

FE MINERALOGY CONTROLS ON GENERATION RATIO OF CHLORATE/PERCHLORATE ON THE MARTIAN SURFACE. Shuai-Yi Qu^{1,2}, He Cui³, Xiu-Zhen Yin³, W Andrew Jackson⁴, Xin Nie⁵, Zhong-Chen Wu⁶, Yu-Yan Sara Zhao^{1,7*} (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 (ClO_4^-) and chlorate (ClO_3^-) have important implications for the modern habitability of Mars, including liquid water, redox environments, bioavailability, and in-situ resource utilization. To date, oxychlorine species (ClO_x^-) 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 ClO_3^- may also present at an equal or higher abundance of the ClO_4^- [4]. The dominance of ClO_4^- or ClO_3^- 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 $\text{ClO}_3^-/\text{ClO}_4^-$ ratios present on Mars are a combination of their generation ratios and subsequent decomposition, yet little is known on the controls of $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios.

Our previous experimental studies indicate that Fe mineralogy may influence the $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios [8]. Here in this work, we systematically investigate the $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios by mixing halite salt or halite solution with Fe-sulfates and Fe-(hydr)oxides under three oxidative conditions (i.e., UV_{254nm} + Mars atm., UV_{254nm} + Earth atm., and ozone). This work in the synthesis of previous experimental studies provides a conceptual model for $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios in different surficial environments on Mars.

Methods: Fe minerals used in this work include three Fe-sulfates (i.e., hydrated Fe^{3+} -sulfate; amorphous Fe^{3+} -sulfate gel (water content 29.99%); a mixture of ferricopiapite and rhombooclase) and four Fe-(hydr)oxides (i.e., 2-line ferrihydrite, akaganeite, goethite, and magnetite). Halite salt was mixed with each Fe mineral (mass ratio 1:7) except for akaganeite, 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 UV_{254nm} lamps for 144 h at 25°C and 1 bar. Simulating Mars atmosphere (i.e., CO_2) 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 O_3 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 ferrihydrite, magnetite, or quartz sand, respectively, and then interacted with O_3 gas for 24 hours. Initial Cl^- , O_3 flow rate and experiment time were the same in both mineral- or solution-zone experiments. The Cl^- , ClO_4^- and ClO_3^- were analyzed by ion chromatography-mass spectrometry. The detection limit of ClO_4^- and ClO_3^- was 0.01 $\mu\text{g}/\text{L}$, and the quantification limit was 0.03 $\mu\text{g}/\text{L}$. The ClO_4^- and ClO_3^- yields were normalized to 1 mole of initial Cl^- for comparison across different experiments.

Results: *The ClO_x^- yields and $\text{ClO}_3^-/\text{ClO}_4^-$ ratios produced by UV irradiation.* As shown in Fig. 1, the ClO_x^- yields by pure halite and Fe-sulfates are similar. By contrast, Fe-(hydr)oxides produce orders of magnitude higher ClO_x^- than the pure halite and Fe-sulfates. The UV+Earth condition produces orders of magnitude higher ClO_x^- than the UV+Mars condition. The $\text{ClO}_3^-/\text{ClO}_4^-$ ratio generated by pure halite is around 2.5. All the Fe-sulfates produce $\text{ClO}_3^-/\text{ClO}_4^-$ ratios close to 0.01, and all the Fe-(hydr)oxides produce $\text{ClO}_3^-/\text{ClO}_4^-$ ratios more than 100. Correlation analysis demonstrates that variations of ClO_3^- primarily control the $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios. The atmospheric conditions (Earth vs. Mars) show no substantial influence on the ClO_3^- or ClO_4^- dominance.

The ClO_x^- yields and $\text{ClO}_3^-/\text{ClO}_4^-$ ratios produced by ozone oxidation. Like found in the UV experiments, mineral-ozone experiments show that ClO_x^- 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, ClO_4^- dominates with Fe-sulfates, and ClO_3^- dominate with Fe-(hydr)oxides. The only exception is the pure halite, of which $\text{ClO}_3^-/\text{ClO}_4^-$ ratio is ~0, reversed to ClO_3^- dominance under UV irradiation.

In the solution-ozone experiments, hydrated Fe-sulfate dissolves to form an acidic $\text{Fe}^{3+}\text{-Na}^+\text{-SO}_4^{2-}\text{-Cl}^-$ solution ($\text{pH} = 1.7$) and produces the lowest ClO_x^- (0.291 mmol) of the four minerals examined. Ferrihydrite, magnetite and quartz without substantial dissolution produce higher ClO_x^- of 4.731 mmol, 4.142 mmol, and 5.142 mmol, respectively. The ClO_x^- 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.

