



RESEARCH ARTICLE

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Key Points:

- Mechanism initiated by radiolysis in the surface can potentially account for observed Martian perchlorate concentrations
- Injection of oxides of chlorine from the surface into the atmosphere is potentially an effective way of forming perchloric acid
- Martian perchlorate is an important oxidant but poorly characterized

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Perchlorate formation on Mars through surface radiolysis-initiated atmospheric chemistry: A potential mechanism

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Abstract Recent observations of the Martian surface by the Phoenix lander and the Sample Analysis at Mars indicate the presence of perchlorate (ClO_4^-). The abundance and isotopic composition of these perchlorates suggest that the mechanisms responsible for their formation in the Martian environment may be unique in our solar system. With this in mind, we propose a potential mechanism for the production of Martian perchlorate: the radiolysis of the Martian surface by galactic cosmic rays, followed by the sublimation of chlorine oxides into the atmosphere and their subsequent synthesis to form perchloric acid (HClO_4) in the atmosphere, and the surface deposition and subsequent mineralization of HClO_4 in the regolith to form surface perchlorates. To evaluate the viability of this mechanism, we employ a one-dimensional chemical model, examining chlorine chemistry in the context of Martian atmospheric chemistry. Considering the chlorine oxide, OClO , we find that an OClO flux as low as 3.2×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ sublimated into the atmosphere from the surface could produce sufficient HClO_4 to explain the perchlorate concentration on Mars, assuming an accumulation depth of 30 cm and integrated over the Amazonian period. Radiolysis provides an efficient pathway for the oxidation of chlorine, bypassing the efficient Cl/HCl recycling mechanism that characterizes HClO_4 formation mechanisms proposed for the Earth but not Mars.

1. Introduction

The naturally occurring perchlorate anion (ClO_4^-) is associated with salts found in several terrestrial dry regions such as the hyperarid Atacama desert [Ericksen, 1983], the Antarctic Dry Valleys [Kounaves et al., 2010a], and the playa evaporite crusts in Bolivia [Orris et al., 2003]. Significant evidence also exists for the presence of natural perchlorates in the rain and snow samples of the high plains regions of Texas and New Mexico [Rajagopalan et al., 2006] and in the rain samples from Florida [Dasgupta et al., 2005]. The largest concentration of perchlorate on Earth was detected in the barren Atacama desert with concentrations as high as 0.6 wt % in the nitrate ore deposits [Ericksen, 1983], whereas the soil concentration is 0.03 wt % [Parker, 2009]. On Earth, chlorine is found primarily in the form of chloride (Cl^-). The Atacama desert, with its high perchlorate concentration, is unique on Earth in exhibiting a perchlorate to chloride ratio average of 1:500 [Catling et al., 2010], whereas most other terrestrial chlorine deposits demonstrate $\text{ClO}_4^-/\text{Cl}^-$ ratios 1 to 3 orders of magnitude smaller [Jackson et al., 2015a].

However, the presence of perchlorate is not limited to the hydrogeochemical systems on Earth. Evidence of Martian perchlorate has been found in the Mars meteorite EETA79001 [Kounaves et al., 2014a]. In addition, the discovery of perchlorate on chondrite meteorites and lunar samples [Jackson et al., 2015b] suggests that perchlorate may be quite common in our solar system.

Nevertheless, the greatest focus of extraterrestrial perchlorate has been observations on the surface of Mars. The Phoenix Mars lander detected perchlorates in the Martian regolith in the north polar region at concentrations of 0.4 to 0.6 wt %. Chemical and spectral analyses of the soil from the Phoenix site indicate that the probable parent is either $\text{Ca}(\text{ClO}_4)_2$ or $\text{Mg}(\text{ClO}_4)_2$ [Hecht et al., 2009; Cull et al., 2010]; the identification of which would have significant implications in our understanding of the evolution of the site. Kounaves et al. [2014b] presented evidence pointing to Ca^{2+} as the dominant parent cation, which would likely indicate a continuously dry region over the 600 Myr age of the site, while the Toner et al. [2015] model suggests a wetter history for the region where $\text{Mg}(\text{ClO}_4)_2$ would be the primary precipitate.

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The evolved gas analysis and gas chromatograph–mass spectrometer experiments on the Sample Analysis at Mars (SAM) instrument in the Mars Science Laboratory (MSL) rover have also revealed the presence of hydrated perchlorates at the Rocknest deposit in Gale Crater in the equatorial region of Mars [Glavin *et al.*, 2013; Ming *et al.*, 2014; Archer *et al.*, 2014; Sutter *et al.*, 2016]. Observations from the Mars Odyssey Gamma Ray Spectrometer demonstrate widespread distribution of chlorine throughout the planet [Keller *et al.*, 2006], and in situ analysis suggests a much larger role played by oxidation in the evolution of chlorine in the Martian environment.

On Earth, perchlorates are widely distributed in both natural and industrial forms due to their ease of solubility in water [Hecht *et al.*, 2009]. The lack of organics on the Martian surface, first indicated by the Viking landers [Biemann *et al.*, 1977], argues that oxidants may have had a role in the destruction of Martian surface organics, although the evidence for surface organics has been debated [Navarro-González *et al.*, 2010; Biemann and Bada, 2011]. In the laboratory, amino acids have been found to decompose from electron radiolysis at a faster rate in the presence of perchlorates [Góbi *et al.*, 2016]. The presence of perchlorate and its effectiveness as an oxidant suggest that understanding the mechanisms responsible for the formation of perchlorates may reveal clues about the evolution of the Martian environment as a whole.

However, despite the possible role perchlorates may have played on the Martian surface, their formation mechanisms have not been resolved to date. UV irradiation of the Martian surface is a possible mechanism for the formation of perchlorate that has been considered. Schuttlefield *et al.* [2011] showed that perchlorate could be formed from the irradiation of halite (NaCl) on titanium dioxide (TiO₂) by ultraviolet (UV) photons under aqueous conditions. A drawback to this study is that there is considerable debate as to whether the Martian sites where perchlorate has been detected has harbored aqueous conditions long enough to produce the concentration of perchlorate detected. Carrier and Kounaves [2015] bypass this inconvenience as they reproduce the large ClO₄⁻/Cl⁻ ratio observed by the Phoenix lander by oxidizing chloride through UV radiation on grains containing halite and silica (SiO₂), with varying amounts of iron, aluminum, and titanium oxides. On the surface, the thin atmosphere of Mars exposes these grains to UV radiation longward of 200 nm. Additional laboratory work and modeling will be necessary to determine the viability of UV-induced oxidation of chlorine through the different epochs of Martian history, but this process may contribute to the perchlorate observed today.

Notwithstanding the apparent pervasiveness of perchlorate in our solar system [Jackson *et al.*, 2015b], the formation mechanisms responsible for its existence may very well differ among the varying environments, as demonstrated by the differing characteristics that these perchlorate samples exhibit. Although chloride deposits do exist on Mars [Osterloo *et al.*, 2008], the measurements at the Phoenix site exhibit much larger perchlorate/chloride ratios (4:1–9:1) [Hecht *et al.*, 2009; Kounaves *et al.*, 2010b] than observed on the Earth, including the Atacama desert. In addition, SAM and the Alpha-Particle X-Ray Spectrometer at Gale Crater find that much of total chlorine is in the form of oxychlorine (10–40%) [Archer *et al.*, 2015], indicating the importance of oxidation in Martian chlorine chemistry. Perchlorate is also greatly enhanced relative to nitrates on Mars (perchlorate/nitrate > 1) in comparison with Earth (perchlorate/nitrate < 10⁻³) or Martian meteorites [Jackson *et al.*, 2015a; Stern *et al.*, 2016]. Furthermore, at the Gale Crater site, SAM has measured the ³⁷Cl/³⁵Cl isotopic ratio to be much lighter and variable than what is typically found on Earth, pointing to a possible atmospheric origin [Farley *et al.*, 2016]. All of these factors suggest that the mechanisms responsible for the formation of perchlorate on Mars might be different than the processes that govern perchlorate production on the Earth or other extraterrestrial environments.

