OXIDANTS GENERATED BY ELECTROSTATIC DISCHARGE IN A MARTIAN ENVIRONMENTAL CHAMBER – IMPLICATION FOR PERCHLORATES FORMATION ON MARS. Zhongchen Wu[1,2,3], Alian Wang[3], [1]Institute of Space Science, Shandong University & Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Shandong University, Weihai 264209, China; [2]Key Laboratory of Planetary Sciences, Chinese Academy of Science, Shanghai, 200030, China; [3]Dept. Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, 63130, USA (alianw@levee.wustl.edu);

Martian Perchlorates and their formation: Perchlorates were detected in the regolith of Phoenix site [1], interpreted by the release of O_2 and chlorinated hydrocarbon at Gale Crater [2, 3], implied by re-analysis of Vicking data [4], and recently suggested by Vis-NIR spectral analysis at four RSL sites [5]. Perchlorates and other oxygen chloride species may exist ubiquitously on Mars [6].

On the basis of terrestrial studies, gas phase photochemical reaction between oxidants and volatile chlorine species was regarded as one important mechanism to generate perchlorates on Mars [7] and was discussed extensively. However, using 1D-photochemical model [7, 8], it was found that sufficient quantity of perchlorate can be modeled by gas phase photochemistry to explain the abundance of ClO_4^- found in Atacama [7], while the modeled photochemical formation of perchlorate is insufficient by orders of magnitude (~10^7) to explain the ClO_4^- concentration measured at Phoenix landing site [8]. Therefore, it suggests that non-gas-phase processes must play a major role in martian perchlorate formation.

Another set of mechanisms, the gas-solid reactions between oxidants and chloride-bearing solids (aerosols, dust grains, mineral surfaces) were proposed. Among them, Electrostatic discharge (ESD) is considered to be an important one, but no detailed experimental study to validate this hypothesis. It was understood that the breakdown electric field strength on Mars (~25 kV/m) [9] is much lower than that on Earth (~30,000 kV/m) [10], and this breakdown electric field strength can be readily reached during the electrostatic discharge (ESD) generated by martian dust storms or dust devils [11].

We designed a set of systematic ESD experiments and conducted them in a Planetary Environment and Analysis Chamber (PEACh) under various martian environmental conditions. Here we report the first observation of oxidant species generated by ESD.

The ESD experiments in a martian chamber: The core unit in this experimental setup is a pair of electrodes, driven by adjustable high voltage with high frequency. The distance between the two electrodes is adjustable as well. The temperature of lower electrode is controlled by a close-loop LN2 circulation. The design of electrodes would allow the solid sample to be placed inside of the plasma generated by ESD, thus to simulate the plasma-solid interaction in controlled environment.

In order to compare the speciation and the quantities of generated oxidants under different conditions, the ESD experiments in PEACh were run in air, in pure CO_2 , and in simulated Mars atmospheric gas mixture (95.0% CO_2, 2.0% N_2, 2.0% Ar, 1.0 % O_2). The pressure range for generating ESD was 1-10 mbar, and the temperature range was 21°C to -80°C.

During dynamic ESD experiments, _we use plasma emission spectroscopy for in situ and instantaneous detection and characterization of the generated oxidant species._ The emission spectra (200 to 975 nm) of low–T plasma excited by the ESD were recorded by a ME5000 Echelle spectrometer (Andor Technology) with a resolution of $\lambda/\Delta\lambda$ = 5000. The plasma emission was collected using a fiber-optic probe (core diameter of 600 μm; length of 4 m), and was fed to the spectrometer via an optical vacuum feedthrough on the wall of PEACh.

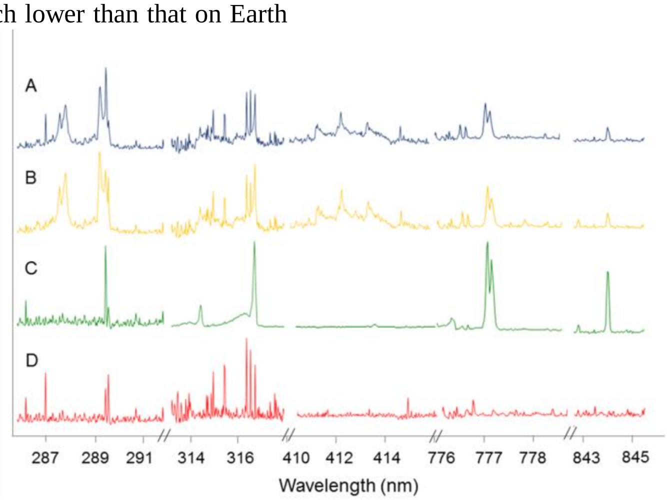

Fig 1. The plasma emission spectra of oxidants generated by ESD in: (A) pure CO_2; (B) simulated martian atmospheric gas mixture (MSG); (C) Air; and (D) spectrometer background noise.

