

MARTIAN CARBONATES GENERATED BY ATMOSPHERE-SURFACE INTERACTION. Alian Wang¹, Yuanchao Yan¹, Jen Houghton¹, Bradley Jolliff¹, Andrew Jackson², Neil Sturchio³, Michael Smith⁴, and Kevin Olsen⁵, ¹Dept. Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University in St. Louis, MO, 63130, USA; ²Dept. Civil, Environmental, and Construction Engineering, Texas Tech University, USA; ³Dept. Earth Science, University of Delaware, USA; ⁴NASA Goddard Space Flight Center, USA, ⁵Dept. Physics, Oxford University, UK; (alianw@levee.wustl.edu)

Heterogeneous electrochemistry: The electrification of atmospheric species (e.g., aerosol, ice particle) and dust particles is very likely a ubiquitous process operating on many planetary bodies. A local electric field will form when charged particles are separated by atmospheric processes, such as dust activities on Mars. Electrostatic discharge (ESD) can happen when the strength of an accumulated electric field grows beyond the *breakdown electric field threshold* of a planet.

An ESD event will generate a large quantity of high-speed-electrons, i.e., electron avalanche, which can collide with atmospheric molecules, such as CO₂, Ar, N₂, O₂, and H₂O on Mars. These collisions will induce molecular ionization, dissociation, and excitation [1], resulting in free radicals, i.e., positively and negatively charged ions, neutral molecules and atoms at excited states [2, 3]. With high electrochemical reactivity and kinetic energy inherited through momentum transfer, they will stimulate the heterogeneous electrochemistry in the planetary atmosphere and at the planetary surface, especially on Mars.

During a set of laboratory investigations supported by the NASA SSW program, we made three major discoveries relevant to Mars:

1. *The phase transformation from chloride (Cl⁻) to chlorate/perchlorate (Cl⁵⁺, Cl⁷⁺), through ESD process under Mars relevant conditions, with high rate and high yield [4];*
2. *The instantaneous release of chlorine as free moving Cl atom at 1st excited state (ClI) from common K, Na, Ca, Mg, Fe, Al-chlorides during medium-strength ESD processes, also has high yields [3];*
3. *The amorphization and dehydration of S, Cl-salts, and the oxidation of Cl, S, Fe made by*

ESD under Mars atmospheric conditions, with relatively high rates [5].

These findings address the following three mission observations on Mars:

1. The high concentration of oxychlorine salts in upper regolith on Mars [6];
2. The correlation of transient atmospheric HCl concentration with martian dust season, especially the global dust storm [7, 8];
3. The high % of X-ray amorphous component in CheMin analyzed samples at Gale Crater, especially their SO₃, Cl, H₂O enrichment [9, 10].

During a new SSW investigation, one of our objectives is the generation of the martian carbonates through atmosphere-surface interaction, especially the heterogeneous electrochemistry, as a possible sink of CO₂ into martian surface materials.

Figure 1. Carbonates detected in 7-hours ESD products from 4 chlorides in 3mb CO₂

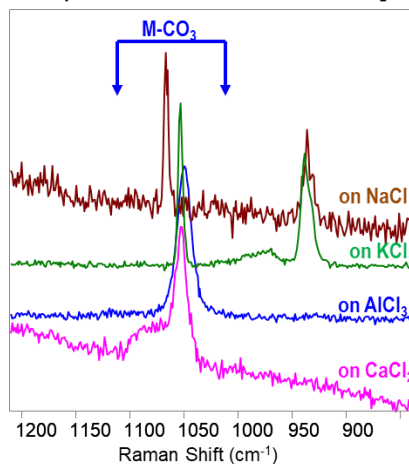
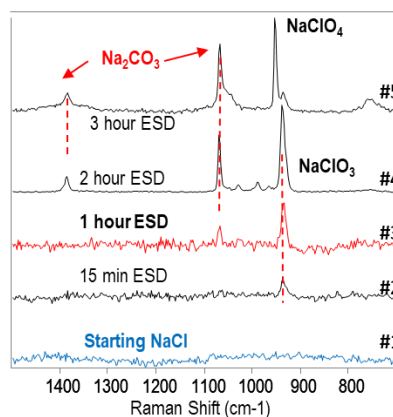


Figure 2. Forming Na₂CO₃ after 1 hour of ESD on NaCl in 3 mb CO₂



Martian carbonates: The rare detection of martian carbonate outcrops has been a mystery in Mars fundamental sciences. The carbonate-rich outcrops (deposited from fluids) have only been detected at a few sites by orbital remote sensing and landed missions, e.g., at Nili Fossae with phyllosilicate-bearing and olivine-rich rock units [11]; at Gusev crater ~16-34 wt.% in Comanche outcrop [12]; and at Jezero crater with olivine and Fe/Mg-smectite [13, 14]. The potential sink for CO₂ (95% in current martian atmosphere) has always been a key question in Mars fundamental sciences.