The formation of perchlorate can occur not only on the surface but also through atmospheric processes or a combination of both. Considering the larger perchlorate concentration and the higher perchlorate/chloride ratio in the Atacama desert than other terrestrial sites, Catling *et al.* [2010] investigated the possibility of atmospheric production of perchlorate in the Atacama. The chemical scheme is based on the formation of perchloric acid (HClO₄) through atmospheric chemistry. HClO₄ is proposed to form through the reaction of hydroxyl radicals (OH) and chlorine trioxide (ClO₃),



which has been positively identified in the laboratory [Kopitzky *et al.*, 2002]. M represents the buffer (background) gas, primarily CO₂, in the Martian atmosphere. As HClO₄ is an end product in atmospheric chlorine chemistry, Catling *et al.* assume that it is deposited onto the Martian surface and incorporated into the surface as perchlorate. With this mechanism, Catling *et al.* are able to explain the perchlorate abundance in the Atacama desert. Smith *et al.* [2014] applied this model to the Martian environment, using volcanism since the Amazonian period as the source of chlorine. Through their model, they calculate a perchlorate production rate of $7.6 \times 10^{-25} \text{ g cm}^{-2} \text{ s}^{-1}$, which falls 7 orders of magnitude short of what is required to explain the perchlorate observations on Mars. As the Catling *et al.* and Smith *et al.* models are identical with regards to chlorine chemistry, we hereafter refer to them as the CS model.

In our study, we considered an alternative for the production of Martian perchlorate. A mechanism for the release of atmospheric chlorine that has not yet been explored from an atmospheric modeling standpoint is the interaction between the chlorine-rich surface and energetic electrons that arise from the deposition of energy from galactic cosmic rays (GCRs). Due to the lack of a thick atmosphere or intrinsic magnetic field, the surface of Mars is exposed to significant levels of energetic GCRs globally. GCR energy deposition is isotropic, having no geographic bias, and thus can impact all regions of the Martian surface. Furthermore, the energies that GCRs deposit are enough to penetrate up to several meters below the surface and would be less sensitive to the opacity provided by an earlier denser atmosphere than ultraviolet radiation. In this vein, we propose an alternative mechanism for producing perchloric acid in the Martian atmosphere via interaction of energetic galactic cosmic rays with the Martian surface. The process begins in the surface, proceeds efficiently in the atmosphere, and ends with perchlorate production in the surface.

2. Radiolysis Mechanism and Model

Radiolysis begins with the engagement of GCRs with the surface causing a cascade of energetic secondary electrons that would be available to interact with the Martian soil. Pavlov *et al.* [2012] demonstrate that Mars receives a dosage of $0.05 \text{ J kg}^{-1} \text{ yr}^{-1}$ of GCRs at the surface that can penetrate to a depth of about 2 m in the Martian surface, producing energetic secondary electrons that interact with the surrounding matter.

This radiolysis process produces chemical compounds that can be released into the atmosphere through sublimation. Kim *et al.* [2013] found a variety of chlorine oxides that are produced from the irradiation of chlorine-doped carbon dioxide ices, using energetic electrons (5 keV) as a proxy for the secondary electrons generated from the interaction of GCRs and the Martian surface. In this study, the radiolysis of the Martian surface by GCRs was simulated by irradiating chlorine-bearing carbon dioxide (CO₂) ices under high vacuum conditions. The irradiation resulted in the formation of dichlorine monoxide (ClOCl), chloryl chloride (ClClO₂), and chlorine dioxide (OClO), irrespective of the CO₂/Cl₂ ratios (2:1–10:1) or the substrate used (silver and NaCl). Additional absorption features of chlorine oxide functional groups (–ClO₃ and –ClO₂) were revealed at higher radiation doses along with the synthesis of dichloromonoxyde (ClOCl). Chlorine monoxide (ClO), which plays a prominent role in the CS scheme, was not produced in the high-energy irradiation. That these products were formed independent of the CO₂ mole fraction demonstrates that chlorine oxides can be formed in Martian ices that are not heavily enriched with CO₂.

The analyzed Martian landing sites are not necessarily examples of environments where ices are in abundance at the surface today. However, Mars has undergone many climatic and obliquity changes throughout its history, whereby glaciation proceeded well into the midlatitudes and possibly low latitudes [Haberle *et al.*, 2003; Wordsworth *et al.*, 2013]. Furthermore, analysis of landforms at the Phoenix site indicates that the ice table is only a few centimeters below the surface [Mellon *et al.*, 2008; Levy *et al.*, 2009]. Given the global distribution of chlorine, it is plausible to assume that much of the Martian surface has been exposed to chlorine-bearing ices throughout much of its history. A pathway converting this chlorine into perchlorate, given its high chemical stability, should result in a substantial global concentration of perchlorate without the need for an aqueous state.

Here we employ a one-dimensional chemical model to investigate chlorine chemistry and the formation of perchloric acid on Mars from chlorine oxides generated as a result of bombardment of chlorine-doped ices by galactic cosmic rays. To conduct this study we add chlorine chemistry to our Mars chemical model,

Table 1. Reactions and Photodissociation Processes Included in the Chemical Model

