elect	tron and per UV	C-photon, at 3 n	nbar CO ₂ and	room tempera	ture in PEACh.			
Starting phase	Experi- ment types	Atmo- sphere in Mars chamber	Calculated total ESD-electron or UVC-photons flux per second (number/s) to whole KI or NaCI sample ^a	Reaction time (h)	Products	Measured total 1 ₂ yield (Mol) in samples ^b	STD				Number of I ₂ in whole samples ^e	Mean reaction rate (number of 1 ₂ molecules per second)	Generation rate (number of 1 ₂ per second) by ESD-electron or by UVC-photons	Ratio of gen- eration rate in Kl exp. (ESD- electron over UVC-photon)
KI KI	ESD Hg-UVC	CO ₂ CO ₂	4.05E+16 7.48E+15	0.5 176	I ₂ I ₂	1.00E-05 6.05E-07	3.88E-06 1.17E-07				6.02E+18 3.64E+17	3.35E+15 5.75E+11	8.26E-02 7.68E-05	1.07E+03
						Measured ClO ₃ con- centration (mg/kg) in samples ^c	STD	Total mass (mg) analyzed by IC-MS/MS	Mass (mg) of ClO ₃ in analyzed samples	Mol of ClO ₃ in analyzed samples ^d	Number of CIO ₃ molecules in analyzed samples ^e	Mean reaction rate (number of ClO ₃ molecules	Generation rate (number of ClO ₃ per second) by one ESD-electron	Ratio of generation rate in NaCl exp (ESD electron

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$$CO_2^+ + O_I + ne^- + M \to CO_3^{2-}$$
 (13)

$$Na^{+} + CO_3^{2-} + M \rightarrow Na_2CO_3 \tag{14}$$

The products at the right side of above equations were observed in our experiments, evidenced by Figs. 4, 5, 6 and Tables 1, 2.

In order to understand the intermediate species in Eq. (11), it would be very useful to comparing our experimental observations with those of Kim et al. (2013). They exposed CO_2 -rich Cl-bearing H₂O ice to energetic electrons and used mid-IR spectroscopy and quadrupole mass spectroscopy to characterize the products upon annealing. Three oxychlorine phases, OCIO, ClOCl, and ClClO₂, were identified after energetic electron irradiation at 100 nA over an area of 3 cm² (i.e., electron flux = $2 \times 10^{15} \text{ s}^{-1} \text{ m}^{-2}$). When using a higher electron flux (1000 nA, $2 \times 10^{16} \text{ s}^{-1} \text{ m}^{-2}$), new IR peaks appeared that were tentatively assigned to ClO_3^- and $ClO_2^$ groups. Our observations are very much in line with theirs except that we used an even higher electron flux of 1.4×10^{20} s⁻¹ m⁻² (Table S1) with a kinetic energy higher than 17.9 eV directly on dry NaCl powder. ClO_3^- and ClO_4^- (at lower concentration) were definitively identified using laser Raman spectroscopy (Fig. 6a) in our experiments. Based on the above comparison, we can tentatively assign the intermediate species in reaction (11) to be OClO, ClOCl, ClClO₂, and possibly ClO_2^- .

Furthermore, because of the existence of O₃ in ESD-generated plasmatic gases (Fig. 5), reaction R3 in Wilson et al. (2016) may be a viable alternative mechanism that forms chlorate:

$$Cl^{-} + O_3 + M \to ClO_3^{-} + M$$
 (15)

Fifteen minutes is the shortest ESD duration for which the Raman peak of NaClO₃ was detectable in an ESD product (Fig. 6a, spectrum 2). To be detectable by ordinary Raman spectroscopy, >1 mol% of the newly formed chlorate must accumulate. Thus, we conclude that NaCl instantaneously transforms into NaClO₃ during ESD-NGD.

4.3. The formation of carbonates

At almost every spots of 2 h and 3 h ESD products examined by Raman (>100 spots on each ESD product), a peak at 1068 cm⁻¹ and a weak peak at 1386 cm⁻¹ of Na₂CO₃ were observed. 1068 cm⁻¹ peak was also observed at many Raman examined spots in 1 h ESD product (Fig. 6a). This observation provides a solid evidence of generation of Na₂CO₃ from NaCl by ESD stimulated plasma chemistry in CO₂ atmosphere, i.e. Eq. (14).

