**Iron Phase Transformations Induced by Plasma Chemistry During Martian Dust Events.** Alian Wang, Yuanchoa, Yan, Bradley L. Jolliff, and Kun Wang, Dept. Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, MO, 63130 (alianw@levee.wustl.edu).

**Introduction:** We have previously shown [1] that a new formation mechanism, namely multiphase (gas-to-solid) redox plasma chemistry induced by dust storms and dust devils on Mars, is responsible for the abundant perchlorate observed during the Phoenix mission to Mars [2], which could not be fully interpreted hitherto by photochemistry [3,4].

Another two potential and important phase transformations that might be affected by this plasma chemistry during martian dust events are the phase transformations of martian sulfates and martian Fe-phases, which will be reported in a pair of abstracts (here and [5]) at 50th LPSC conference.

**Fe-phase transformations on Mars:** Fe-minerals consist one type of highly variable and abundant phases at the Martian surface, in primary basaltic minerals and in secondary alteration products. Based on the overall lower level of aqueous alteration degree of martian basalts [6,7], we anticipate the amounts of cations released into the aqueous environment following a descending order from (Mg, Fe), to Ca, to (Na, K). In the case of SO₄-bearing solutions, Mg-sulfates could precipitate from a combination of evaporative and diagenetic processes. The fate of released Fe in aqueous solution is more complicated, and would greatly depend on both the pH and the oxidation state [8]. Direct precipitation of Fe-oxides and Fe-hydroxides [9] and formation of ferrous and ferric sulfates [10,11] are possible pathways. The actual occurrences of both were evidenced on Mars by two types of mission observations: (1) orbital remote sensing data that suggested a spatial correlation between Mg-sulfates and Fe-oxides; (2) the detections of Fe-sulfates by orbital remote sensing at much lower occurrence than Mg-sulfate.

Laboratory experiments added more fundamental understandings of Fe-geochemical cycles on Mars. When liquid water was involved (in depositional and diagenetic processes, even at low water/rock ratio), it was found that the oxidation from Fe²⁺ to Fe³⁺ happens very fast [12,13]. However when involving only H₂O vapor, (e.g., the post-depositional sulfates-atmosphere interaction, relevant to obliquity change), there is a quite large T-RH stability field for Fe²⁺-sulfates, with Fe²⁺ to Fe³⁺ oxidation occurs only at extreme RHs [14].

Some observations on Mars indicate even more complex diageneis. For example, at Meridiani Planum, jarosite was found in Burn Formation outcrop rocks: 10% jarosite on average in rock interior determined by APXS and Mössbauer data analysis [15]. However, jarosite was NOT detected in Mössbauer analyses of regolith targets at the same site [Table 3 of 16]. For some rocks (named as McKittrick, Kentucky, Bylot), the amount of jarosite detected at “as is” rock surfaces was less than the amount found at RATed targets of the same rock, accompanied by the higher Fe³⁺/Fe_total ratio in “as is” rocks.

These observations suggest that some later diagenesis reactions may have happened, different from aqueous chemistry and vapor-solid reaction, which were responsible for the destruction of Fe-sulfates at dry martian surface. Considering the frequency, time duration, and spatial coverage of dust storm and dust devils on Mars [more details in 5], the effect of plasma chemistry (induced by electrostatic discharge (ESD) during martian dust events) on the destruction of surface Fe-phase should be experimentally evaluated.

**Experiments, Fe-bearing samples, and Analyses:** The ESD experiments were conducted in a Mars Chamber (the PEACH, [17]). The chamber was first evacuated to 3x10⁻² mbar to remove air and then filled with pure CO₂. The atmospheric pressure was kept at 3 ± 0.1 mbar. The ESD was generated at about 300 V and 22 mA across the electrodes. Consistent with our early experiments [1], the ESD was generated in the normal glow discharge (NGD) regime, with a similar electron flux 1.43x10¹⁰ electrons per (second m²), about 10⁴ times lower than the calculated electron flux for ESD-NGD type that could occur in dust events.

The starting Fe-phases used in the experiments are martian relevant ferrous and ferric sulfates, chlorides, and sulfides, including FeSO₄·7H₂O, Na-jarosite (NaFe₅(SO₄)₂(OH)₆) and its 1:1 mixture with MgSO₄·7H₂O, FeCl₂·4H₂O, Pyrite (FeS₂), with more to be tested before LPSC. Each of these samples was grounded and sieved, and a grain size range of 88 μm > d > 63 μm was used to ensure the comparable reaction rate information for tested samples. The ESD experiments on each sample were run at 15 min, 1hr, 2hrs, 3hrs, 7hrs, and in some cases up to 64 hrs.