Reaction	Rate Coefficient	Reference
$O + O + M \rightarrow O_2 + M$	$5.2 \times 10^{-35} e^{900/T}$	<i>Tsang and Hampson</i> [1986]
$O_2 + O + M \rightarrow O_3 + M$	$1.2 \times 10^{-27} T^{-2.4}$	<i>Krasnopolsky</i> [2010]
$O_3 + O + M \rightarrow O_2 + O_2$	$8.0 \times 10^{-12} e^{-2060/T}$	<i>Atkinson et al.</i> [1989]
$H_2 + O(^1D) \rightarrow OH + H$	1.1×10^{-10}	<i>DeMore et al.</i> [1997]
$H + H + M \rightarrow H_2 + M$	$2.7 \times 10^{-31} T^{-0.6}$	<i>Baulch et al.</i> [1992]
$H + O_2 + M \rightarrow HO_2 + M$	$1.5 \times 10^{-27} T^{-1.6}$	<i>DeMore et al.</i> [1997]
$H + O_3 \rightarrow O_2 + OH$	$1.4 \times 10^{-10} e^{-470/T}$	<i>DeMore et al.</i> [1997]
$H_2O + O(^1D) \rightarrow OH + OH$	2.2×10^{-10}	<i>DeMore et al.</i> [1997]
$OH + CO \rightarrow CO_2 + H$	$4.9 \times 10^{-15} T^{0.6}$	<i>Sander et al.</i> [2011]
$OH + O \rightarrow O_2 + H$	$2.2 \times 10^{-11} e^{120/T}$	<i>DeMore et al.</i> [1997]
$OH + O_3 \rightarrow O_2 + HO_2$	$1.6 \times 10^{-12} e^{-940/T}$	<i>DeMore et al.</i> [1997]
$HO_2 + O \rightarrow O_2 + OH$	$2.9 \times 10^{-11} e^{200/T}$	<i>Atkinson et al.</i> [1989]
$HO_2 + O_3 \rightarrow 2O_2 + OH$	$1.1 \times 10^{-14} e^{-500/T}$	<i>DeMore et al.</i> [1997]
$HO_2 + H \rightarrow OH + OH$	7.2×10^{-11}	<i>Atkinson et al.</i> [1989]
$HO_2 + H \rightarrow H_2 + O_2$	5.6×10^{-12}	<i>Atkinson et al.</i> [1989]
$HO_2 + H \rightarrow H_2O + O$	2.4×10^{-12}	<i>Atkinson et al.</i> [1989]
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$1.5 \times 10^{-12} e^{19/T}$	<i>Christensen et al.</i> [2002]
$HO_2 + OH \rightarrow O_2 + H_2O$	$4.8 \times 10^{-11} e^{250/T}$	<i>DeMore et al.</i> [1997]
$H_2O_2 + OH \rightarrow HO_2 + H_2O$	$2.9 \times 10^{-12} e^{-161/T}$	<i>DeMore et al.</i> [1997]
$O(^1D) + M \rightarrow O + M$	$7.4 \times 10^{-11} e^{120/T}$	<i>DeMore et al.</i> [1997]
$CO_2^+ + H_2 \rightarrow HCO_2^+ + H$	4.7×10^{-10}	<i>Anicich and Huntress</i> [1986]
$HCO_2^+ + e^- \rightarrow CO_2 + H$	$8.7 \times 10^{-6} T^{-0.5}$	<i>Prasad and Huntress</i> [1980]
$O^+ + CO_2 \rightarrow O_2^+ + CO$	9.6×10^{-10}	<i>Anicich and Huntress</i> [1986]
$CO_2^+ + O \rightarrow O_2^+ + CO$	1.6×10^{-10}	<i>Anicich and Huntress</i> [1986]
$CO_2^+ + O \rightarrow O^+ + CO_2$	1.0×10^{-10}	<i>Anicich and Huntress</i> [1986]
$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2$	5.3×10^{-11}	<i>Anicich and Huntress</i> [1986]
$CO_2^+ + e^- \rightarrow CO + O$	$6.9 \times 10^{-6} T^{-0.5}$	<i>Prasad and Huntress</i> [1980]
$O_2^+ + e^- \rightarrow O + O$	$3.5 \times 10^{-6} T^{-0.5}$	<i>Prasad and Huntress</i> [1980]
$O_2^+ + N \rightarrow NO^+ + O$	1.2×10^{-10}	<i>Anicich and Huntress</i> [1986]
$O_2^+ + NO \rightarrow NO^+ + O_2$	4.4×10^{-10}	<i>Anicich and Huntress</i> [1986]
$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$	8.0×10^{-10}	<i>Anicich and Huntress</i> [1986]
$N_2^+ + O \rightarrow NO^+ + N(^2D)$	$1.7 \times 10^{-9} T^{-0.44}$	<i>McFarland et al.</i> [1974]
$N_2^+ + e^- \rightarrow N(^2D) + N(^2D)$	$1.8 \times 10^{-6} T^{-0.4}$	<i>Prasad and Huntress</i> [1980]
$NO^+ + e^- \rightarrow N(^2D) + O$	$1.2 \times 10^{-4} T^{-1.0}$	<i>Prasad and Huntress</i> [1980]
$N^+ + CO_2 \rightarrow CO_2^+ + N$	5.0×10^{-10}	<i>Anicich and Huntress</i> [1986]
$N^+ + CO_2 \rightarrow CO^+ + NO$	5.0×10^{-10}	<i>Anicich and Huntress</i> [1986]
$CO^+ + CO_2 \rightarrow CO_2^+ + CO$	1.1×10^{-9}	<i>Anicich and Huntress</i> [1986]
$N^+ + CO \rightarrow CO^+ + N$	4.0×10^{-10}	<i>Anicich and Huntress</i> [1986]
$N + O \rightarrow NO + hv$	$4.8 \times 10^{-16} T^{-0.5}$	<i>Du and Dalgarno</i> [1990]
$N + O + M \rightarrow NO + M$	$8.2 \times 10^{-31} T^{-0.65}$	<i>Du and Dalgarno</i> [1990]
$N + O_2 \rightarrow NO + O$	$1.5 \times 10^{-11} e^{-3600/T}$	<i>Sander et al.</i> [2011]
$N + O_3 \rightarrow NO + O_2$	1.0×10^{-16}	<i>Barnett et al.</i> [1987]
$N + OH \rightarrow NO + H$	$3.1 \times 10^{-9} T^{-0.69} e^{-48/T}$	<i>Smith and Stewart</i> [1994]
$N + HO_2 \rightarrow NO + OH$	2.2×10^{-11}	<i>Brune et al.</i> [1983]
$N(^2D) + CO_2 \rightarrow NO + CO$	3.5×10^{-13}	<i>Herron</i> [1999]
$N(^2D) + O \rightarrow N + O$	6.9×10^{-13}	<i>Fell et al.</i> [1990]
$N(^2D) + N_2 \rightarrow N + N_2$	1.7×10^{-14}	<i>Herron</i> [1999]
$N_2 + O(^1D) \rightarrow N_2 + O$	$1.8 \times 10^{-11} e^{110/T}$	<i>DeMore et al.</i> [1997]
$N_2 + O(^1D) + M \rightarrow N_2O + M$	$1.1 \times 10^{-35} T^{-0.6}$	<i>DeMore et al.</i> [1997]
$NO + O + M \rightarrow NO_2 + M$	$4.6 \times 10^{-28} T^{-1.5}$	<i>DeMore et al.</i> [1997]
$NO + O_3 \rightarrow NO_2 + O_2$	$2.0 \times 10^{-12} e^{-1400/T}$	<i>DeMore et al.</i> [1997]
$NO + HO_2 \rightarrow NO_2 + OH$	$3.5 \times 10^{-12} e^{250/T}$	<i>DeMore et al.</i> [1997]
$NO + OH + M \rightarrow HNO_2 + M$	$1.9 \times 10^{-24} T^{-2.6}$	<i>DeMore et al.</i> [1997]
$NO + N \rightarrow N_2 + O$	$2.1 \times 10^{-11} e^{100/T}$	<i>DeMore et al.</i> [1997]
$NO + N(^2D) \rightarrow N_2 + O$	6.9×10^{-11}	<i>Fell et al.</i> [1990]
$NO_2 + O \rightarrow NO + O_2$	$6.5 \times 10^{-12} e^{120/T}$	<i>DeMore et al.</i> [1997]
$NO_2 + O + M \rightarrow NO_3 + M$	$8.0 \times 10^{-27} T^{-2.0}$	<i>DeMore et al.</i> [1997]
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.2 \times 10^{-13} e^{-2450/T}$	<i>DeMore et al.</i> [1997]
$NO_2 + OH + M \rightarrow HNO_3 + M$	$1.9 \times 10^{-19} T^{-4.4}$	<i>DeMore et al.</i> [1997]
$NO_2 + N \rightarrow N_2O + O$	$5.8 \times 10^{-12} e^{220/T}$	<i>DeMore et al.</i> [1997]
$NO_3 + O \rightarrow NO_2 + O_2$	1.0×10^{-11}	<i>DeMore et al.</i> [1997]

Table 1. (continued)

