FE MINERALOGY CONTROLS ON GENERATION RATIO OF CHLORATE/PERCHLORATE ON THE MARTIAN SURFACE. Shuai-Yi Qu1,2, He Cui3, Xiuzhen Yin4, W Andrew Jackson4, Xin Nie5, Zhong-Chen Wu6, Yu-Yan Sara Zhao1,7# (Email: zhaoyuyan@mail.gyig.ac.cn). 1Center for Lunar and Planetary Sciences, Institute of Geochemistry Chinese Academy of Sciences, Guiyang 550081, China; 2 University of Chinese Academy of Sciences, Beijing 100049, China; 3Technical Center of Qingdao Customs, Qingdao 266002, China; 4Department of Civil Engineering, Texas Tech University, Lubbock, TX 79409-1022, USA; 5State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry Chinese Academy of Sciences, Guiyang 550081, China; 6Institute of Space Science, Shandong University, Weihai 264209, China; 7CAS Center for Excellence in Comparative Planetology, Hefei 230026, China.

Introduction: The perchlorate (ClO₄⁻) and chlorate (ClO₃⁻) have important implications for the modern habitability of Mars, including liquid water, redox environments, bioavailability, and in-situ resource utilization. To date, oxychlorine species (ClO₃⁻) are suggested to be ubiquitously present on the martian surface, but the specific speciations are not well-constrained. The perchlorate has been identified in the soil at the Phoenix site and in the martian meteorites [1-3]. Further reanalysis of the Phoenix soil data suggests that ClO₄⁻ may also present at an equal or higher abundance of the ClO₃⁻ [4]. The dominance of ClO₄⁻ or ClO₃⁻ is critical because the two species show different capabilities to depress the freezing points of water, and their chemical activity and bioavailability are also different [e.g., 5-7]. The ClO₄⁻/ClO₃⁻ ratios present on Mars are a combination of their generation ratios and subsequent decomposition, yet little is known on the controls of ClO₄⁻/ClO₃⁻ generation ratios.

Our previous experimental studies indicate that Fe mineralogy may influence the ClO₄⁻/ClO₃⁻ generation ratios [8]. Here in this work, we systematically investigate the ClO₄⁻/ClO₃⁻ generation ratios by mixing halite salt or halite solution with Fe-sulfates and Fe-(hydr)oxides under three oxidative conditions (i.e., UV₂54nm + Mars atm., UV₂54nm + Earth atm., and ozone). This work in the synthesis of previous experimental studies provides a conceptual model for ClO₄⁻/ClO₃⁻ generation ratios in different surficial environments on Mars.

Methods: Fe minerals used in this work include three Fe-sulfates (i.e., hydrated Fe³⁺-sulfate; amorphous Fe³⁺-sulfate gel (water content 29.99%); a mixture of ferricopiapite and rhomboclase) and four Fe-(hydr)oxides (i.e., 2-line ferrhydrite, akaganite, goethite, and magnetite). Halite salt was mixed with each Fe mineral (mass ratio 1:7) except for akaganite, which already includes chloride in its structure. Pure halite salt was also examined as the control experiment.

For the ultraviolet (UV) experiments, two aliquots of the mineral mixtures were exposed to the UV₂54nm lamps for 144 h at 25°C and 1 bar. Simulating Mars atmosphere (i.e., CO₂) and Earth atmosphere (dry ambient air) were flushing through the chamber at a rate of 0.7 L/min. For mineral-ozone experiments, the same initial mineral mixtures as used in the UV experiments were placed in the reaction vessel, under conditions of constant O₃ concentration (30 mg/L) and continuous flow (30 mL/min) for 24 hours. To examine the role of liquid water, 100 ml 0.34 M NaCl solution was mixed with 3.5 g of hydrated Fe-sulfate, 2-line ferrhydrite, magnetite, or quartz sand, respectively, and then interacted with O₃ gas for 24 hours. Initial Cl⁻, O₃ flow rate and experiment time were the same in both mineral- or solution-zone experiments. The Cl⁻, ClO₃⁻ and ClO₄⁻ were analyzed by ion chromatography-mass spectrometry. The detection limit of ClO₄⁻ and ClO₃⁻ was 0.01 µg/L, and the quantification limit was 0.03 µg/L. The ClO₃⁻ and ClO₄⁻ yields were normalized to 1 mole of initial Cl⁻ for comparison across different experiments.

Results: The ClO₄⁻ yields and ClO₃⁻/ClO₄⁻ ratios produced by UV irradiation. As shown in Fig. 1, the ClO₄⁻ yields by pure halite and Fe-sulfates are similar. By contrast, Fe-(hydr)oxides produce orders of magnitude higher ClO₄⁻ than the pure halite and Fe-sulfates. The UV+Earth condition produces orders of magnitude higher ClO₄⁻ than the UV+Mars condition. The ClO₄⁻/ClO₃⁻ ratio generated by pure halite is around 2.5. All the Fe-sulfates produce ClO₄⁻/ClO₃⁻ ratios close to 0.01, and all the Fe-(hydr)oxides produce ClO₄⁻/ClO₃⁻ ratios more than 100. Correlation analysis demonstrates that variations of ClO₄⁻ primarily control the ClO₄⁻/ClO₃⁻ generation ratios. The atmospheric conditions (Earth vs. Mars) show no substantial influence on the ClO₃⁻ or ClO₄⁻ dominance.