All ESD reaction products were first analyzed by Raman spectroscopy using a Renishaw-inVia Raman system (532 nm excitation, 0.5-0.3 mW, ~1 μm beam diameter at focus). For some samples, in situ plasma emission spectroscopy was taken in the PEACH to detect the release of free radicals from the CO₂ atmosphere or from the samples. XRD and VNIR analyses of
a few reaction products were made using a Bruker D8 Diffractometer and an ASD spectrometer.

**Results:** The break-down of FeSO$_4$·7H$_2$O by ESD was faster than that of MgSO$_4$·7H$_2$O. After 15 min of ESD, no FeSO$_4$·7H$_2$O phase remains. All 78 spots check by Raman spectroscopy have mixed spectra of FeSO$_4$·4H$_2$O (supported by VNIR spectra) and amorphous FeSO$_4$·xH$_2$O. After an 1hr ESD reaction, no Raman peaks of crystalline phases were left. In a 2hrs ESD product, a continuous reduction of H$_2$O content in the structure of amorphous phases was revealed by a progressive shift upward of its central peak position, from 1014 to 1063 cm$^{-1}$, accompanied with a spectral background increase, especially centered at 850 and 230 cm$^{-1}$ (Fig. 1). The oxidation of Fe$^{2+}$ to Fe$^{3+}$ was seen as the Raman peaks of Fe(OH)SO$_4$ and jarosite. XRD analysis of a 7hrs ESD product suggests a total amorphization.

After a 64hrs ESD reaction, the alteration of pure Na-jarosite was barely observable, by an increased intensity of a broad Raman peak near 560 cm$^{-1}$ and a raised background below 700 cm$^{-1}$ from dark-colored grains mainly. The peaks of hematite and Na$_2$SO$_4$ were seen only at two spots among >300 spots checked. However when using a mixture of Na-jarosite and MgSO$_4$·7H$_2$O (at 1:1 ratio) to start, the Raman peaks of hematite and goethite were observed from a few dark-colored grains in the ESD products of much shorter durations, e.g., 1, 2, 3, 7hrs. The release of OH radicals by MgSO$_4$·7H$_2$O under ESD (confirmed by *in situ* observation of OH plasma line in the PEACH) might be the key to increase the rate of Na-jarosite alteration.

The ESD-induced alteration of FeCl$_3$·4H$_2$O apparently occurs in stages (Fig. 2 shows typical Raman spectra). Following the development of alteration, structural H$_2$O was gradually lost (#1→#2), then hematite Fe$_2$O$_3$ was formed (#2→#3; mixture of #2 & #3 was seen). The end-phase formed later in long-duration ESD products (3hrs & 7hrs). XRD analysis of 7hrs ESD product indicates the formation of FeOCl and FeCl$_2$·2H$_2$O.

A natural pyrite FeS$_2$ (Huanzala, Peru) was used as the starting phase for ESD experiments. After 3 to 14 hrs of ESD reaction, the phase changes were revealed by the appearance of multiple doubles in the spectral ranges of two strong and sharp Raman peaks of pyrite (Fig. 3). These doublets occur in a much wider ranges (Δν$=10.5$ cm$^{-1}$ and Δν$=6.0$ cm$^{-1}$) than that of original pyrite sample (379.8–374.6 cm$^{-1}$, Δν=5.2 cm$^{-1}$ and 344.3–340.6 cm$^{-1}$, Δν=3.7 cm$^{-1}$). Instead of only one peak in each spectral range of original pyrite, the multiple doublets of ESD products reveal at least seven peaks in range #1 and four peaks in range #2 (Fig. 3). This Raman data suggests the phases with slightly different chemistry from FeS$_2$. The XRD pattern of a 14hrs ESD product shows four extra lines near 26°. Other FeS$_3$ phases, Fe$_7$S$_8$, Fe$_3$S$_4$, Fe$_{10}$S$_{11}$, Fe$_{11}$S$_{12}$, can have these XRD lines. In VNIR spectra, a band center shift was observed in 14hrs ESD product from the starting FeS$_2$.

**Conclusion:** The effects on Fe-phases by ESD-NGD in martian dust events were found to be dehydration, amorphization, oxidation of Fe$^{2+}$, the loss of S from sulfides and loss of Cl from chlorides.

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