Reaction	Rate Coefficient	Reference
$\text{NO}_3 + \text{H} \rightarrow \text{NO}_2 + \text{OH}$	1.1×10^{-10}	Boodaghians <i>et al.</i> [1988]
$\text{NO}_3 + \text{OH} \rightarrow \text{NO}_2 + \text{HO}_2$	2.0×10^{-11}	Atkinson <i>et al.</i> [2004]
$\text{NO}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{NO}_2$	$1.5 \times 10^{-11} e^{170/T}$	DeMore <i>et al.</i> [1997]
$\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$9.8 \times 10^{-21} T^{-3.9}$	DeMore <i>et al.</i> [1997]
$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{N}_2 + \text{O}_2$	4.9×10^{-11}	DeMore <i>et al.</i> [1997]
$\text{N}_2\text{O} + \text{O}(^1\text{D}) \rightarrow \text{NO} + \text{NO}$	6.7×10^{-11}	DeMore <i>et al.</i> [1997]
$\text{HNO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$2.5 \times 10^{-12} e^{260/T}$	Atkinson <i>et al.</i> [2004]
$\text{HNO}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$8.3 \times 10^{-15} e^{850/T}$	Smith <i>et al.</i> [1984]
$\text{H} + \text{CO} + \text{M} \rightarrow \text{HCO} + \text{M}$	$5.3 \times 10^{-34} e^{-370/T}$	Baulch <i>et al.</i> [1994]
$\text{HCO} + \text{O} \rightarrow \text{OH} + \text{CO}$	5.0×10^{-11}	Baulch <i>et al.</i> [1992]
$\text{HCO} + \text{O} \rightarrow \text{CO}_2 + \text{H}$	5.0×10^{-11}	Baulch <i>et al.</i> [1992]
$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	$2.2 \times 10^{-12} e^{170/T}$	Nesbitt <i>et al.</i> [1999]
$\text{HCO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	1.5×10^{-10}	Baulch <i>et al.</i> [1992]
$\text{HCO} + \text{HO}_2 \rightarrow \text{H}_2\text{CO} + \text{O}_2$	5.0×10^{-11}	Tsang and Hampson [1986]
$\text{HCO} + \text{HCO} \rightarrow \text{H}_2\text{CO} + \text{CO}$	5.0×10^{-11}	Baulch <i>et al.</i> [1992]
$\text{H}_2\text{CO} + \text{O} \rightarrow \text{HCO} + \text{OH}$	$6.9 \times 10^{-13} T^{0.6} e^{-1390/T}$	Baulch <i>et al.</i> [1992]
$\text{H}_2\text{CO} + \text{H} \rightarrow \text{HCO} + \text{H}_2$	$2.1 \times 10^{-16} T^{1.6} e^{-1090/T}$	Baulch <i>et al.</i> [1994]
$\text{H}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	1.0×10^{-11}	DeMore <i>et al.</i> [1997]
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{HCl} + \text{O}$	1.5×10^{-11}	Chichinin [2000]
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{Cl} + \text{OH}$	9.8×10^{-11}	Chichinin [2000]
$\text{HCl} + \text{O}(^1\text{D}) \rightarrow \text{ClO} + \text{H}$	3.7×10^{-11}	Chichinin [2000]
$\text{HCl} + \text{O} \rightarrow \text{Cl} + \text{OH}$	$1.0 \times 10^{-11} e^{-3300/T}$	DeMore <i>et al.</i> [1997]
$\text{HCl} + \text{H} \rightarrow \text{Cl} + \text{H}_2$	$2.4 \times 10^{-11} e^{-1730/T}$	Allison <i>et al.</i> [1996]
$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$2.6 \times 10^{-12} e^{-350/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.3 \times 10^{-11} e^{-200/T}$	Sander <i>et al.</i> [2011]
$\text{Cl} + \text{O}_3 + \text{M} \rightarrow \text{ClO}_3 + \text{M}$	1.0×10^{-31}	Simonaitis and Hecklen [1975]
$\text{Cl} + \text{O}_2 + \text{M} \rightarrow \text{ClOO} + \text{M}$	$1.1 \times 10^{-25} T^{-3.1}$	Sander <i>et al.</i> [2011]
$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$3.1 \times 10^{-11} e^{-2270/T}$	Sander <i>et al.</i> [2011]
$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	$1.8 \times 10^{-11} e^{170/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{OH}$	$4.1 \times 10^{-11} e^{-450/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.1 \times 10^{-11} e^{-980/T}$	Atkinson <i>et al.</i> [2007]
$\text{Cl} + \text{Cl} + \text{M} \rightarrow \text{Cl}_2 + \text{M}$	$3.5 \times 10^{-33} e^{820/T}$	Baulch <i>et al.</i> [1981]
$\text{ClO} + \text{CO} \rightarrow \text{products}$	$1.0 \times 10^{-12} e^{-3700/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{CO} + \text{M} \rightarrow \text{ClCO} + \text{M}$	$3.4 \times 10^{-24} T^{-3.8}$	Yung and Demore [1999]
$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	$2.8 \times 10^{-11} e^{85/T}$	Sander <i>et al.</i> [2011]
$\text{ClO} + \text{O} + \text{M} \rightarrow \text{OCIO} + \text{M}$	$k_0 = 8.6 \times 10^{-21} T^{-4.1} e^{-420/T}$ $k_\infty = 4.3 \times 10^{-11} T^{-0.03} e^{43/T}$	Zhu and Lin [2003]
$\text{ClO} + \text{OH} \rightarrow \text{Cl} + \text{HO}_2$	$7.4 \times 10^{-12} e^{270/T}$	Sander <i>et al.</i> [2011]
$\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$	$6.0 \times 10^{-13} e^{230/T}$	Sander <i>et al.</i> [2011]
$\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$	$8.1 \times 10^{-11} e^{-30/T}$	DeMore <i>et al.</i> [1997]
$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$6.4 \times 10^{-12} e^{290/T}$	DeMore <i>et al.</i> [1997]
$\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}$	$k_0 = 4.8 \times 10^{-23} T^{-3.4}$ $k_\infty = 7.6 \times 10^{-7} T^{-1.9}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{NO}_3 \rightarrow \text{ClO} + \text{NO}_2$	2.4×10^{-11}	Atkinson <i>et al.</i> [2007]
$\text{HOCl} + \text{O} \rightarrow \text{ClO} + \text{OH}$	1.7×10^{-13}	Atkinson <i>et al.</i> [2007]
$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$3.0 \times 10^{-12} e^{-500/T}$	DeMore <i>et al.</i> [1997]
$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$2.7 \times 10^{-12} e^{220/T}$	Sander <i>et al.</i> [2011]
$\text{Cl} + \text{HOCl} \rightarrow \text{HCl} + \text{ClO}$	$1.25 \times 10^{-12} e^{-130/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{OH}$	$1.25 \times 10^{-12} e^{-130/T}$	DeMore <i>et al.</i> [1997]
$\text{OCIO} + \text{NO} \rightarrow \text{ClO} + \text{NO}_2$	$2.5 \times 10^{-12} e^{-600/T}$	DeMore <i>et al.</i> [1997]
$\text{ClO} + \text{NO}_3 \rightarrow \text{ClOO} + \text{NO}_2$	4.7×10^{-13}	DeMore <i>et al.</i> [1997]
$\text{OCIO} + \text{O} \rightarrow \text{ClO} + \text{O}_2$	$2.4 \times 10^{-12} e^{-960/T}$	DeMore <i>et al.</i> [1997]
$\text{OCIO} + \text{O} + \text{M} \rightarrow \text{ClO}_3 + \text{M}$	$k_0 = 1.4 \times 10^{-23} T^{-3.1}$ $k_\infty = 8.3 \times 10^{-12}$	Sander <i>et al.</i> [2011]
$\text{OCIO} + \text{OH} \rightarrow \text{HOCl} + \text{O}_2$	$4.5 \times 10^{-13} e^{800/T}$	Atkinson <i>et al.</i> [2007]
$\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$	$1.1 \times 10^{-29} e^{-1820/T}$	Atkinson <i>et al.</i> [2007]
$\text{ClO} + \text{O} + \text{M} \rightarrow \text{OCIO} + \text{M}$	$k_0 = 8.6 \times 10^{-21} T^{-4.1} e^{-420/T}$ $k_\infty = 4.3 \times 10^{-11} T^{-0.03} e^{43/T}$	Zhu and Lin [2003]
$\text{Cl} + \text{OCIO} \rightarrow \text{ClO} + \text{ClO}$	$3.4 \times 10^{-11} e^{160/T}$	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{ClOO} \rightarrow \text{Cl}_2 + \text{O}_2$	2.3×10^{-10}	DeMore <i>et al.</i> [1997]
$\text{Cl} + \text{ClOO} \rightarrow \text{ClO} + \text{ClO}$	1.2×10^{-11}	DeMore <i>et al.</i> [1997]

Table 1. (continued)

