

OXIDANTS GENERATED BY ELECTROSTATIC DISCHARGE IN A MARTIAN ENVIRONMENTAL CHAMBER – IMPLICATION FOR PERCHLORATES FORMATION ON MARS.

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Martian Perchlorates and their formation: Perchlorates were detected in the regolith of Phoenix site [1], interpreted by the release of O₂ and chlorinated hydrocarbon at Gale Crater [2, 3], implied by re-analysis of Viking 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 ClO₄⁻ found in Atacama [7], while the modeled photochemical formation of perchlorate is insufficient by orders of magnitude (~10⁷) to explain the ClO₄⁻ 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 obser-

vation 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 CO₂, and in simulated Mars atmospheric gas mixture (95.0% CO₂, 2.0% N₂, 2.0% Ar, 1.0 % O₂). 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.

In this work, the emission spectra of plasma generated by ESD in pure CO₂, 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

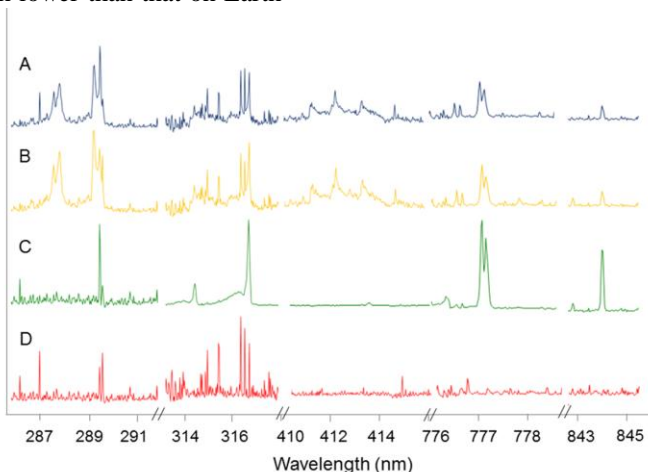


Fig 1. The plasma emission spectra of oxidants generated by ESD in: (A) pure CO₂; (B) simulated martian atmospheric gas mixture (MSG); (C) Air; and (D) spectrometer background noise.

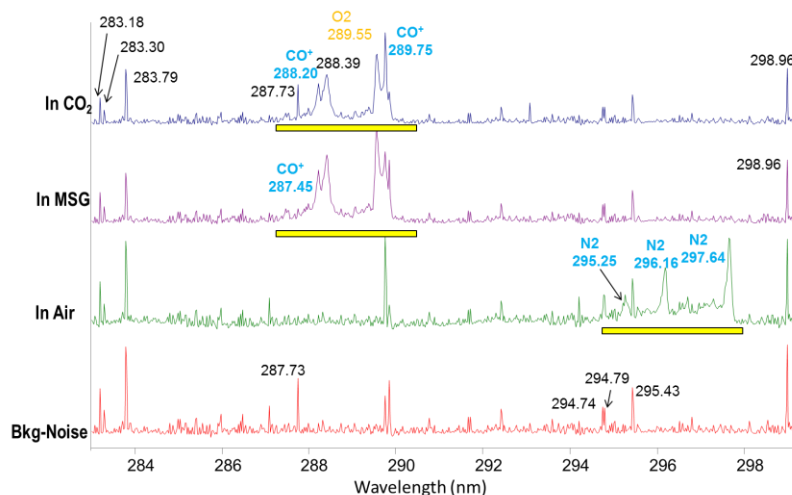


Figure 2. Example of plasma emission line assignments in a UV spectral range (colored marks = confirmed lines of oxidants in CO₂ or MSG, or N₂ in air; black marks = false lines due to non-even responses of ICCD pixels)

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 CO₂ and in MSG, 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 CO₂ and in MSG concentrate typically in the UV spectral range between 280 nm and 430 nm, and in NIR spectral range between 770 nm 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 CO₂ and MSG atmosphere.

The data from *in situ* and *instantaneous* plasma spectroscopy told us that the ESD-plasma emissions in air (1-10 mbar) are dominated by those from N₂ or N₂⁺. The ESD-plasma emissions in CO₂ and MSG are dominated by those from CO⁺ (288.20, 289.75, 287.45 nm), CO₂⁺ (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), O₂⁺ (414.07, 775.84 nm) and O₂ (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 CO₂ and MSG are mainly due to the dissociation of CO₂ 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. O₃ was formed later and was detected in a different experiment. Quantified data will be reported at the conference.

Andor ME5000 recorded spectrum in CO₂

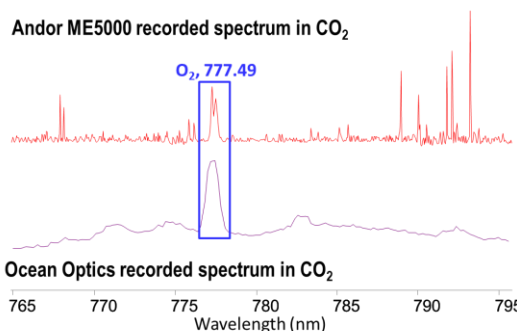


Figure 3. Confirmation of plasma emission line assignment

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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