The ClO₄⁻ yields and ClO₃⁻/ClO₄⁻ ratios produced by ozone oxidation. Like found in the UV experiments, mineral-ozone experiments show that ClO₄⁻ production by Fe-(hydr)oxide mixtures (3.81 to 97.66 mmol) are orders of magnitude higher than those produced by Fe-sulfate mixtures (0.001 to 0.02 mmol). Also, ClO₄⁻ dominates with Fe-sulfates, and ClO₃⁻ dominate with Fe-(hydr)oxides. The only exception is the pure halite, of which ClO₄⁻/ClO₃⁻ ratio is ~0, reversed to ClO₄⁻ dominance under UV irradiation.
In the solution-ozone experiments, hydrated Fe-sulfate dissolves to form an acidic Fe$^{3+}$-Na$^+$-SO$_4^{2-}$-Cl$^-$ solution (pH = 1.7) and produces the lowest ClO$_3^-$ (0.291 mmol) of the four minerals examined. Ferrihydrite, magnetite and quartz without substantial dissolution produce higher ClO$_3^-$ of 4.731 mmol, 4.142 mmol, and 5.142 mmol, respectively. The ClO$_3^-$ yields of solution-ozone experiments strongly correlate to the specific surface area of the minerals. The mineral surface mainly provides an interface for the ozone oxidation processes. With ozone, the solutions/suspensions consistently produce predominant ClO$_3^-$ regardless of the mineral types.

Factors controlling ClO$_3^-$/ClO$_4^-$ generation ratios. Our results demonstrate that the characteristics of minerals (e.g., catalyst, surface area, acidity) and physical states of initial chloride (solid, liquid, gas) are the primary factors that control ClO$_3^-$/ClO$_4^-$ generation ratios. Oxidation methods (UV vs. ozone) and atmospheric O$_2$ contents are secondary factors. Depending on the specific system, mineral characteristics and physical states of chloride may simultaneously contribute to the ClO$_3^-$ production rates and ClO$_3^-$/ClO$_4^-$ generation ratios.

Implications for Mars: This study in the synthesis of previous experimental studies highlight the ClO$_3^-$/ClO$_4^-$ generation ratios in different surficial environments relevant to Mars (Fig. 2). In the atmosphere, when ozone oxidation is in effect, the gaseous HCl, aerosol/dust of chloride salts, or chloride-Fe sulfate mixtures would produce ClO$_3^-$ $>>$ ClO$_4^-$.

Aerosols/dusts of chloride-Fe-(hydr)oxide mixtures or aqueous chloride would result in ClO$_3^-$ $>>$ ClO$_4^-$, when UV irradiation is primarily effective, the ClO$_3^-$/ClO$_4^-$ generation patterns of the suspensions in the atmosphere and minerals on the ground are controlled by the type of minerals. Specifically, Fe-sulfates, as observed in the Paso Robles soils of Gusev Crater, would result in ClO$_3^-$ $>>$ ClO$_4^-$, Non-Fe-sulfates, halides, silicates, or non-Fe oxides would produce ClO$_3^-$ $\geq$ ClO$_4^-$. Fe-(hydr)oxides, which are ubiquitous present in the martian soils and some local areas where Fe-oxidation processes occur [9,10], would result in ClO$_3^-$ $>>$ ClO$_4^-$. 

Our model strongly supports the ClO$_3^-$ dominant of the ClO$_4^-$ species on Mars, facilitated by the (hyper)arid climate and ubiquitous Fe-(hydr)oxides since the Amazonian. Therefore, the chlorate rather than perchlorate should be the key species in the future discussion on the ClO$_3^-$ related redox environments, habitability, interference in in-situ organic analysis, and in-situ resource utilization for Mars.

**Fig. 1.** The ClO$_3^-$ yields of different mineral mixtures under three oxidative conditions. The ClO$_3^-$ yields are normalized to 1 mole of initial Cl$^-$ for comparison. On each bar, the dark and light colors represent ClO$_3^-$ and ClO$_4^-$ fraction, respectively, of the total ClO$_3^-$.  

**Fig. 2.** The conceptual model for ClO$_3^-$/ClO$_4^-$ generation ratios in different surficial environments of present Mars. Our model strongly supports the ClO$_3^-$ dominant of the ClO$_4^-$ species on Mars, facilitated by the (hyper)arid climate and ubiquitous Fe-(hydr)oxides since the Amazonian.