Reaction	Rate Coefficient	Reference
$\text{ClO} + \text{O}_3 \rightarrow \text{ClOO} + \text{O}_2$	$1.0 \times 10^{-12} e^{-3600/T}$	<i>DeMore et al.</i> [1997]
$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	$1.0 \times 10^{-12} e^{-4000/T}$	<i>DeMore et al.</i> [1997]
$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$1.0 \times 10^{-12} e^{-1590/T}$	<i>Atkinson et al.</i> [2007]
$\text{ClO} + \text{ClO} \rightarrow \text{ClOO} + \text{Cl}$	$3.0 \times 10^{-11} e^{-2450/T}$	<i>Atkinson et al.</i> [2007]
$\text{ClO} + \text{ClO} \rightarrow \text{OCIO} + \text{Cl}$	$3.5 \times 10^{-13} e^{-1370/T}$	<i>Atkinson et al.</i> [2007]
$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	$k_0 = 2.2 \times 10^{-21} T^{-4.5}$ $k_\infty = 1.8 \times 10^{-6} T^{-2.4}$	<i>Sander et al.</i> [2011]
$\text{ClO}_3 + \text{OH} + \text{M} \rightarrow \text{HClO}_4 + \text{M}$	$k_0 = 1.9 \times 10^{36} T^{-15.3} e^{-5542/T}$ $k_\infty = 3.2 \times 10^{-10} T^{0.07} e^{-25/T}$	<i>Zhu and Lin</i> [2001]
$\text{ClO}_3 + \text{OH} \rightarrow \text{OCIO} + \text{HO}_2$	$2.1 \times 10^{-10} T^{0.09} e^{-18/T}$	<i>Zhu and Lin</i> [2001]
$\text{ClO} + \text{ClO}_3 \rightarrow \text{ClOO} + \text{ClOO}$	$1.9 \times 10^{-18} T^{2.28} e^{-2417/T}$	<i>Xu and Lin</i> [2003]
$\text{ClO} + \text{ClO}_3 \rightarrow \text{OCIO} + \text{OCIO}$	$1.4 \times 10^{-18} T^{2.11} e^{-2870/T}$	<i>Xu and Lin</i> [2003]
$\text{ClO} + \text{ClO}_3 + \text{M} \rightarrow \text{Cl}_2\text{O}_4 + \text{M}$	$k_0 = 1.4 \times 10^{-1} T^{-10.2} e^{-1597/T}$ $k_\infty = 1.4 \times 10^{-10} T^{0.09} e^{-82/T}$	<i>Xu and Lin</i> [2003]
$\text{OCIO} + \text{O}_3 \rightarrow \text{ClO}_3 + \text{O}_2$	$2.1 \times 10^{-12} e^{-4700/T}$	<i>Atkinson et al.</i> [2007]
$\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + \text{ClO}$	$6.2 \times 10^{-11} e^{130/T}$	<i>Atkinson et al.</i> [1997]
$\text{Cl} + \text{Cl}_2\text{O}_2 \rightarrow \text{Cl}_2 + \text{ClOO}$	1.0×10^{-10}	<i>Atkinson et al.</i> [1997]
$\text{Cl}_2\text{O}_2 + \text{NO} \rightarrow \text{Cl}_2\text{O} + \text{NO}_2$	1.0×10^{-15}	<i>Ingham et al.</i> [2005]
$\text{Cl} + \text{NO} + \text{M} \rightarrow \text{ClNO} + \text{M}$	$2.2 \times 10^{-27} T^{-1.8}$	<i>Sander et al.</i> [2011]
$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	$5.8 \times 10^{-11} e^{100/T}$	<i>DeMore et al.</i> [1997]
$\text{Cl}_2\text{O} + \text{O} \rightarrow \text{ClO} + \text{ClO}$	$2.7 \times 10^{-11} e^{-530/T}$	<i>Atkinson et al.</i> [1997]
$\text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$	$k_0 = 1.4 \times 10^{-26} e^{-7690/T}$ $k_\infty = 7.9 \times 10^{15} e^{-8820/T}$	<i>Atkinson et al.</i> [2007]
	$f_c = 0.45$	
$\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{ClO} + \text{Cl}$	2.0×10^{-10}	<i>Sander et al.</i> [2011]
$\text{Cl}_2 + \text{O}(^1\text{D}) \rightarrow \text{Cl}_2 + \text{O}$	6.8×10^{-11}	<i>Sander et al.</i> [2011]
$\text{Cl}_2 + \text{OH} \rightarrow \text{HOCl} + \text{Cl}$	$1.4 \times 10^{-12} e^{-900/T}$	<i>DeMore et al.</i> [1997]
$\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClONO} + \text{M}$	$k_0 = 1.2 \times 10^{-25} T^{-2.0}$ $k_\infty = 3.0 \times 10^{-8} T^{-1.0}$	<i>DeMore et al.</i> [1997]
$\text{Cl} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_2 + \text{M}$	$k_0 = 1.6 \times 10^{-26} T^{-2.0}$ $k_\infty = 3.0 \times 10^{-8} T^{-1.0}$	<i>DeMore et al.</i> [1997]
$\text{ClONO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_2$	1.0×10^{-13}	<i>Atkinson et al.</i> [2007]
$\text{ClONO}_2 + \text{O} \rightarrow \text{ClONO} + \text{O}_2$	$2.9 \times 10^{-12} e^{-800/T}$	<i>DeMore et al.</i> [1997]
$\text{ClONO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_3$	$6.0 \times 10^{-13} e^{-330/T}$	<i>Atkinson et al.</i> [2007]
$\text{ClONO}_2 + \text{OH} \rightarrow \text{ClO} + \text{HNO}_3$	$6.0 \times 10^{-13} e^{-330/T}$	<i>Atkinson et al.</i> [2007]
$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	$6.2 \times 10^{-12} e^{145/T}$	<i>Atkinson et al.</i> [2007]
$\text{ClCO} + \text{O} \rightarrow \text{Cl} + \text{CO}_2$	3.0×10^{-11}	<i>Yung and Demore</i> [1999]
$\text{ClCO} + \text{O} \rightarrow \text{ClO} + \text{CO}$	3.0×10^{-12}	<i>Yung and Demore</i> [1999]
$\text{ClCO} + \text{H} \rightarrow \text{HCl} + \text{CO}$	1.0×10^{-11}	<i>Yung and Demore</i> [1999]
$\text{ClCO} + \text{Cl} \rightarrow \text{Cl}_2 + \text{CO}$	1.0×10^{-11}	<i>Yung and Demore</i> [1999]
$\text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}$		<i>Nakata et al.</i> [1965], <i>Shemansky</i> [1972], <i>Okabe</i> [1978], <i>Fox and Dalgarno</i> [1979], <i>Lewis and Carver</i> [1983], <i>Gallagher et al.</i> [1988], <i>Shaw et al.</i> [1995], and <i>Lu et al.</i> [2014]
$\rightarrow \text{CO} + \text{O}(^1\text{D})$		
$\rightarrow \text{C} + \text{O}_2$		
$\rightarrow \text{CO}_2^+ + e^-$		
$\rightarrow \text{CO} + \text{O}^+ + e^-$		
$\rightarrow \text{O} + \text{CO}^+ + e^-$		
$\text{CO} + h\nu \rightarrow \text{C} + \text{O}$		<i>Wight et al.</i> [1976], <i>Okabe</i> [1978], and <i>Gallagher et al.</i> [1988]
$\rightarrow \text{CO}^+ + e^-$		
$\text{O} + h\nu \rightarrow \text{O}^+ + e^-$		<i>Fennelly and Torr</i> [1992]
$\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$		<i>Watanabe et al.</i> [1953], <i>Samson and</i> <i>Cairns</i> [1964], <i>Ogawa</i> [1971], and <i>Sander</i> <i>et al.</i> [2011]
$\rightarrow \text{O}(^1\text{D}) + \text{O}$		
$\rightarrow \text{O}_2^+ + e^-$		
$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$		<i>Lindner</i> [1988] and <i>Sander et al.</i> [2011]
$\rightarrow \text{O}_2 + \text{O}(^1\text{D})$		
$\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H}$		<i>Thompson et al.</i> [1963], <i>Watanabe and</i> <i>Jursa</i> [1964], and <i>Haddad and</i> <i>Samson</i> [1986]
$\rightarrow \text{O}(^1\text{D}) + \text{H}_2$		
$\rightarrow \text{O} + 2\text{H}$		

Table 1. (continued)

Reaction	Rate Coefficient	Reference
$\text{HO}_2 + hv \rightarrow \text{OH} + \text{O}$		<i>Okabe</i> [1978]
$\text{H}_2\text{O}_2 + hv \rightarrow \text{OH} + \text{OH}$ $\rightarrow \text{HO}_2 + \text{H}$		<i>Okabe</i> [1978] and <i>Gerlach-Meyer et al.</i> [1987]
$\text{N}_2 + hv \rightarrow \text{N} + \text{N}(^2\text{D})$ $\rightarrow \text{N}_2^+ + e^-$ $\rightarrow \text{N}^+ + \text{N} + e^-$		<i>Zipf and McLaughlin</i> [1978], <i>Shaw et al.</i> [1992], and <i>Chan et al.</i> [1993]
$\text{NO} + hv \rightarrow \text{N} + \text{O}$		<i>Thompson et al.</i> [1963] and <i>Watanabe et al.</i> [1967]
$\text{NO}_2 + hv \rightarrow \text{NO} + \text{O}$ $\text{N}_2\text{O} + hv \rightarrow \text{N}_2 + \text{O}(^1\text{D})$		<i>Atkinson et al.</i> [2004] <i>Zelikoff et al.</i> [1953] and <i>Thompson et al.</i> [1963]
$\text{N}_2\text{O}_5 + hv \rightarrow \text{NO}_2 + \text{NO}_3$ $\text{HNO}_2 + hv \rightarrow \text{OH} + \text{NO}$ $\text{HNO}_3 + hv \rightarrow \text{OH} + \text{NO}_2$ $\text{HCO} + hv \rightarrow \text{CO} + \text{H}$ $\text{H}_2\text{CO} + hv \rightarrow \text{HCO} + \text{H}$ $\rightarrow \text{CO} + \text{H}_2$ $\rightarrow \text{CO} + 2\text{H}$		<i>Sander et al.</i> [2011] <i>Sander et al.</i> [2011] <i>Sander et al.</i> [2011] <i>Hochanadel et al.</i> [1980] <i>Gentieu and Mentall</i> [1970], <i>Glicker and Stief</i> [1971], <i>Moortgat et al.</i> [1983], and <i>Suto et al.</i> [1986]
$\text{HCl} + hv \rightarrow \text{Cl} + \text{H}$ $\text{ClO} + hv \rightarrow \text{Cl} + \text{O}$ $\text{HOCl} + hv \rightarrow \text{Cl} + \text{OH}$ $\text{ClOO} + hv \rightarrow \text{ClO} + \text{O}$ $\text{OCIO} + hv \rightarrow \text{ClO} + \text{O}$ $\text{Cl}_2 + hv \rightarrow \text{Cl} + \text{Cl}$ $\text{Cl}_2\text{O} + hv \rightarrow \text{Cl} + \text{ClO}$ $\text{Cl}_2\text{O}_2 + hv \rightarrow \text{Cl} + \text{ClOO}$ $\rightarrow \text{ClO} + \text{ClO}$		<i>Sander et al.</i> [2011] <i>Sander et al.</i> [2011]
$\text{ClNO} + hv \rightarrow \text{Cl} + \text{NO}$ $\text{ClNO}_2 + hv \rightarrow \text{Cl} + \text{NO}_2$ $\text{ClONO} + hv \rightarrow \text{Cl} + \text{NO}_2$ $\text{ClO}_3 + hv \rightarrow \text{ClO} + \text{O}_2$ $\text{Cl}_2\text{O}_4 + hv \rightarrow \text{ClOO} + \text{ClOO}$		<i>Sander et al.</i> [2011] <i>Ghosh et al.</i> [2012] <i>Sander et al.</i> [2011] <i>Sander et al.</i> [2011] <i>Sander et al.</i> [2011]

