PERCHLORATE FORMATION THROUGH ELECTROCHEMISTRY IN MARTIAN ATMOSPHERE-SURFACE INTERACTION. Alian Wang1, Y. C. Yan1, J. Houghton1, Kun Wang1, Z. C. Wu2, 1Dept. Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, 63130, USA; 2Institute of Space Science, Shandong University, Weihai 264209, China (alianw@levee.wustl.edu);

Electrochemistry in Mars surface processes: 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 consid- ered responsible for the majority of secondary phases, e.g., silica, phyllosili- cates, and salts [1]. The finding of perchlorate by Phoenix mission [2, 3], with abnormally high ClO2/Cl ratio, brought up the importance of photochemistry processes [4]. Through the efforts of modeling, experiments, and ter- restrial analog studies, the role of photochemistry in the generation of chloride/perchlorates was supported, its importance in Cl-cycle on Mars is also implied [4-7].

Nevertheless when going into the quantitative de- tails, it was found that 1D photochemistry model was unable (by seven order of magnitudes less, 10−7) to account for the abnormally high ClO2/Cl ratio found by Phoenix [8]. In addition, a set of abnormally negative δ37Cl was recently found in all seven solid samples analyzed by MSL-SAM instrument at Gale Crater [9]. 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 [4, 7]. These discrepan- cies posted a call for a NEW mechanism that would potentially take the major responsibility for Cl-bearing phase transformations on Mars.

We proposed [10-12] 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−) to oxychlorine salts (Cl3+, Cl5+, Cl7+) by Mars atmosphere–surface interaction. A recent modeling paper [13] also suggests the role of electro-chemistry process, induced by Galactic Cosmic Ray (GCR), Solar Cosmic Ray (SCR), and Solar Energetic Particles (SEPs).

In order to validate this hypothesis, we conducted two sets of simulated electrostatic discharge (ESD) experiments in a Mars chamber under the conditions of Mars surface atmospheric pressure, composition, and temperature [14]. In these experiments, we identified various oxidant species generated from Mars atmospheric species by ESD [11]. In this abstract, we report the first observation chloride and perchlorate formed from chloride induced by ESD. Combined with our two other reports [14, 11], it supports our hypothesis that electrochemistry process can be a major contributing mechanism in Cl-bearing phase transformations and therefore is very important for Cl-cycle on Mars.

ESD experiments in PEAC: we have built an apparatus and realized stable ESD in our Planetary Environ- ment and Analysis Chamber (PEACh), which is capable of maintaining Mars atmospheric pressure, composition (pure CO2, CO2+H2O, and Mars Simulating Gas Mixture, MSGM), and a well-controlled sample temperature (T) range relevant to Mars surface and shallow subsurface. Furthermore, our PEACh is equipped with four in situ sensors for the characterization of molecular species as solid, liquid, and plasma.

Our first set of ESD experiments concentrated on identifying the oxidant species generated from simulat- ed Mars atmosphere. In pure CO2, CO2+H2O, and a MSGM of 95% CO2, 2% N2, 2% Ar and 1% O2, the major oxidants identified by in situ plasma optical spectroscopy are: CO2+, O (I), Ar (I), N2, Hα, and OH− [11]. Our second set of experiments concentrated in Cl-bearing phase transformation stimulated by ESD. A powdered NaCl sample was the starting phase.

Identification of new molecular species: We use laser Raman spectroscopy to characterize the molecular species generated in the electrochemistry reaction between plasmatic oxidants and NaCl. Fig. 2 shows the Raman spectra measured in situ on the solid samples in ESD sample cup (shown as insert of Fig. 1).

Note the starting phase NaCl does not have a finger- print Raman peak owing to the ionic nature of Na − Cl bond (bottom spectrum in Fig. 2). A Raman peak at 936 cm−1 first appears in a sample after 15 min ESD experiment in PEACh at 3 mbar CO2 (Fig. 2), suggest- ing the instantaneous formation of an oxychlorine salt. The intensity of this peak increases following the lengthening of the ESD duration (to 3 hours). The as- signment of this peak, as NaClO2, was based on our previous study on Raman spectral features of oxychlorine salts M[ClOx]y·zH2O (M=Na, Mg, Ca, x=1, 2, 3, 4; y=1, 2; z=0, 1, 2, 4, 6) at different pressures and temperatures relevant to Mars surface and shallow subsurface [12]. At a few sampling spots, a Raman peak
near 954 cm\(^{-1}\) appears, suggesting the occurrence of NaClO\(_4\), which obviously is a minor component in the ESD products. Furthermore, a strong peak at 1068 cm\(^{-1}\) and a weak peak at 1386 cm\(^{-1}\) appear later in every Raman spot, whose positions suggest the occurrence of Na\(_2\)CO\(_3\).

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

\[
\text{Na}^- + \text{Cl}^- \rightarrow \text{Na}^+ & \text{Cl}^- \\
\text{Cl}^- + \text{O(I)} \rightarrow \text{some middle phases} \rightarrow \text{ClO}_2^- \text{or ClO}_4^- \\
\text{Na}^+ + \text{ClO}_3^- \text{or ClO}_4^- \rightarrow \text{NaClO}_3 \text{or NaClO}_4 \\
\text{CO}_2^+ + \text{O(I)} \rightarrow \text{CO}_2^2- \\
\text{Na}^+ + \text{CO}_3^- \rightarrow \text{Na}_2\text{CO}_3
\]

By using the relative peak intensity values, and by making multi-spot Raman analysis on an ESD sample, we can achieve a semi-quantitative estimation on the yield of NaClO\(_3\) and NaClO\(_4\), and their relative concentrations.

**Quantification of oxychlorine species in ESD products using Ion Chromatography (IC):** We prepared two ESD samples for IC analysis using an A-Supp7-250 anion column (45°C, 3mM Na\(_2\)CO\(_3\) 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 analysis is 1mM. We also consistently found a second IC peak (referred as ClO\(_4\) for now) that only appear in ESD products.

The ESD sample cup has a diameter of 19 mm and a depth of 2.5 mm. We took at least four layers of sample from each ESD sample cup, and analyzed them separately by IC. The samples with ESD duration of 3 hours, 10 hours, and a blank sample of starting NaCl were analyzed. Fig. 3a shows the detected ClO\(_3\) (in ppm) from four layers of two ESD samples.

The IC data first confirmed that the generated oxychlorine salt is dominantly 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. 3a, 3b) of both oxychlorine species, implying a link to an atmosphere-surface interaction.

Although at this moment, we cannot fully identify and quantify the ClO\(_3\) 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 ClO\(_3\) or forming ClO\(_4\)) to occur in our specific plasma-solid electrochemical reaction, which needs further investigation.

**Conclusion:** This study demonstrated the formation of oxychlorine salts from chloride stimulated by electrostatic discharge in an environment [14] 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.

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