We notice that <5 wt.% carbonates was found in the surface soil at the landing site of Opportunity rover (Christensen et al., 2004), that contributes MiniTES spectrum. The frequent occurrence of Na₂CO₃ in ESD products of short durations (1-3 h) supports a possibility of ESD stimulated plasma chemistry contributing some carbonates found in martian surface soils. More ESD experiments with difference starting chlorides and quantitative analysis of carbonate yield are needed.

5. Implications to Mars

5.1. Potential ESD-generating atmospheric events on Mars

Past volcanic eruptions, current grain saltation, dust devils, and dust storms on Mars have been actively investigated for electrification and electrostatic discharge using numerical modeling, laboratory experiments, and terrestrial field tests (Atreya et al., 2006; Delory et al., 2006; Esposito et al., 2016; Farrell et al., 2004, 2015; Forward et al., 2009; Harrison et al., 2016; Jackson and Farrell, 2006; Jackson et al., 2010; Kim et al., 2013; Krauss et al., 2003; Melnik and Parrot, 1998; Schmidt et al., 1998; Wilson et al., 2016;

I

I

over UV photon)

ESD-electron UVC-photon

or by one

per second)

for ClO₃

1.02E+03

5.11E-03 5.01E-06

2.07E+14 3.75E+10

2.24E+18 8.92E+16

3.71E-06 1.48E-07

3.10E-01 1.24E-02

1.003E+02 1.006E+02

3.10E+01 1.20E+00

3.09E+02 1.23E+01

Cl03

3 661

4.05E+16 7.48E+15

C 22

ESD Hg-UVC

NaCl NaCl

^a Calculated total ESD-electron or UVC-photons flux per second (number/s) to whole Ki or NaCl sample, based on measurements, details in Table S1.

Measured total 12 yield in Mol from the entire reaction product from KI, by a standard iodometry procedure.

Measured ClO₃ concentration in mg/kg in \sim 100 mg reaction product used in IC-MS/MS analysis. Molar mass of ClO₃ is 83.5 g.

Avogadro number is 6.022×1023 atoms per mole

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Winn et al., 1974; Yan et al., 2017; Zhai et al., 2006). Two flight E-field sensors were selected for two missions to Mars: one mission was canceled (ECHOS/MATADOR (Farrell et al., 2004) for the 2003 Mars Surveyor), and one mission crashed during landing (MicroARES (Harrison et al., 2016) for the 2016 ExoMars-EDM). At this stage, without actual E-field measurements from Mars, a hypothesis regarding the occurrence of ESD in atmospheric events has been validated by terrestrial field tests (Esposito et al., 2016; Farrell et al., 2004; Harrison et al., 2016; Jackson and Farrell, 2006; Schmidt et al., 1998) and laboratory experiments (Farrell et al., 2017).

Dust devils were observed by all landed missions on Mars. The size, duration, speed, and mean occurrence rates of dust devils were quantified at Gusev Crater based on Spirit rover observations during three dust seasons (Greeley et al., 2006, 2010). On average, global dust storms occur once every two Martian years. Regional and local dust storms occur every year with well-documented temporal and areal coverages (Wang and Richardson, 2015). For these dust events, the lifted dust flux has been used for quantification. For example, Whelley and Greeley (2008) found that the annual global dust flux lifted by dust devils was approximately equal to 1/2 of the annual dust flux by all local/regional dust storms in a nonglobal-dust-storm year on Mars and 1/2 of that lifted by a global dust storm at its peak. The E-field measurements generated by terrestrial dust devils have revealed a range of up to 60 kv/m (Jackson and Farrell, 2006). At this level, ESD does not occur on Earth but would occur on Mars because the BEFT on Mars is <1% of the BEFT on Earth. Based on these values, we anticipate ESD to occur during dust devils and dust storms on Mars.