details of which can be found in *Wong et al.* [2003] and *Atreya and Gu* [1994], which solves the steady state continuity-diffusion equation in spherical coordinates

$$P_i - L_i = \frac{1}{r^2} \frac{\partial(r^2 \Phi_i)}{\partial r}, \quad (1)$$

where P_i = the chemical production rate of species i ; L_i = the chemical loss rate of species i ; $r = (R_0 + z)$, where R_0 = the radius of Mars and z = the altitude; and Φ_i = the vertical flux of species i , which can be expressed as

$$\Phi_i = -D_i \left[n \frac{\partial f_i}{\partial z} + f_i \frac{\partial n}{\partial z} + \frac{nf_i}{T} \frac{\partial T}{\partial z} + \frac{nf_i}{H_i} \right] - Kn \frac{\partial f_i}{\partial z}, \quad (2)$$

where n = the atmospheric number density, f_i = the mole fraction of species i , D_i = the molecular diffusion coefficient of species i , K = the eddy diffusion coefficient, T = the temperature, and H_i = the scale height of species i . These equations are solved for 51 species, considering CO_2 - H_2O - NO_x chemistry with charged particles, for 220 altitude levels, spaced 1 km apart. Table 1 includes the chemical reactions relevant to the present model. In our nominal model we assume that chlorine oxides from radiolysis are synthesized in the form of chlorine dioxide (OCIO) sublimated into the atmosphere and thus, apply an upward flux of OCIO molecules at the lower boundary to serve as the source of chlorine in the model. The OCIO lower boundary flux is taken as an input parameter. We adopt the CS model assumption that the perchloric acid

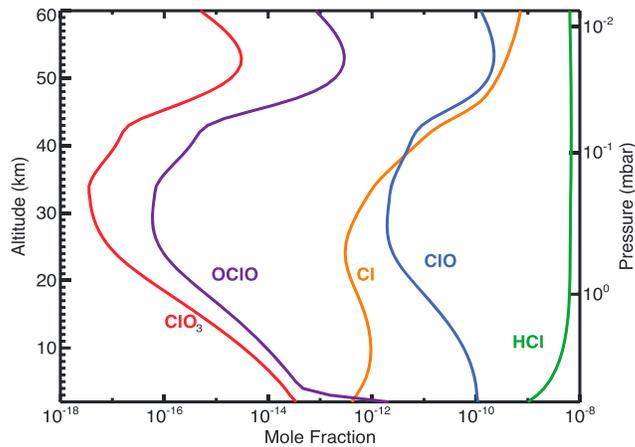
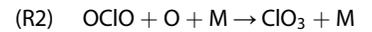


Figure 1. Mole fraction profiles for important chlorine species for the $10^9 \text{ cm}^{-2} \text{ s}^{-1}$ OCIO flux level.

produced in the atmosphere is deposited onto the surface and incorporated into the surface as perchlorate following mineralization.

3. Chlorine Chemistry

In our nominal model, the flux of OCIO from the surface provides a direct source to chlorine trioxide (ClO_3), the precursor to perchloric acid. This pathway proceeds through a three-body association mechanism with atomic oxygen



[Colussi *et al.*, 1992]. The CS model also includes OCIO as a possible path-

way to perchloric acid [Catling *et al.*, 2010; Smith *et al.*, 2014]. Chlorine monoxide (ClO) formation provides an alternative reaction channel



that dominates at low atmospheric pressures. However, at higher pressures near the surface, the association mechanism (reaction (R2)) becomes significant, making it the most important nonphotolytic destruction mechanism for OCIO below 10 km. Figure 1 shows the large dropoff in ClO_3 mole fraction away from the near-surface region as a result of the decreasing importance of reaction (R2) at lower pressures. Chlorine trioxide is also formed through the reaction

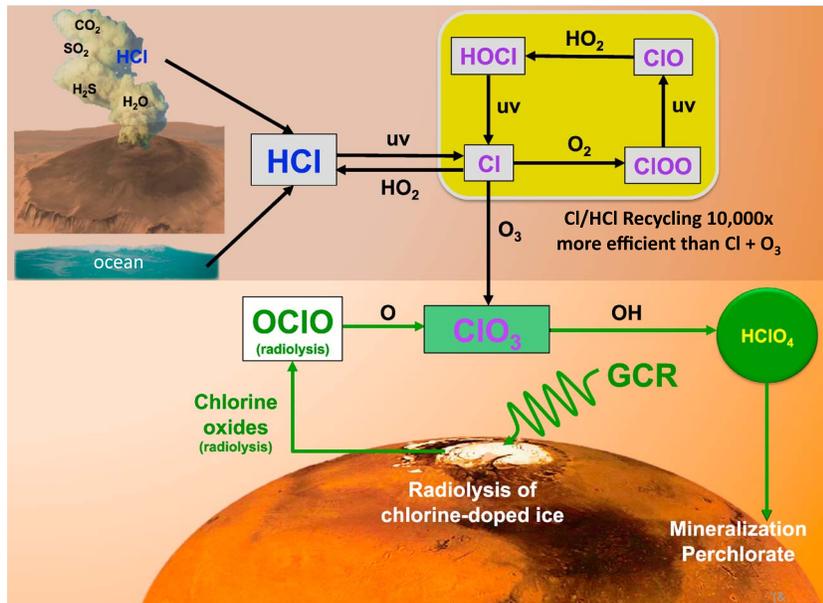


Figure 2. HCl, which is generated by volcanic activity in the Smith *et al.* [2014] model, is photolysed to form free Cl atoms that can combine with O_3 to form ClO_3 molecules. However, in the Martian atmosphere, most of these free atoms will participate in a Cl/HCl recycling mechanism, labeled in yellow. Our alternative for forming ClO_3 , from the release of OCIO through radiolysis/sublimation, bypasses this recycling mechanism, paving the way for perchlorate mineralization.

an important reaction in the proposed catalytic depletion of ozone in the Earth's polar stratosphere, along with the dissociation mechanism



Reaction (R3) is the primary mechanism for forming the perchloric acid precursor in the atmospheric perchlorate formation studies in the CS model. Free chlorine atoms, generated by the photolysis of hydrogen chloride (HCl), are part of a very efficient recycling mechanism, illustrated in Figure 2, which we refer to as the Cl/HCl recycling mechanism. This mechanism acts to maintain the HCl abundance, impeding the association pathway to ClO₃. The Cl/HCl recycling mechanism is further intensified in the Martian context by the lower atmospheric pressures that undermine ClO₃ formation through the Cl channel as compared to the Earth, for instance. This mechanism is shepherded by the Cl + O₂ association reaction



Considering that the mole fraction of O₂ is about 5 orders of magnitude larger than O₃ near the surface, and $k(R3)/k(R2) \sim 0.1$, the Cl/HCl recycling mechanism is about 10,000 times more efficient than the ClO₃-producing channel through reaction (R3).

