MARTIAN DUST ACTIVITY CAN QUANTITATIVELY ACCOUNT FOR THE OBSERVED CARBONATES, PERCHLORATES IN TOP SOIL AND HCL IN ATMOSPHERE.

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Introduction: Frictional electrification is a common process in our solar system, with Martian dust activities known to be a powerful source of electrical charge buildup. Furthermore, the thin atmosphere on Mars makes the breakdown of accumulated electrical fields, in form of electrostatic discharge (ESD), much easier to occur (a hundred times easier than on Earth). ESD generates a huge amount of energetic electrons that collide with Martian atmospheric molecules and generate free radicals. These free radicals react with the Martian molecules (at the surface and in the atmosphere) to generate new species.

We have experimentally demonstrated that heterogeneous electrochemistry stimulated by mid-strength Martian dust events can decompose common chloride salts, which is accompanied by the release of chlorine atoms into the atmosphere and the generation of (per)chlorates (chlorates and perchlorates) and carbonates[1,2,3,4].

Here we report the first set of quantifications on the yields of (per)chlorates, carbonates (as solid salts), and chlorine (as released gas) generated by ESD on two typical chlorides (KCl and $MgCl_2$), with ESD strength matching that of mid-strength Martian dust activity. Based on these results, we calculate the total abundances of those species produced from limited chloride sources on Mars[5,6,7] by global dust storms[8] during defined durations in the Amazonian period.

Experiments: We conducted 26 sets of ESD experiments on chloride salts in a Mars reaction chamber (at 3mbar CO_2), with a range of electron flux densities that match those for mid-strength dust events on Mars. KCl and $MgCl_2$ were selected for this study, to represent two groups of common chlorides (KCl, NaCl, and $CaCl_2$ vs. $MgCl_2$, $AlCl_3$, and $FeCl_2$) that demonstrated distinct behaviors in three aspects[2,4].

The characterization and quantification of four types of new species in the reaction products (post-ESD-remaining salts, Cl-bearing films, and exhaust gases) were accomplished by using Sequential ion chromatography-mass spectroscopy-mass spectroscopy (IC-MS/MS), Ion Chromatography (IC), Thermo-flash elemental analyzer, associated with the wet-chemical procedure. Gas sensors and *in situ* Raman, MIR spectroscopy, and XRD were also used.

Results: In the spectra of post-ESD-on-KCl remaining salts, the characteristic Raman and MIR spectral peaks of carbonates and chlorates were readily observed (Figure 1a, b) at very low concentrations (< 1 mol%). The quantification by IC-MS/MS shows the released Cl^{-1} from both chlorides are *at percent level*, while the formed (per)chlorates are per thousand level (Figure 1c). The abundances of Cl^{+1}, Cl^{+3}, Cl^{+5}, and Cl^{+7} in exhaust gases reduce (from 10^-3 to 10^-9,

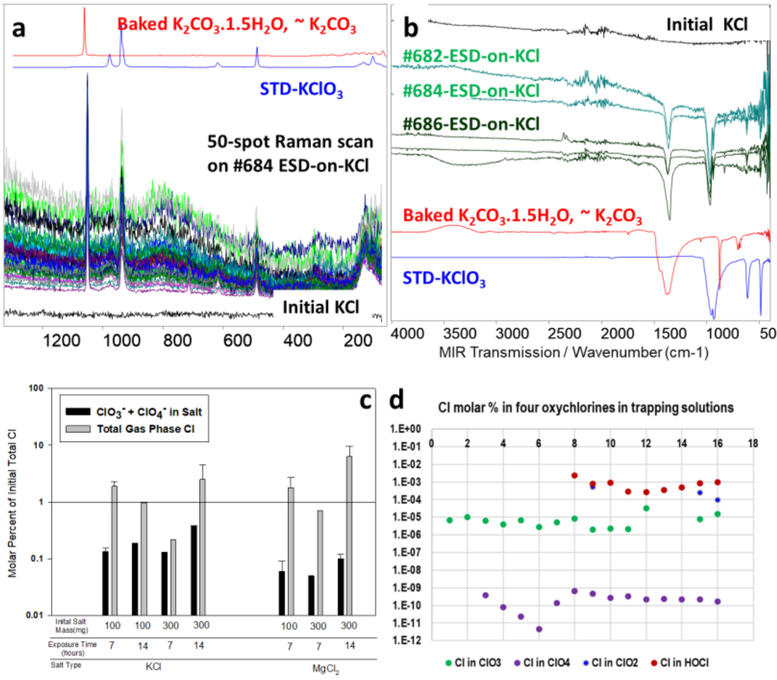

Figure 1. Characterization and quantifications of new species in reaction products (a) Raman and (b) Mid-IR spectra of post-ESD remaining salts; (c) IC-MS/MS revealed ClO_3^-, ClO_4^- in salts compared with release Cl^- in exhaust gases; (d) Cl^{+1}, Cl^{+3}, Cl^{+5}, and Cl^{+7} in exhaust gases.

