

# Radiation-Induced Formation of Chlorine Oxides and Their Potential Role in the Origin of Martian Perchlorates

Yong S. Kim,<sup>†</sup> Kellie P. Wo,<sup>†,‡</sup> Surajit Maity,<sup>†</sup> Sushil K. Atreya,<sup>‡</sup> and Ralf I. Kaiser<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States

<sup>‡</sup>Department of Chemistry, Wellesley College, Wellesley, Massachusetts 02481, United States

<sup>‡</sup>Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, Michigan 48109, United States

## Supporting Information

**ABSTRACT:** Carbon dioxide (CO<sub>2</sub>) rich chlorine-bearing ices were exposed to energetic electrons in laboratory simulation experiments to investigate the formation of chlorine oxides (Cl<sub>x</sub>O<sub>y</sub>) in the condensed phase on Mars. The radiolysis-induced synthesis of chlorine oxides (Cl<sub>x</sub>O<sub>y</sub>) was complementarily monitored online and in situ via infrared spectroscopy (IR) and quadrupole mass spectrometry (QMS). Three discrete chlorine oxides were identified: chlorine dioxide (OClO), dichlorine monoxide (ClOCl), and chloryl chloride (ClClO<sub>2</sub>). Higher irradiation doses support the facile production of ClO<sub>3</sub><sup>-</sup> and ClO<sub>2</sub>-bearing high-order chlorine oxides. We attribute manifolds of chlorine oxides, as invoked herein, to the potential origin of perchlorates as found on Mars.

Air-borne chlorine oxides (Cl<sub>x</sub>O<sub>y</sub>) remain atmospheric and environmental concerns on planet Earth. They are prone to degrade the protective ozone (O<sub>3</sub>) shield in catalytic cycles.<sup>1</sup> Atmospheric interactions of chlorine monoxide (ClO) and its dimer (ClOCl) have been connected to ozone depletion in the stratosphere.<sup>2</sup> Laboratory measurements further suggest that high-order chlorine oxides might play an atmospheric role. Stratospheric chlorine dioxide (OClO) is proposed to be involved in the formation of transient chlorine oxides in the terrestrial atmosphere such as dichlorine hexaoxide (O<sub>2</sub>ClOClO<sub>3</sub>) and chloryl chloride (ClClO<sub>2</sub>).<sup>3</sup> The involvement of chlorine trioxide (ClO<sub>3</sub>) remains uncertain in the irreversible pathway to dichlorine hexaoxide, which in turn decomposes into chlorine tetraoxide (ClO<sub>4</sub>) and chlorine dioxide (OClO). Moisture contacts in any stage trigger a transformation to eventually yield perchloric acid (HClO<sub>4</sub>).<sup>4</sup> Rarely occurring on Earth except in the Atacama desert at levels up to 0.6 wt %, natural perchlorate (ClO<sub>4</sub><sup>-</sup>) is regarded a potential oxidant in aqueous media.<sup>5</sup> Perchlorate has been also classified as an emerging pollutant, which is widely present in the environments such in aerosols, groundwater, surface water, seawater, and in the arctic snow, the origin of which may trace back to stratospheric chlorine, photochemical reactions, and lightening.<sup>6</sup>

Interestingly, perchlorates exist beyond earthly surroundings; they were first detected in the Martian soil at the north polar landing site of the Phoenix spacecraft (NASA) in 2008 at levels of 0.4–0.6 wt %.<sup>7,8</sup> The Martian surface temperature was determined below 245 K at the landing site, where the surface

pressure is about 6 mbar with partial pressures of up to 5 mbar of carbon dioxide (CO<sub>2</sub>).<sup>9</sup> Recently, perchlorates have been tentatively identified at the southern equatorial landing site of the Curiosity rover,<sup>2,3</sup> and their concentrations are similar to those found by Phoenix at this entirely different location on Mars. The location and extent of Martian polar ice deposits changes periodically due to obliquity changes; hence, where the perchlorates are detected today does not necessarily imply that is where they formed originally. Martian surface minerals were suggested to catalyze the oxidation of chlorides to perchlorate.<sup>10</sup> Martian perchlorate may also originate from an atmospheric chemistry involving chlorine volatiles; Martian volcanism in the past was suggested to be the active chlorine source in form of molecular chlorine (Cl<sub>2</sub>) and hydrogen chloride (HCl).<sup>5</sup>