In contrast, chlorine dioxide provides an effective pathway for forming ClO₃. The association reaction (R2) bypasses the Cl/HCl recycling mechanism, directly forming the chlorine trioxide complex. Unlike the Cl + O₃ reaction, association is the preferred pathway for OClO + O near the Martian surface. At 10 km, the ratio of the rate coefficients of the two OClO + O pathways $k(R1)/k(R1a) = 3.5$, while for Cl + O₃, $k(R2)/k(R2a) = 9.4 \times 10^{-4}$. Thus, the three-body association mechanism forming ClO₃ is favored over the two-body ClO-forming process in OClO + O, while the mechanism yielding ClO and O₂ products dominates in the Cl + O₃ reaction.

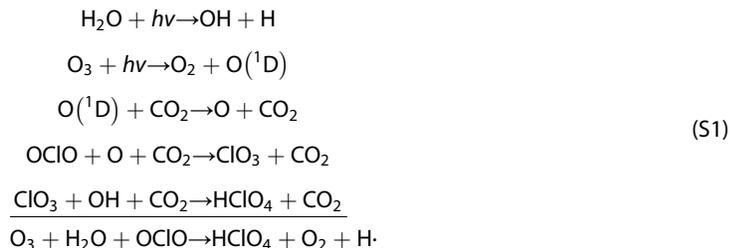
ClO₃ is proposed to react with OH, yielding two pathways, an association reaction that produces perchloric acid



and an addition/decomposition mechanism that is proposed to yield HO₂ and OClO



The pathway to perchloric acid through direct injection of chlorine dioxide into the atmosphere proceeds as follows:



Water vapor, in the atmosphere, provides the important hydroxyl radicals that support this oxidation process. As on Earth, ozone (O₃) also plays an important, albeit indirect, role in the formation of perchloric acid in supplying the necessary oxygen atoms. A secondary source of O atoms in the lower atmosphere is from CO₂ photolysis, so

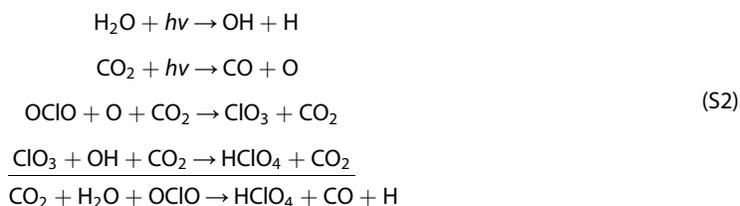


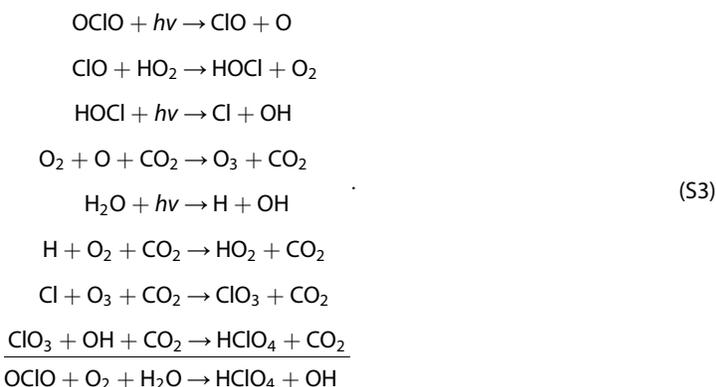
Table 2. Integrated Production Rates for Important Reactions as a Function of OCIO Flux^a

OCIO Flux	10 ⁴	10 ⁵	10 ⁶	10 ⁷	10 ⁸	10 ⁹	10 ¹⁰	2 × 10 ¹⁰	3 × 10 ¹⁰	10 ¹¹
OCIO + O → ClO ₃	2.0 (2)	2.0 (3)	2.0 (4)	2.0 (5)	2.1 (6)	2.3 (7)	5.8 (8)	1.8 (9)	2.0 (9)	1.6 (9)
Cl + O ₃ → ClO ₃	3.2 (1)	3.2 (2)	3.2 (3)	3.2 (4)	3.3 (5)	3.6 (6)	6.6 (7)	2.6 (8)	5.1 (8)	3.3 (8)
OH + ClO ₃ → HClO ₄	4.6 (-1)	4.6 (0)	4.6 (1)	4.6 (2)	4.5 (3)	3.7 (4)	1.4 (5)	1.6 (5)	1.4 (5)	8.0 (4)
ClO + ClO ₃	1.7 (-4)	1.7 (-2)	1.7 (0)	1.7 (2)	1.7 (4)	1.4 (6)	8.3 (7)	3.7 (8)	6.6 (8)	4.0 (8)

^a2.0(2) = 2.0 × 10². All values in units of cm⁻² s⁻¹.

also contributes to perchloric acid formation. The viability of these chemical schemes lies with the availability of OH radicals, which get consumed by carbon monoxide (CO) molecules. A reduction in CO abundance would coincide with an increase in HClO₄ production.

Reaction (R3) does serve as a minor source for ClO₃ under these assumptions, yielding a ClO₃ production rate of ~15% that of reaction (R2) over most of the range of OCIO fluxes considered. The path from OCIO to perchloric acid through reaction (R3) involves a larger variety of chlorine species, which includes part of the Cl/HCl efficient recycling mechanism:



Many of the reactions involved in the above chemical schemes are pressure-dependent reactions, involving a third-body, CO₂. This illustrates that perchlorate production from these mechanisms can only significantly take place at low altitudes (<10 km) and high pressures (>2 mbar).

4. Model Results and Comparison With Catling *et al.*/Smith *et al.* Volcanic Mechanism

To analyze the effect of an influx of chlorine oxides on the formation of perchloric acid, the OCIO boundary flux from the surface was varied from 10³ to 6 × 10¹¹ molecules cm⁻² s⁻¹. The results are displayed in Table 2. As OCIO is injected into the atmosphere, ultraviolet radiation longward of 200 nm, transparent to CO₂ and most of Mars' atmospheric constituents, efficiently destroys chlorine dioxide at a rate of ~500 times that of O addition. The result is the formation of ClO, a cog in the Cl/HCl recycling mechanism that acts as a tourniquet to ClO₃ formation. Thus, at low OCIO fluxes, the production of HClO₄ is limited. Perchloric acid production increases proportionally with OCIO flux up to about 10⁸ cm⁻² s⁻¹. Above this flux level, the flux of OCIO produces enough ClO molecules to diminish the availability of ClO₃ to be converted to HClO₄, as ClO + ClO₃ competes with OH + ClO₃. As a result, perchloric acid production peaks at an OCIO flux of 2 × 10¹⁰ cm⁻² s⁻¹, decreasing thereafter with increasing OCIO flux, as shown in Figure 3.

Smith *et al.* [2014] derived a ClO₄⁻ concentration of 2.8–4.8 × 10⁻⁸ wt % from a perchloric acid deposition rate of 4.6 × 10⁻³ molecules cm⁻² s⁻¹, assuming a soil density of 1 g cm⁻³, a deposition time of 3 × 10⁹ years, and a soil mixing depth of 1.5–2.6 m. Using these assumptions, an HClO₄ production rate of 3.8 × 10⁴ molecules cm⁻² s⁻¹ is necessary to account for the observed Martian perchlorate concentration in the north polar region [Hecht *et al.*, 2009]. Under our nominal scheme, a flux of 10⁹ OCIO molecules cm⁻² s⁻¹, generated by radiolysis, would provide the necessary yield of perchloric acid. As Table 1 shows, higher OCIO fluxes would also produce the requisite amount of HClO₄.

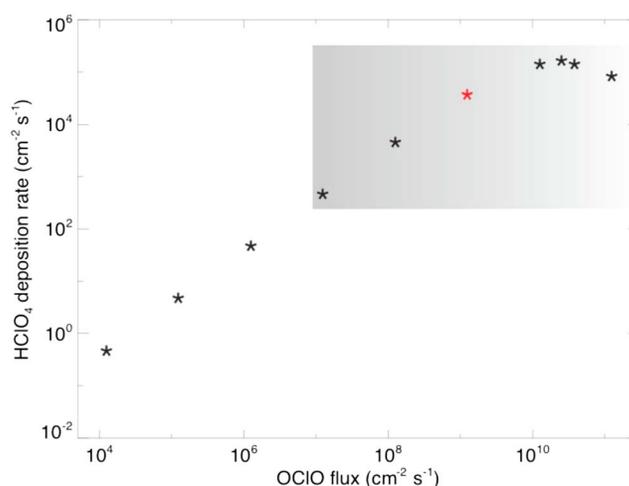


Figure 3. Plot of the model-calculated deposition rate of perchloric acid versus the input chlorine dioxide surface flux. The rectangular area represents the values that could explain the observed perchlorate abundances on the Martian surface.

pole, with uncertainties of about 40% [Smith *et al.*, 2009]. Considering that periods of high obliquity would bring glaciation down to lower latitudes, it is not unreasonable to consider that the CO mixing ratio could be at these levels at low and middle latitudes during chlorine oxide sublimation. Reducing the CO mole fraction in our model from 8.0×10^{-4} to 2.0×10^{-4} decreases the required OCIO surface flux to 1.6×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$.