Carbonates formed by atmospheric processes were suggested by some mission observations and meteorite studies. For example, Ca-carbonate (3-5 wt.%) in the soil around Phoenix landing site was judged to be

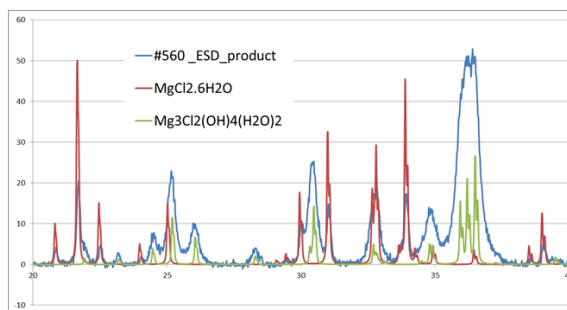
formed by the interaction of atmospheric CO_2 with liquid water films on particle surfaces in the past [15]. At Gale crater, SAM detected CO_2 evolved from 450-800 °C that was consistent with the contribution from Fe & Mg-rich carbonates [16]. Carbonates were found in martian meteorites, at < 1 vol.% [17]. The carbonates in ALH84001 have been studied extensively [18,19,20]. Based on triple oxygen isotope study of carbonates in ALH84001, Farquhar et al. [21] suggested two oxygen isotope reservoirs: the atmosphere and the silicate planet, at the time of carbonate growth in this meteorite. The cause of the triple oxygen isotope anomaly ($\Delta^{17}\text{O}$) in “atmospheric” carbonates was suggested [21] to be the isotopic exchange between CO_2 and $\text{O}(\text{ID})$ produced by the photodecomposition of O_3 .

Evidences of carbonate formation through heterogeneous electrochemistry: we have observed evidences of carbonate formation in atmosphere-salts interaction, i.e., ESD process on common chlorides under martian atmospheric conditions [3, 5].

Figure 1 shows the Raman spectra collected at the surfaces of KCl, NaCl, CaCl_2 , and AlCl_3 powder after 7-hours ESD processes. The Raman peaks between 1050-1100 cm^{-1} (a range marked by blue arrows in Fig.1) are symmetric stretching vibration modes (ν_1) of CO_3^{2-} in carbonates. The exact ν_1 peak positions of K_2CO_3 , Na_2CO_3 , CaCO_3 , and $\text{Al}_2(\text{CO}_3)_3$ are different. In addition, the formation rate of carbonate is very high, evidenced (Figure 2) by the appearance of ν_1 peak of Na_2CO_3 after only one hour of ESD process on NaCl powder in a simulation chamber at 3 mb CO_2 .

To quantify the yields of carbonates through ESD, we dissolved the 7-hours ESD product from MgCl_2 and from CaCl_2 into $\text{DI-H}_2\text{O}$. Based on the huge difference in solubility between MgCO_3 and MgCl_2 -Mg-oxychlorine salts (0.18g vs. 56-142g, in 100g H_2O), CaCO_3 and CaCl_2 -Ca-oxychlorine salts (0.0007g vs. 81-197g, in 100g H_2O), we extracted MgCO_3 and CaCO_3 from the insoluble residuals. We found the intriguingly high carbonate yield: *MgCO_3 at 2.37 wt. % and CaCO_3 at 0.55 wt. % in top-layer of ESD products.* These successful extractions confirmed the *in situ* Raman observation of carbonate peaks in ESD products (Fig. 1, 2). They further demonstrated that the

Figure 3. XRD patterns of 7hr ESD product from MgCl_2 in 3mb CO_2 , compared with standards



$\text{Mg}_2\text{Cl}_2(\text{OH})_4.2\text{H}_2\text{O}$ was found by XRD measurement (Figure 3) in the top layer of the ESD product from MgCl_2 , after a few days exposure in laboratory. The forming of OH/ H_2O -bearing species demonstrated that some additional species with high chemical reactivity were generated by ESD process in 3 mb CO_2 , which need further study. Additional Raman, Mid-IR, and VNIR measurements all support this observation.

On-going study: We plan to use a different technology [22] for the extraction of carbonates from ESD products, with quantitative information. Thus the carbonate yield can be precisely evaluated, and to be compared with other process such as photochemistry.

We will conduct the isotopic analysis of carbon and oxygen in these carbonates with atmospheric origin, which will be significant for understanding the electrochemical processes that generated them.

Simultaneously, the extraction, purification, and isotopic analysis of chlorate (KClO_3) and perchlorate (KClO_4) from ESD on KCl in 3mb CO_2 are ongoing. The results will be reported at the conference.

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References: [1] Jackson et al., (2010), JGR-P; [2] Bak et al., (2017), EPSL; [3] Wang et al., (2020a), JGR-P; [4] Wu et al., (2018), EPSL. [5] Wang et al., (2020b), JGR-P; [6] Hecht et al., (2009), Science; [7] Olsen et al., (2021), A&A; [8] Korabiev et al., (2021), Science Advances; [9] Vaniman et al., (2014), Science; [10] Morrison et al., (2018), Am. Mineral., [11] Ehlmann et al., (2008), Science; [12] Morris et al., (2010), Science; [13] Goudge et al., (2015), JGR-P; (2017), EPSL; [14] Horgan et al., (2020), ICARUS; [15] Boynton et al., (2009), Science; [16] Sutter et al., (2019), in *Volatiles in Martian Crust*; [17] Bridges et al., (2001), Space Science Reviews; [18] Valley et al., (1997), Science; [19] Borg et al., (1999), Science; [20] Eiler et al., (2002), GCA; [21] Farquhar et al., (1998), Science; [21] Lide (2001), *Handbook of Chemistry and Physics*; [22] McCrea (1950), J. Chem. Phys..

carbonate yield from various chlorides is affected by the chemical bonding between the metal ion and chlorine.

In addition to the formation of carbonates and oxychlorates, the heterogeneous electrochemical reactions are complicated with multiple active products. For example,