However, the formation mechanism of perchlorates on Mars is still unresolved. Current gas phase models converge qualitatively that chlorine oxides such as chlorine monoxide (ClO) and chlorine dioxide (OClO) are crucial reaction intermediates, which might be oxidized by ozone or atomic oxygen up to dichlorine heptaoxide (Cl<sub>2</sub>O<sub>7</sub>).<sup>11</sup> The latter presents the anhydride of perchloric acid (HClO<sub>4</sub>). Therefore, upon reaction with water, dichlorine heptaoxide can form perchloric acid (HClO<sub>4</sub>), which transforms to perchlorates. Nevertheless, no model can provide a quantitative agreement between predicted and observed perchlorate concentrations on Mars; the crucial bottleneck of the proposed chemical reaction networks is their inability to produce sufficient concentrations of chlorine oxides like chlorine monoxide and chlorine dioxide in the gas phase.<sup>5</sup> This may translate in significantly misinterpreting the origin of perchlorates observed by Phoenix. Therefore, current models need to address that a hitherto undiscovered source and formation route(s) of chlorine oxides must exist on Mars.

Here, we demonstrate that chlorine oxides can be formed easily in simulation experiments mimicking the Martian environment via the interaction of energetic electrons and carbon dioxide rich chlorine-bearing ices in the condensed (solid) phase. The yield of the chlorine oxides is invariant on the carbon dioxide concentration suggesting that carbon dioxide acts as an excess reagent in the experiments and also on Mars. Further, chlorine appears to be ubiquitous on Mars. It

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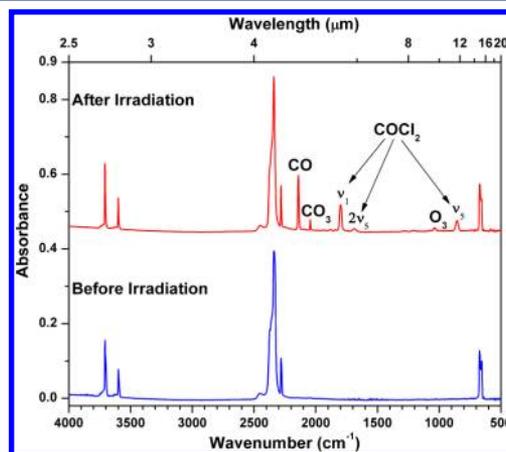
has been found in every soil ever analyzed on Mars in situ or from orbit. Chlorine was first detected on the surface of Mars in 1976 at two very different sites of the Viking Landers: Chryse Planitia and Utopia Planitia. The detected level was found to be 0.3–1.2 wt %.<sup>12</sup> An average concentration of 0.49 wt % chlorine was measured by the 2001 Mars Odyssey  $\gamma$ -ray spectrometer (GRS) from equator to midlatitudes in both hemispheres;<sup>13</sup> the GRS is ineffective at high latitudes. The Shergottite-Nakhilite-Chassignite meteorites also indicate relatively large concentrations of chlorine in the Martian mantle and crust.<sup>14</sup> Further, chlorine would also be distributed over the planet due to widespread aeolian transport.

Upon warming up the ices, the chlorine oxides sublime and are “injected” into the photochemical chlorine/oxygen gas phase chemistry. The synthesis of chlorine oxides and subsequent injection into the gas phase upon warming up, i.e., during the Martian Spring, may present the missing source of chlorine oxides necessary to rationalize the detection of Martian perchlorates quantitatively. The knowledge on the formation of perchlorates on Mars is also of crucial importance from the astrobiological viewpoint.

Perchlorates are extremely stable, making them suitable as oxidizers in rocket fuel where controlled combustion is required. On the other hand, they have the potential of becoming strong oxidizers if mineral phase reactions or other surface processes release their oxygen in the Martian soil over time. In that case, perchlorates, together with any other surface oxidants such as hydrogen peroxide and superoxides, and the solar ultraviolet photons (UV) could destroy organic molecules including biologically relevant molecules, on the Martian surface.<sup>7b</sup>