The 166 kv/m E-field (Schmidt et al., 1998) detected in saltating sand on Earth suggests that with every wind event on Mars carrying sand and dust, near-surface E-fields could develop, and ESD might occur. A new experimental observation made by Bak et al. (2017) has revealed that the wind abrasion of silicates can give rise to oxidants in the form of hydrogen peroxide (H_2O_2) and hydroxyl radical (·OH), and observed glow discharge under Mars atmospheric composition and pressure. E-fields and ESD from saltation are expected to be more ubiquitous than those from dust devils and storms.

Catling et al. (2010) suggested that chlorine species in past volcanic plume processed by photochemistry can be a possible source for the perchlorates. We note herein that volcano plumes also contain vigorous electrical processes such as triboelectric grain charging and impulsive intense discharging. The vigorous electrical activity should modify the gas near the volcanic vent. Especially given the high opacities in the dust-loaded plume, the conversion of HCl in plume by ESD might have a rate that exceeds photochemical activity. Such ESD effects could be included in future volcanic plume atmospheric models of the chlorine chemical processes.

5.2. Estimating the electron density and drift velocity for ESD-NGD in Martian dust events

The electron drift velocity, Townsend coefficient, and electron density have been modeled by several teams for Townsend dark discharge (TDD) in Martian dust events (Jackson et al., 2010; Delory et al., 2006). Although no such model study exists for normal glow discharge (NGD), some extrapolations from these models can be reasonably made based on physics (Gallo, 1975) and the measured values of BEFT, which are ~25 kv/m for TDD (Farrell et al., 2015) and ~34 kv/m for NGD (Yan et al., 2017) in CO₂ at the Mars-relevant atmospheric pressure.

Based on the gas discharge phenomena described in literatures, the major difference between NGD and TDD is that the former has a much higher current (i.e., electron density in electron avalanche) than TDD, 10^7-10^8 times from point F–G to point C in Fig. S1

(Gallo, 1975), and a lower voltage drop because of the shielding effect of space charges.

A simplified way to estimate the electron density for NGD would be to extrapolate from Delory's (2006) model of TDD for Martian dust events. From the model-calculated electron density N_e (m⁻³) vs. *E* (kv/m) (in Fig. 4 of Delory et al., 2006), we can find an N_e value of $\sim 5 \times 10^{18}$ m⁻³ for 34 kv/m (assumed NGD-like), which is approximately 10⁷ times the N_e value (3 × 10¹¹ m⁻³) for 25 kv/m (TDD) and thus is consistent with the basic concept (Gallo, 1975, Fig. S1).

On the other hand, the model-calculated electron drift velocity V d (m/s) vs. *E* (kv/m) (in Fig. 4 of Delory et al., 2006) tends to flatten out after 20 kv/m. This result suggests that the electron drift velocity for 25 kv/m ($\sim 3 \times 10^5$ m/s in TDD) can probably be used for 34 kv/m (assumed NGD-like), which is consistent with the fact that similar collision processes occur in TDD and NGD.

A combination of the two, with largely increased electron density in NGD and the same electron velocity for both, would result in a very conservative estimation of the electron flux, $1.5 \times 10^{24} \text{ s}^{-1} \text{ m}^{-2}$, for the ESD-NGD that may occur in Martian dust events. This value sets the up-scaling factor of 10^4 from the electron flux $1.42 \times 10^{20} \text{ s}^{-1} \text{ m}^{-2}$ (Table S1) in our ESD-NGD experimental setting, which will be used in the discussion of next section.

5.3. Scaling the oxidation power of ESD vs. UVC to Mars

Two sets of comparative experiments on KI and NaCl oxidations revealed an oxidation power of ESD (per electron) that was 10^3 times that of UVC (per photon) in our experimental setting (Table 2). To scale this ratio to Martian conditions, we first assumed an average Martian UVC (200–280 nm) flux of 3.18–3.73 W m⁻² modeled in previous studies (Cockell et al., 2005; Schuerger et al., 2003). The power density of the Hg lamp used in our KI and NaCl oxidation experiments was 20.7 W m⁻² (2.07×10^{-6} J s⁻¹ mm⁻²) at 200–260 nm (Table S1). This comparison means that the I₂ yield in our UVC-KI experiment and the ClO₃ yield in out UVC-NaCl experiment should be downscaled approximately 5 times to match the average daytime UVC flux on Mars.

