

Oxidation of Halite (NaCl) during Global Dust Storms on Mars

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Introduction

The present-day Martian surface is highly oxidized: multiple-valency elements are found in their oxidized states and incorporated into oxidized minerals. Among these, chlorates (XClO_3 ; $\text{X} = \text{cations}$) and perchlorates (XClO_4 ; $\text{X} = \text{cations}$) are particularly significant since they can be antifreezes forming liquid brine and oxidants providing bioavailable chemical energy [1, 2]. Several proposed mechanisms for chlorate and perchlorate formation on Mars have focused on homogeneous gas-phase photochemistry [3]. However, photochemical mechanisms alone cannot account for the perchlorate concentration or the high $\text{ClO}_4^-:\text{Cl}^-$ ratio measured by in-situ instruments [3]. Electrostatic discharge events [4] and UV irradiation onto halite (NaCl)-silicate mixtures [5] can be two additional formation mechanisms for the large amounts of perchlorate observed. [5] reproduced the high $\text{ClO}_4^-:\text{Cl}^-$ ratio measured by the Phoenix lander through exposing halite-silicate mixtures to UV radiation in the presence of catalysts, under a 14mbar 10% O_2 atmosphere. The previous study [4] also suggested that Martian perchlorates underwent radiolytic degradation over time, implying that perchlorates were part of a dynamic chlorine cycle.

The chlorine cycle on Mars includes the seasonal appearance of hydrogen chloride (HCl) in the atmosphere, particularly during the months around the southern hemisphere's summer. This phenomenon, observed by ESA's ExoMars Trace Gas Orbiter [6], coincides with the occurrence of the dust storm season. This finding suggests the existence of an efficient and dynamic chlorine exchange between atmospheric gases and dust particles.

In the present study, we propose a new mechanism forming chlorates and perchlorates during dust storms, in which halite dust grains are lifted into the Martian troposphere and stratosphere. NASA's MAVEN spacecraft has found dust transport up to 150 km altitude during dust storm [7]. In the stratosphere, halite grain may undergo heterogeneous (gas-solid) reactions with atomic oxygen formed through CO_2 photolysis. This process may form chlorates and/or perchlorates on the surface of halite grains, which subsequently settle on the surface. In this study, we performed laboratory experiments to simulate the reaction between halite (NaCl) grain and O atom in the stratosphere of Mars. Then, we discuss the role of this reaction in the chlorine cycle on Mars.

Methods

In the experiments, we irradiated NaCl disks (diameter 10mm, thickness 2mm: IR System Co., Ltd.) with atomic oxygen formed by cold plasma (13.56 MHz RF power supply, Nihon Koshuha). The experimental system was an open system with a continuous gas supply and evacuation with a rotary pump (Figure 1).

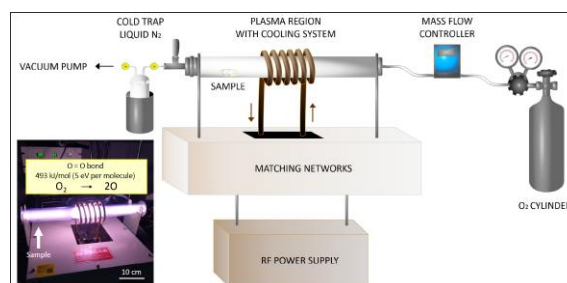


Figure1. A schematic diagram of the experimental setup for RF plasma irradiation

Pure O_2 gas (>99.999% by volume; Taiyo Nippon Sanso, Japan) was continuously intro-

duced into the quartz glass reaction tube using a mass-flow controller with a flow rate of 1 standard $\text{cm}^3 \text{min}^{-1}$ (sccm), ensuring a stable pressure of approximately 100 Pa inside the quartz tube. We set a NaCl disk inside the quartz tube during the O atom irradiation. In the downstream of the quartz tube, a cold trap with liquid N_2 (at 77K) was set to trap gaseous species produced through irradiation of O atoms onto NaCl. In the cold trap, 10mL of ultrapure water was introduced before the irradiation.

After irradiation for different times, the NaCl disk was extracted and analyzed using Time of Flight – Secondary Ions Mass Spectrometry (TOF-SIMS 5-100-AD, ION-TOF GmbH). TOF-SIMS provides depth profiles of ClO_x ($x = 0-4$) from the surface of the irradiated NaCl disk to assess chlorate and perchlorate formation. In the cold trap with liquid N_2 , whitish ice flakes were precipitated after the irradiation. The ice flakes were dissolved in the ultrapure water upon a rise of the temperature to the room temperature. The ultrapure water was dissolved 10 times and analyzed by ion chromatography (Dionex-2000 ICS-1100, ThermoFisher Scientific), where the separation of anionic species in solution involved an IonPac AS22 column (ThermoFisher Scientific).