In this work, the emission spectra of plasma generated by ESD in pure CO_2, air and martian simulating gas (MSG) mixture were recorded at various working parameters. The effect of discharge parameter (excited voltage, discharge distant) and martian environmental condition (temperature and atmospheric pressure) on the spectral features were systematically studied. The

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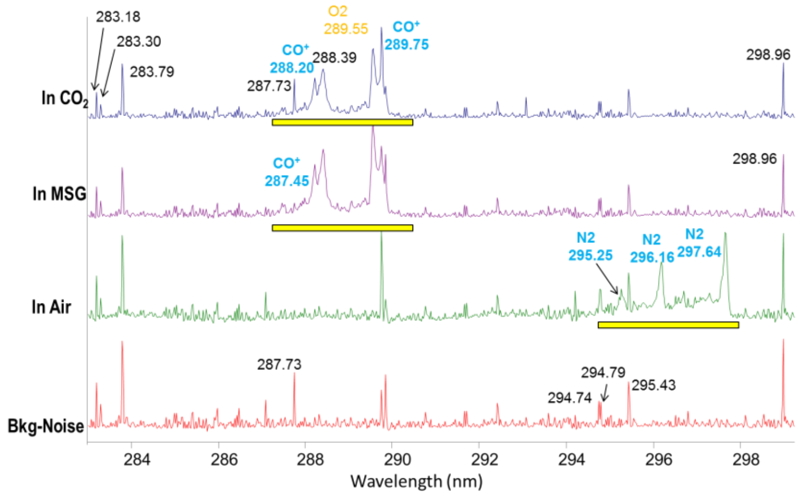

Figure 2. Example of plasma emission line assignments in a UV spectral range (colored marks = confirmed lines of oxidants in Co2 or MSG, or N2 in air; black marks = false lines due to non-even responses of ICCD pixels)

optimized ESD-plasma generation conditions in the laboratory experimental setting were found.

The identification of oxidants generated by ESD: Fig. 1 compares a typical plasma emission spectrum generated by ESD in pure CO_2 and in SMG, at optimized working parameters, with those from plasma generated in air by ESD, and also shows the spectrometer background noise .

We have found that the plasma emission lines generated by ESD in pure CO_2 and in MSG concentrate typically in the UV spectral range between 280 nm and 430 nm, and in NIR spectral range between 770nm and 850 nm. By carefully line-by-line comparison with (1) the data in literature [12, 13], (2) the plasma lines in air generated by ESD, and (3) to exclude the false "lines" in low level background noise produced by non-even response of pixels in the ICCD of Andor spectrometer, we were able to identify the plasma lines contributed by ESD generated major oxidants in CO_2 and MSG atmosphere.

The data from *in situ and instantanous* plasma spectroscopy told us that the ESD-plasma emissions in air (1-10 mbar) are dominated by those from N_2 or N_2^+. The ESD-plasma emissions in CO_2 and MSG are dominated by those from CO^+ (288.20, 289.75, 287.45 nm), CO_2^+ (324.75, 326.42, 337.30, 353.41, 367.48, 410.98, 412.37, 413.95, 415.96 nm), O (777.46, 844.66 nm), O_2^+ (414.07, 775.84 nm) and O_2 (328.55, 367.09 nm). In addition, weak emission lines of atomic nitrogen ions (354.64, 391.43, 427.81 nm) and Ar (750.44 nm) can also be detected in MSG (Fig. 2 shows an example of plasma emission line assignment).

The Andor ME5000 spectrometer that we used to record plasma emission has a high spectral resolution but low optical throughput. In order to verify above assignments for the observed plasma emission lines, we used a set of three Ocean Optics spectrometers (239-340 nm, 381-469 nm, 450-911 nm) to repeat the full set of ESD-plasma line measurements. The Ocean Optics spectrometers have a lower spectral resolution but a much higher optical throughput, thus very high S/N. We found (Figure 3) that the second set of measurements can confirm our previous major line assignments.

Apparently, all instantaneously identified emission lines in CO_2 and MSG are mainly due to the dissociation of CO_2 by ESD. The atomic oxygen (shown as strong emission lines at 777.46 and 844.66 nm) is chemically extremely reactive and readily to interact with martian surface materials. O_3 was formed and was detected in a different experiment. Quantified data will be reported at the conference.

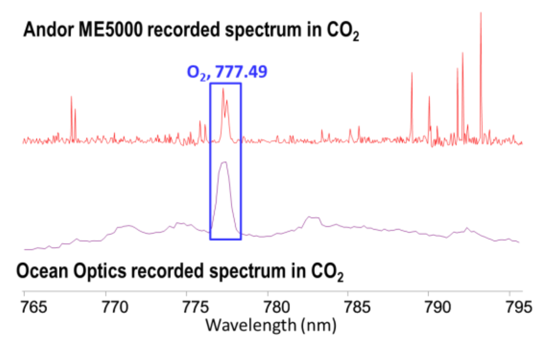

Figure 3. Confirmation of plasma emission line assignment

Conclusion: We demonstrated that wide variety and large amount of oxidants were generated by Electrostatic Discharge (ESD) under Mars relevant conditions.

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