Because there is no E-field measurement made on Mars, we only refer to the modeling results (e.g., Delory et al., 2006) for potential ESD processes in dust events (dust storm, dust devil, and grain saltation) on Mars. We noted that there were two important unknowns, the first is the time duration that an ESD would occur during a dust event (in percent of time duration of a dust event); the second is the type of ESD (TDD or NGD) that would occur in a specific dust event. Because of these unknowns, we would scale the electron flux $1.42 \times 10^{20} \text{ s}^{-1} \text{ m}^{-2}$ (7th column of Table S1) in our ESD-KI and ESD-NaCl experiment into two extreme cases. For a weak ESD that remains in Townsend Dark Discharge (TDD) regime, the modeled electron flux is 9×10^{16} s⁻¹ m⁻² (at 25 kV/m in Fig. 4 of Delory et al., 2006), roughly 6×10^{-4} times of that in our experiments. For a stronger ESD that develops to Normal Glow Discharge (NGD) regime, a higher electron flux would be generated with similar electron drift velocity. This extrapolation described in section 5.2 gave an electron flux of 1.5×10^{24} s⁻¹ m⁻², roughly 10⁴ times of that in our ESD-KI and ESD-NaCl experiment. The wide range ($\sim 10^{7-8}$) in modeled ESD (from TDD to NGD) electron flux is consistent with the wide 10⁸ range of discharge current between NGD (point G in Fig. S1, $I_{NGD} \sim 10^{-2}$ A) and TDD (point C in Fig. S1, $I_{\text{TDD}} \sim 10^{-10}$ A, Gallo, 1975).

We now combine the two-step scaling: (1) down-scaling 5 times for UVC on Mars, and (2) down-scaling 6×10^{-4} for weak ESD-TDD and up-scaling 10^4 for strong ESD-NGD on Mars. We found that the oxidation power ratio of 10^3 per ESD electron over that per UVC photon (Table 2), revealed by two sets of compara-

tive experiments on KI and NaCl oxidations, would translate to be an ESD oxidation power of about 10^{-1} (TDD) to 10^7 (NGD) times (in a dust event) that of average UVC on current Mars. Since we do not have E-field measurements in the saltation layer at Mars, we cannot quantify the field strength itself or its duration for a direct comparison to UVC. However, the process is potent.

6. Conclusion

Our study revealed (1) the instantaneous generation of highly reactive free radicals during ESD in simulated Mars atmospheric compositions and pressure; (2) the extreme fast transformation from NaCl to NaClO₃ and NaClO₄ through the interaction with free radicals. (3) Quantitatively, the oxidation power by ESD (per electron) was 10^3 times that by UVC (per photon) in our experimental setting, which translated to modeled Mars conditions of either 10% or 10^7 times UVC, depending on the type of ESD (TDD or NGD) in a specific dust event.

Considering the current areal and temporal coverages of atmospheric dust events on Mars and their anticipated frequent occurrences in the Amazonian period, the accumulated ESD product (e.g., oxychlorines) on Mars could be substantial.

This result, in general, might fill the huge gap (seven orders of magnitude, 10^{-7}) in perchlorate concentration, indicated by Smith et al. (2014), between the modeled value when considering only photochemistry mechanism and the actually measured ClO₄ concentration in regolith of Phoenix landing site (Hecht et al., 2009; Kounaves et al., 2014a, 2014b).

In conclusion, we suggest that plasma chemical processes during Martian atmosphere-surface interactions can be an additional important formation mechanism for the large amounts of oxychlorines observed during the Phoenix, Curiosity, and Vikings missions on Mars.

Author contributions

ZCW and AW designed the whole set of experiments. ZCW, AW, and YCY conducted ESD, plasma, Raman experiments and data analyses. KW and JH conducted IC measurements and data analyses. AJ conducted IC-MS/MS measurements and data analysis. ZCW, AW, and WMF drafted the manuscript. All co-authors contributed to discussions, interpretations, and writing.

Competing financial interests

The authors declare no competing financial interests.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2018.08.040.

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