Results

TOF-SIMS analysis shows the formation of hypochlorite, chlorate and perchlorate on the irradiated surface of NaCl (Figure 2). In TOF-SIMS analysis, the surface materials are sputtered through the irradiation of a primary ion beam onto the sample. Thereby, the sputter time in Fig. 2 corresponds to the depth from the surface. The depth profile of Cl^- , ClO^- , ClO_3^- , and ClO_4^- from the surface before the irradiation shows that there are no significant signals of ClO_3^- or ClO_4^- . The ClO^- signals throughout the sample before the O irradiation may be due to H_2O molecules adsorbed on NaCl sample. After

30 minutes of O atom irradiation, however, a high level of ClO_4^- appears at the surface of the disk until 100s of sputter time. The ClO_3^- and ClO^- levels are about 1/10 of that of ClO_4^- at the surface. After 5 hours of O irradiation, the ClO_4^- level at the surface does not change significantly, whereas ClO_4^- signals appear at greater depth in the sample. The near constant ClO_4^- levels after 30 minutes and 5 hours suggest that the ClO_4^- formation at the surface becomes saturated after 30 minutes of atomic O irradiation. The deepening of ClO_4^- in the sample after 5 hours of O irradiation would be because the surface NaClO_4 may be sputtered by irradiation of O atoms. The surface sputtering would allow O atoms to enter into the greater depth in the sample.

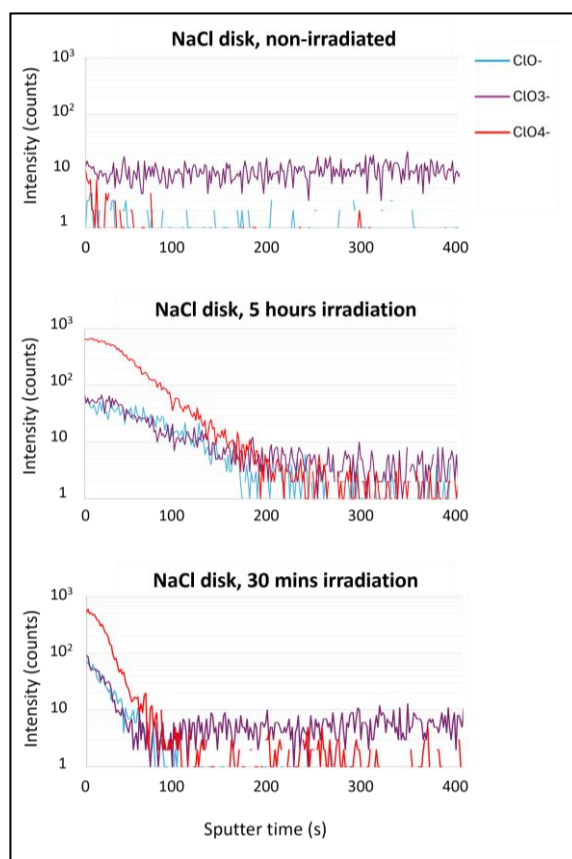


Figure 2. TOF-SIMS analysis shows the formation of ClO^- , ClO_3^- and ClO_4^- after atomic oxygen irradiation. On the top is a non-irradiated sample, for reference.

The idea of surface sputtering may be supported by the results of IC analysis for the entrapped ice materials in the cold trap. Our results of IC analysis show the presence of a small peak corresponding to perchlorate (ClO_4^-) at the retention time of 23.5 minutes (Figure 3). The peaks due to ClO^- and ClO_3^- are less than the detection limits.

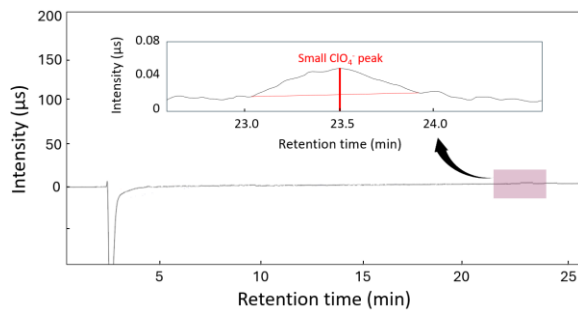


Figure 3. Overall chromatogram, with enlarged section at retention time of 23.5 minutes.

Discussion

The atomic O flux in our experiments can be estimated as $\sim 10^{15}$ atoms/second based on the O_2 pressure in the quartz tube and the dissociation fraction of O_2 into O, latter of which has been estimated about 10% for RF plasma [8]. Given the fact that the surface of our sample was saturated with ClO_4^- in 30 minutes, the O atoms number required to form ClO_4 on NaCl is estimated as 2×10^{18} atoms. On the other hand, atomic O densities in different altitudes of the Martian atmosphere have been estimated based on NASA's MAVEN NGIMS in situ measurements and photochemical models [9, 10]. According to the previous studies [9, 10], the collision of O with 2×10^{18} atoms onto NaCl surface can be achieved in 3.6×10^4 years in the stratosphere, and 3.6×10^6 years in the troposphere, assuming low solar activity.

Global dust storms occur every 3–5 years on Mars. Our scenario of NaCl oxidation would work only at the timing of global dust storms; however, the estimated timescale for ClO_4 for-

mation is geologically short.

Our findings suggest that NaCl on the surface may have been oxidized to ClO_4 during repeated global dust storms over Mars history. The surface perchlorates on NaCl grain would then deliquesce forming liquid brine and sinter into soils on current and past Mars [1]. Then, new NaCl surface would appear and be oxidized in subsequent global dust storms. We suggest the significant role of dust storms in driving surface and atmospheric chemistry, representing a key advance in Martian geochemical studies.

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