A preliminary experimental study of Cl cycle on present day Mars. Wenshuo Mao[1], Zhongchen Wu[1]*, Xiaohui Fu[1,2]*, Jiang Zhang[1], Yuheng Ni[1](Email:z.c.wu@sdu.edu.cn).[1]Shandong Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, School of Space Science and Physics, Institute of Space Sciences, Shandong University, Weihai, China. [2]CAS Center for Excellence in Comparative Planetology, Hefei 230026, China.

Introduction: Mars missions (orbiters, landers and rovers) have revealed the widespread distribution of chloride on the surface of Mars. Chlorine is one of the highly mobile elements that have been actively involved in surface geological processes on ancient and modern Mars. Its valence states also changes by the redox reaction of photochemistry[1,2], cosmic gamma rays[3], and multiphase redox plasma chemistry caused by electrostatic discharge (ESD)[4]. Recently, Korablev et al. (2021)[5] reported the halogen gas HCl (1-4 ppbv) was firstly detected by ExoMars Trace Gas Orbiter in the atmosphere of Mars after dust storm events4. This is the most typical example of the current active Cl cycle on Mars.

Oxychlorides have also been discovered on Mars such as Phoenix landing site[6], Curiosity landing site[7], which indicates ClOx species (i.e. perchlorate, chlorate) are important components of the chlorine budget, ubiquitous on the surface of Mars, and persistent throughout the history of Martian geological evolution. Furthermore, perchlorate was found in Martian meteorites EETA79001 and Tissint[8,9].

Except of the stable perchlorate, chlorate, other oxidized forms of chlorine may also transiently exist on the surface of Mars, such as pypocholoride, chlorite, and so on as intermediates or unstable end reaction products in the Cl cycle (Figure1). The presence and variety of chlorine and oxychlorine on Mars are very important indicators of the oxidizing processes in the ancient and modern Martian environment such as a sink of water, the formation of brines at low temperatures and destroy organic molecules[10].

The formation and decomposition mechanisms of perchlorate on Mars: Several formation mechanisms have been proposed to explain high abundance of oxychlorines in the Martian soils: ultraviolet (UV) photocatalysis[2,3], energetic electrons[11], cosmic gamma rays[3], and multiphase redox plasma chemistry caused by electrostatic discharge (ESD)[4]. However, when perchlorates were exposed to energetic electrons and gamma rays, reduction reactions might take place to form chlorates (ClO_3^-), hypochlorite (ClO^-), oxygen (O_2), and chlorine dioxide (ClO_2)[12,13]. Our experiments indicated that oxychlorine will undergo oxidation-reduction reactions and form chlorine dioxide during the ESD process.

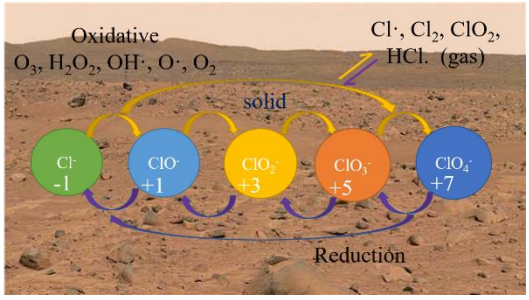

Figure1. Potential evolution path of Cl cycle on Mars surface.

Experiments: The ESD normal glow discharge (NGD) were conducted in a Mars chamber which is capable of maintaining Mars atmospheric pressure, composition (pure CO_2 or Mars atmosphere simulation gas) and one ClO_2 gas sensor for end gas detection.

Herein, our ESD-NGD experiment is carried out in a pure CO_2 gas. The oxychlorine samples selected for our experiments were $NaClO_2$, $NaClO_3$ and $NaClO_4$ with time durations of 30 minutes to 5 hours.

We used Mid-IR attenuated total reflectance (ATR) spectra to characterize the oxychlorine species generated by electrochemistry in ESD process.

Results: We observed the significant enrichment of ClO_3^- in the ESD products with $NaClO_2$ and $NaClO_4$ as starting material (ClO_2^- > ClO_3^- and ClO_4^- > ClO_3^-) (Figure 2). It was also noted the ClO4- presented in the ESD products with $NaClO_3$ as starting materials (ClO_3^- > ClO_4^-) (Figure 2). In addition, CO_3^{2-} was also detected in all ESD products (all oxychlorine starting material). A small amount ClO_2 gas have detected in all ESD products exhaust by ClO_2 sensor.

Implications: Our results indicated that oxychlorine undergoes redox reactions during the ESD process except of oxidizing reaction, and release ClO_2 gas. $Cl^- \leftrightharpoons ClO_2^- \leftrightharpoons ClO_3^- \leftrightharpoons ClO_4^-$ objectively generates/exists in the solid-solid reaction during ESD process. The release of gas ClO_2 is also an important part of the gas-solid reaction which played an important role in the Cl cycle on present day Mars. Our next step of this project is ongoing in two aspects 1) characterize other gas species in the exhaust gas, e.g. Cl_2, HCl. 2) quantitative analysis the ESD products to clarify the Cl cycle reaction path.

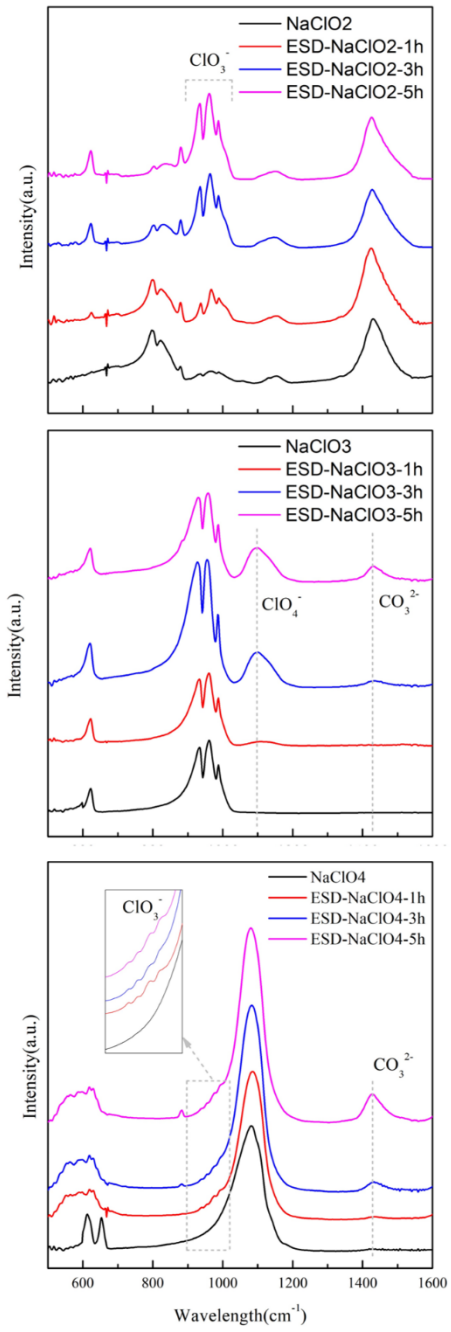

Figure 2. Mid-IR spectra of starting oxychlorine and ESD products. a) $NaClO_2$ and ESD products. b) $NaClO_3$ and ESD products. c) $NaClO_4$ and ESD products.

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