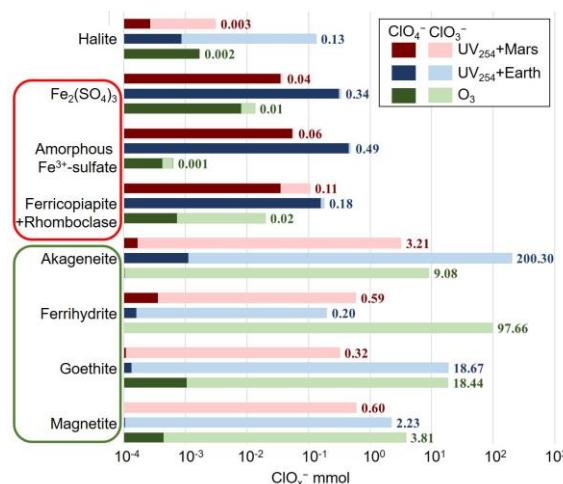


Fig. 1. The ClO_x^- yields of different mineral mixtures under three oxidative conditions. The ClO_x^- yields are normalized to 1 mole of initial Cl^- for comparison. On each bar, the dark and light colors represent ClO_4^- and ClO_3^- fraction, respectively, of the total ClO_x^- .

Factors controlling $\text{ClO}_3^-/\text{ClO}_4^-$ 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 $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios. Oxidation methods (UV vs. ozone) and atmospheric O_2 contents are only secondary factors. Depending on the specific system, mineral characteristics and physical states of chloride may simultaneously contribute to the ClO_x^- production rates and $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios.

Implications for Mars: This study in the synthesis of previous experimental studies highlight the $\text{ClO}_3^-/\text{ClO}_4^-$ 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 $\text{ClO}_4^- \gg \text{ClO}_3^-$.

ClO_3^- . Aerosols/dusts of chloride-Fe-(hydr)oxide mixtures or aqueous chloride would result in $\text{ClO}_3^- \gg \text{ClO}_4^-$. When UV irradiation is primarily effective, the $\text{ClO}_3^-/\text{ClO}_4^-$ 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 $\text{ClO}_4^- \gg \text{ClO}_3^-$. Non-Fe-sulfates, halides, silicates, or non-Fe oxides would produce $\text{ClO}_3^- \geq \text{ClO}_4^-$. 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 $\text{ClO}_3^- \gg \text{ClO}_4^-$.

Our model strongly supports the ClO_3^- dominant of the ClO_x^- 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_x^- related redox environments, habitability, interference in in-situ organic analysis, and in-situ resource utilization for Mars.

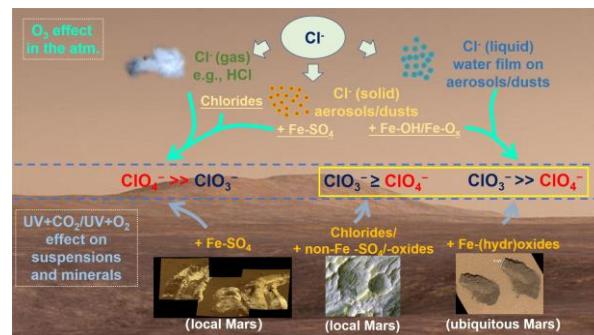


Fig. 2. The conceptual model for $\text{ClO}_3^-/\text{ClO}_4^-$ generation ratios in different surficial environments of present Mars. Our model strongly supports the ClO_3^- dominant of the ClO_x^- species on Mars, facilitated by the (hyper)arid climate and ubiquitous Fe-(hydr)oxides since the Amazonian.

- References:**
- [1] Hecht, M. H. et al. (2009) *Science*, 325, 64-67.
 - [2] Kounaves, S. P. et al. (2014) *Icarus*, 229, 206-213.
 - [3] Jaramillo, E. A. (2019) *Geophys Res Lett*, 46, 3090-3098.
 - [4] M Toner, J. D. et al. (2014) *Geochim Cosmochim Ac*, 136, 142-168.
 - [5] Hanley, J. et al. (2012) *Geophys Res Lett*, 39.
 - [6] Brundrett, M. et al. (2019) *Acs Earth Space Chem* 3, 700-710.
 - [7] Jackson, W. A. et al. (2015) *Geochim Cosmochim Ac*, 164, 502-522.
 - [8] Zhao, Y. Y. S. et al. (2018) *Earth Planet Sc Lett* 497, 102-112.
 - [9] McLennan, S. M. et al. (2005) *Earth Planet Sc Lett*, 240, 95-121.
 - [10] Bish, D. L. (2013) *Science* 341.