We utilized 5 keV electrons as a radiation source to mimic the interaction of energetic secondary electrons produced in the track of galactic cosmic rays once they interact with carbon dioxide rich ices on the Martian surface up to a couple meters deep.<sup>15</sup> Currently on Martian surface, the Radiation Assessment Detector (RAD) onboard NASA's Curiosity rover is in operation to assess radiation levels of those particles that penetrate easily through the tenuous atmosphere lacking a magnetic field.<sup>16</sup> We conducted the experiments under ultrahigh vacuum conditions (UHV)<sup>17</sup> with chlorine ( $\text{Cl}_2$ ) doped carbon dioxide ices at temperatures between 10 and 80 K. On Mars, chlorine can be easily formed via radiolysis of chlorides ( $\text{Cl}^-$ )<sup>18</sup> embedded in carbon dioxide frost. Premixed carbon dioxide and chlorine gases were deposited onto either a crystalline silver substrate or a layer of sodium chloride (NaCl). A highly polished silver substrate was selected due to the high reflectivity of silver in the mid-infrared regime;<sup>17</sup> sodium chloride was utilized since chlorides are present on Mars, on which carbon dioxide can condense, and to investigate the effects of the substrate on the yield of chlorine oxides. Carbon dioxide to chlorine ratios between 2:1 and 10:1 can be achieved. These samples were irradiated isothermally with electron currents of 0 (blank experiment), 100, and 1000 nA over an area of 3 cm<sup>2</sup>; higher currents shall be avoided to eliminate any heating of the ices by the impinging electrons. We would like to stress that the Galactic Cosmic Rays are distributed isotropically and have little preference for polar latitudes over equatorial latitudes—unlike Earth—as Mars is a nonmagnetic planet for all practical purposes.<sup>19</sup> The remnant crustal magnetic field at Mars, which is much weaker than the global magnetic field of Earth, indicates magnetic process on ancient Mars.

Sets of mid-infrared spectra were recorded online and in situ before and after, as well as during the irradiation of the ices (Figure 1). The irradiation leads to the appearance of new

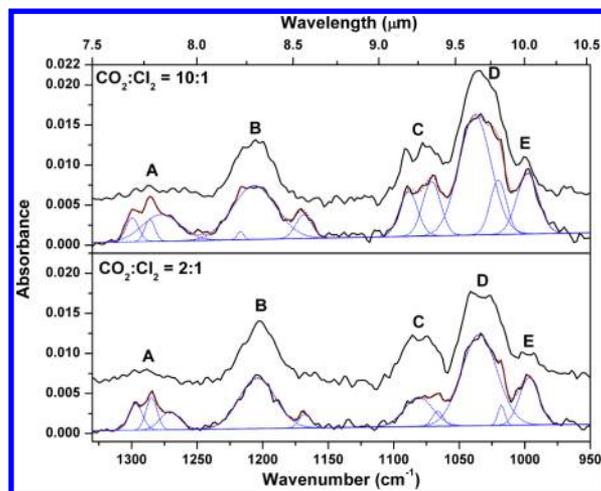


**Figure 1.** Midinfrared spectra recorded before and after the isothermal electron irradiation of carbon dioxide/chlorine ices on a highly polished silver substrate. Newly formed species are annotated.

absorption features. These are carbon monoxide (CO) at 2041 cm<sup>-1</sup>, carbon trioxide (CO<sub>3</sub>) at 2044 cm<sup>-1</sup>, and ozone (O<sub>3</sub>) at about 1040 cm<sup>-1</sup>.<sup>17</sup> Three additional features emerged at 1798, 1688, and 856 cm<sup>-1</sup> and were attributed to phosgene (COCl<sub>2</sub>).<sup>20</sup> These products were formed reproducibly by varying carbon dioxide to chlorine mixing ratios, the irradiation temperatures (10–80 K), and even the substrates (silver vs sodium chloride). After the isothermal irradiation, chlorine oxides could not be observed in the spectral window of 1350–950 cm<sup>-1</sup>, where diagnostic  $\nu(\text{Cl}-\text{O})$  stretching bands of Cl<sub>x</sub>O<sub>y</sub> are known to occur.<sup>3b,4,21</sup> However, upon annealing of the irradiated ices, prominent features appeared in the range of 1350–950 cm<sup>-1</sup>. For the low dose exposure and a target temperature reaching about 100 K, two absorptions emerged at around 1204 and 1038 cm<sup>-1</sup>. These absorptions are characteristic of chloryl chloride (ClClO<sub>2</sub>) as identified previously in photolyzed ices of chlorine dioxide (OClO) and of dichlorine monoxide (ClOCl).<sup>21c</sup> Weak absorptions of OClO were identified at about 1080 and 920 cm<sup>-1</sup>.<sup>21c</sup> A definitive identification of ClOCl or ClO was not feasible because their infrared absorptions overlap with either the reactant molecules or the phosgene product.<sup>4,21c</sup>