Figure 1d) following the change of their valence state.

The quantification of total carbon in four post-ESD-remaining salts was made using Thermo-flash elemental analyzer, ~ 0.47 and 0.23 microgram C per milligram salt ($MgCl_2$ and KCl) were found, which correspond 0.37 mol% $MgCO_3$ and 0.29 mol% K_2CO_3. In other words, an average of ~0.33 mol% of cation in the initial chloride was taken by carbonates when formed by the ESD reactions in CO_2.

A large amount of Cl released by 7hours-ESD (> 1 mol%) suggests the decomposition of original chloride molecules. Some of the liberated cations (K^+ or Mg^{2+}) went into (per)chlorates, some went into carbonates. However, some remaining liberated cations must have gone into an additional molecular form. We hypothesize that some oxides (MgO or K_2O) were formed, and used wet chemistry plus XRD analysis and gravimetric measurements of the post-ESD-on-$MgCl_2$ remaining salts to identify and quantify. The result supports that MgO is the molecular form of the rest of liberated Mg^{2+}, with a produced quantity (0.7 - 2.8 mol%) that matches the released Cl^-, i.e., both are *at the percent level*.

Our analyses quantified a complete set of products from the electrochemically-induced decomposition of chlorides when impacted by energetic electrons under Mars's relevant atmospheric conditions (electron flux densities match mid-strength Martian dust events). The quantifications approximately (in the order of magnitude) closed the mass balances of chlorine and cations, i.e., *at the percent level*. It also revealed the yield of (per)chlorates *at the per thousand leve*l, and the yield of carbonate, *at the sub-percent level*.

Scale to Mars: We conducted a calculation using (1) the mean values of three quantifications of this study, (2) the lowest end of available chloride sources on Mars[5,6,7], and (3) the average temporal and areal coverage of Martian global dust storms (GDS)[8] with an arbitrarily selected 0.0001 ESD-probability[4], to find the duration (in %) of the Amazonian period that would be needed to reach ***the highest reported perchlorate abundances (0.7 wt%)[9,10] and carbonate abundances (5 wt%)[11,12,13].*** Only the effect of dust activities (& GDS only) was counted in this calculation. The (per)chlorates contributed by photochemistry[13,14] or by galactic cosmic ray impact[15], and the carbonates contributed by ground carbonate-bearing outcrops and distributed by aeolian processes were ignored.

We found the observed high abundances of (per)chlorate and carbonate can be accumulated (by GDS) after ~ 4.6 x10^8 Martian years and ~ 7.0 x10^8 Martian years, respectively. These time durations correspond to ~ 16% and ~ 24% of the Amazonian period.

Furthermore, we used a different approach to scale the Cl released from chlorides by ESD to the observed HCl in atmosphere by TGO mission in MY34 or MY35[16,17]. Since HCl has a lifetime of at least a few months, the accumulation of released Cl in a GDS-dust season was considered. We assumed the thickness of lifted topsoil by a GDS to be 1 cm to 10 cm (a conservative estimation), and took NaCl to represent the affected chlorides, the total released number of Cl atoms from the limited chloride source areas on Mars during an average Martian year would be 2.32x10^{31} to 7.42x10^{32}. Assuming all Cl atoms reacted with H to form HCl and the HCl molecules are distributed into the atmosphere below 40 km, ***the HCl number density*** would be in the range of 4.0x10^6 to 1.3x10^8 molecule/cm^3. This estimated range matches the observed range of 2x10^6 to 2x10^8 molecule/cm^3 by the TGO mission[17] in an atmospheric layer of 10-40 km.

Conclusion: This new study provides the first set of quantifications of the (per)chlorate, carbonate, and oxide in the post-ESD remaining salt, as well as Cl and ClOx (x=1-4) in the exhaust gas, from ESD process with known duration and a strength comparable with the mid-strength martian dust activities. Based on these quantifications, our calculation indicates that Martian global dust storm can account for the abundance of the above species observed by landed and orbital missions. Furthermore, it supports that the heterogeneous electrochemistry induced by Martian dust activities is a major driving force in martian global chlorine cycle.

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