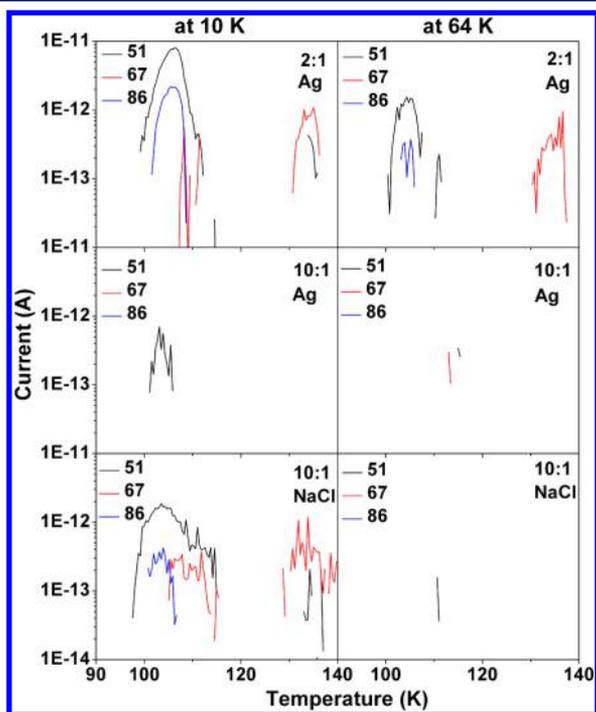
At higher irradiation dose (1000 nA), additional absorption features of chlorine oxides appeared upon annealing of the irradiated samples to 100 K (Figure 2). We identified five major peaks labeled from A to E. These features were deconvoluted and compiled in Table S1 with the corresponding molecular structures of the chlorine oxides listed in Figure S1. A comparison with literature data suggests that absorptions in group A arise from the -ClO<sub>3</sub> group as found in Cl<sub>2</sub>O<sub>4</sub>, Cl<sub>2</sub>O<sub>6</sub>, and Cl<sub>2</sub>O<sub>7</sub>. Within group B, this deconvolution leads to the detection of the -ClO<sub>2</sub> functional group as present in Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>3</sub>. The deconvolution of the absorptions C and D supports the existence of -ClO<sub>2</sub> and/or -ClO<sub>3</sub> functional groups. Finally, OClOCl was identified tentatively to be the carrier of group E at 998 cm<sup>-1</sup>.<sup>21c</sup>

Having identified individual chlorine oxides (OClOCl, ClClO<sub>2</sub>, OClO) as well as functional groups (-ClO<sub>2</sub>, -ClO<sub>3</sub>) via infrared spectroscopy, we are correlating now the infrared



**Figure 2.** Infrared spectra at 100 K of chlorine/oxygen-bearing molecules in electron-irradiated (1000 nA) ices. Each panel contains two offset spectra obtained from samples irradiated at 10 K (upper) and 64 K (lower). A minimum set of Gaussians (blue-dotted) are used to deconvolute these features. Resulting fits (red-dotted) are also shown. Absorption features are compiled in Table S1.

spectra with data obtained via a mass spectrometric analysis of the chlorine oxides released into the gas phase upon warming of the irradiated samples (Figure 3). Three ion currents were



**Figure 3.** Ion current of  $m/z = 51$  ( $^{35}\text{ClO}^+$ ),  $67$  ( $^{35}\text{ClO}_2^+$ ), and  $86$  ( $^{35}\text{Cl}_2\text{O}^+$ ) vs the target temperature obtained recorded during the warm-up phase (0.5 K/min) after an isothermal irradiation at 1000 nA at 10 and 64 K. Ag, silver substrate; NaCl, sodium chloride substrate.

observed at mass to charge ratios ( $m/z$ ) of 51 ( $^{35}\text{ClO}^+$ ), 67 ( $^{35}\text{ClO}_2^+$ ), and 86 ( $^{35}\text{Cl}_2\text{O}^+$ ) in the range of 90–140 K. We would like to stress that none of these ion currents appeared in the blank experiments (no irradiation). Signal at  $m/z = 86$  ( $^{35}\text{Cl}_2\text{O}^+$ ) in the range of 95–110 K can be attributed to subliming ClOCl molecules. As evident from electron-impact

induced fragmentation pattern from chlorine oxides (Table S2), ClOCl molecules should also undergo dissociative ionization forming the  $^{35}\text{ClO}^+$  ion ( $m/z = 51$ ).<sup>22</sup> A close inspection of Figure 3 indicates that the ion profile of  $m/z = 51$  in the range of 95–110 K follows similar patterns of the ion profile of  $m/z = 86$ . Therefore, we propose that at least in the range of 95–110 K, ions of  $m/z = 51$  originate from dissociative ionization of ClOCl molecules in the electron impact ionizer. However, signal at  $m/z = 51$  also extends to temperatures of 115 K. Therefore, a second molecule must exist which yields  $^{35}\text{ClO}^+$  ions at  $m/z = 51$  upon ionization. This ion current also correlates with the ion profile of  $m/z = 67$  ( $^{35}\text{ClO}_2^+$ ). Therefore, we may conclude that signal at  $m/z = 67$  and 51 at temperatures up to 115 K originates from subliming ClO<sub>2</sub> molecules. Note that the ion current at  $m/z = 67$  ( $^{35}\text{ClO}_2^+$ ) depicts a second peak in the range of 130–140 K. Therefore, another carrier must exist, which leads to  $^{35}\text{ClO}_2^+$  ions in the electron impact ionizer of the mass spectrometer. This conclusion can be also supported from the infrared spectroscopic analysis. Here, as signal rises at  $m/z = 67$  ( $^{35}\text{ClO}_2^+$ ) from 110–115 and 130–140 K, OClO and ClClO<sub>2</sub> decrease and ultimately disappear in the infrared spectra, respectively; the sublimation from the solid state into the gas phase leads to the increase of ion signal at  $m/z = 67$ . To summarize, the mass spectrometric data correlated with the infrared spectroscopic analysis suggest the sublimation of at least three distinct chlorine oxides, i.e., Cl<sub>2</sub>O, ClO<sub>2</sub>, and ClClO<sub>2</sub>. Note that we were unable to detect any parent masses of higher chlorine oxides in our experiment; therefore, these higher chlorine oxides, which are the carriers of the -ClO<sub>2</sub> and/or -ClO<sub>3</sub> functional groups, likely decompose thermally upon annealing of the samples. Alternatively, the ion currents of the parents and of their fragments are too weak to be detected within our signal-to-noise.

In conclusion, we have demonstrated the facile, radiation-induced formation of at least three distinct chlorine oxides in electron-irradiated chlorine doped carbon dioxide ices: OClO, ClOCl, and ClClO<sub>2</sub>; OClOCl was assigned tentatively. At higher irradiation doses, the formation of higher chlorine oxides carrying the -ClO<sub>3</sub> and -ClO<sub>2</sub> groups could be verified. It is important to highlight that the yield of these species is invariant on the carbon dioxide concentration investigated here suggesting that carbon dioxide acts as an excess reagent. The latter releases energetic (suprathermal) oxygen atoms upon exposure to energetic electrons during the irradiation,<sup>17a</sup> which in turn react with molecular and/or atomic chlorine to form the experimentally observed chlorine oxides. Upon annealing the irradiated ices, i.e., simulating the transition from the Martian winter to spring, these chlorine oxides can be “injected” into the photochemical chlorine–oxygen cycle leading ultimately to perchlorates on Mars. Therefore, our laboratory experiments propose that the radiation-induced formation of chlorine oxides might present the missing source of chlorine oxides to account for the formation of perchlorates on Mars. Note that Schuttlefield et al. proposed that a UV illumination of naturally occurring semiconducting minerals is capable of oxidizing chloride ion to perchlorate in aqueous solution.<sup>10</sup> This pathway might have yielded perchlorates in the ancient past, when liquid water existed on Mars. On the other hand, the reaction mechanism proposed here via interaction of ionizing radiation with chlorine- and carbon dioxide-bearing ices does not require the presence of liquid water and can even lead to the formation of chlorine oxides and ultimately perchlorates today.

## ■ ASSOCIATED CONTENT

## S Supporting Information

Tables S1, S2 and Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

## Corresponding Author

ralfk@hawaii.edu

## Notes

The authors declare no competing financial interest.

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