Mixing depth is another area of considerable uncertainty. Smith *et al.* assumed a mixing depth of 1.5–2.6 m, taking 3 times the e -folding depth calculated by Zent [1998]. Zent [1998] calculated $1/e$ mixing depths for post-Noachian conditions of 0.51–0.85 m. However, the level of mixing in driving oxidants down from the surface through the regolith at the Phoenix site is still up to debate. Mellon *et al.* [2008] examined periglacial landforms at the Phoenix landing site and found small-scale polygons of about 3–6 m in diameter and rock sorting that they argue is indicative of cryoturbation overturning of the surface on the order of a few meters in depth over the past few million years. Gallagher *et al.* [2011] found landforms 25 km east of the Phoenix landing site that they indicate are consistent with freeze-thaw cycles that accompany the overturning of the surface. However, Levy *et al.* [2009] did not find any evidence of rock sorting at the Phoenix landing site and concluded that landforms were consistent with a dry, quiescent history with only ice sublimation, as opposed to the dry cryoturbation or freeze-thaw scenarios. The Zent model demonstrates that only the top 30 cm is likely to undergo complete oxidation and that oxidation falls off considerably below the top tens of centimeters of crust. We consider this conservative scenario and use this depth to calculate a lower limit for OCIO flux. The HClO_4 production rate necessary to account for the observed concentration of perchlorate accumulated in the top 30 cm of the surface since the Amazonian period is 7.7×10^3 molecules $\text{cm}^{-2} \text{s}^{-1}$, corresponding to a OCIO flux of 3.2×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$. We take this value as our lower limit for OCIO flux under this mechanism (Figure 3).

The results of the nominal model can be directly compared with the CS model. Using the same background atmosphere the nominal model calculates an HClO_4 production rate of about 7 orders of magnitude greater than the CS model. Part of the discrepancy is associated with a larger chlorine flux into the atmosphere. Smith *et al.* include a volcanic flux of 6.0×10^4 HCl molecules $\text{cm}^{-2} \text{s}^{-1}$, while our nominal model calculates the requisite rate of HClO_4 production with a chlorine flux larger than Smith *et al.* by a factor of 1.7×10^4 . The radiolysis method can potentially release significantly more chlorine into the atmosphere than volcanism, as the radiolysis mechanism is not bound by the energy budget of the planet but rather by the energy input into the atmosphere from external sources. Moreover, this energy input is available throughout the entire planet and throughout all of Martian history, as opposed to volcanism, which has geographic limitations and a more limited timeframe [Craddock and Greeley, 2009]. We add that this process may operate in parallel with other perchlorate-forming processes, such as UV-induced oxidation as suggested by Carrier and Kounaves [2015].

However, the required amount of HClO_4 production depends on the assumptions used in the calculations. HClO_4 production is very dependent on the hydroxyl (OH) mole fraction. OH, supplied by H_2O ((S1)), is highly sensitive to the CO abundance, as CO is the major sink for hydroxyl radicals. The quadrupole mass spectrometer on the SAM suite measured the CO mole fraction at $7.49 \pm 0.026 \times 10^{-4}$ at the Gale Crater low-latitude site [Franz *et al.*, 2015]. In contrast, the Compact Reconnaissance Imaging Spectrometer on the Mars Reconnaissance Orbiter, which measured a globally averaged CO mole fraction of 700 ppm, sampled the north pole CO mole fraction at 200 ppm and 400 ppm at the south

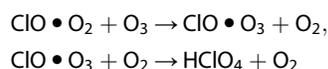
Another difference between the nominal model and the CS model pertains to the OH + ClO₃ reaction. In their study on chlorine chemistry in the Atacama, CS reduced the rate coefficients for OH + ClO₃ (reaction (R1)) and Cl + O₃ (reaction (R3)) by a factor of 30 in order to match their HCl profile with observations. Reaction (R3) has not been measured in the laboratory, and *Simonaitis and Heicklen [1975]* used OH + NO as an analogy to estimate the reaction (R3). Reaction (R3) is a less important reaction in our scheme as chlorine flows to ClO₃ primarily through OClO, rather than through the Cl/HCl mechanism as in the CS model. So the CS rate coefficient for reaction (R3) has been adopted in the nominal model. However, for reaction (R1) *Zhu and Lin [2001]* conducted a theoretical ab initio calculation of the OH + ClO₃ reaction complex. Their calculations found that the association/decomposition pathway (reaction (R1a)) lacks a reaction barrier and proceeds with a minimal temperature dependence from 300 to 3000 K. In addition, the HClO₄-producing pathway at high pressures proceeds at rates comparable to the (reaction (R1a)) channel in this temperature range. CS considered this rate coefficient in their Atacama study but dismissed it citing difficulty in matching the HCl profile. Considering the behavior of the OH + ClO₃ complex, we find it difficult to believe that the rate coefficient would drop by a factor of 30 between 300 K and Martian temperatures, and given the lack of evidence to the contrary, we adopt the Zhu and Lin rate coefficient for reaction (R1). This difference accounts for a factor of 30 difference in the HClO₄ yield between the nominal model and the CS Mars model.

The remaining difference stems from the greater efficiency in chlorine incorporation into HClO₄ via OClO as opposed to the efficient recycling mechanism of Cl/HCl. It is more difficult to explain the larger perchlorate/chloride ratios found on Mars through an atmospheric mechanism involving HCl as the high efficiency of the Cl/HCl cycle prevents a large yield of HClO₄ in relation to HCl. The CS mechanism appears to be a more viable way of forming perchlorate in the Atacama or Antarctic Dry Valleys, where the ClO₄⁻/Cl⁻ ratio are ~1:500 [*Catling et al., 2010*] and 1:1500–3000 [*Kounaves et al., 2010a*], respectively. However, in the nominal scheme the independence of perchlorate formation to the HCl abundance would permit perchlorate/chloride ratios near or greater than unity, more indicative of what is found on the surface of Mars [*Hecht et al., 2009; Kounaves et al., 2010b; Archer et al., 2015*].

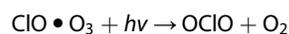
5. Other Possible Sources of Perchlorate

Our calculations are based on the assumption that chlorine oxides formed through radiolysis are injected via sublimation into the atmosphere in the form of OClO. The study of *Kim et al. [2013]* shows that irradiation of chlorine-doped ice yields ClOOCl and ClOCl as well, along with evidence for higher-order chlorine oxides. ClOOCl and ClOCl form ClO through photolysis, which can lead to HClO₄ formation, albeit less efficiently than OClO. Molecules that contain –ClO₂ and –ClO₃ functional groups can also be sources of HClO₄ through ClO₃ or OClO. For instance, Cl₂O₆ rapidly decomposes into OClO and O₂ in the gas phase [*López and Sicre, 1990*]. More investigation regarding the identification and kinetics of these compounds are needed.

ClO₃ chemistry itself could also provide additional mechanisms for perchloric acid formation. ClO₃ has been positively identified by *Grothe and Willner [1994]* and *Kopitzky et al. [2002]*. The photolysis of ClO₃ results in the formation of ClO and O₂. However, there is evidence of a ClO•O₂ complex forming from the photolysis of ClO₃ at 255 nm [*Kopitzky et al., 2002*]. ClO•O₂ may potentially provide a rapid pathway to HClO₄ through



or to OClO through the photolysis of the ClO•O₃ complex



[*Prasad and Lee, 1994*], but much more work is necessary in understanding the stability and dynamics of ClO•O₂ and ClO•O₃ in order to evaluate the viability of these pathways.

In addition, a further source of OClO could be the irradiation of perchlorate salts themselves. *Quinn et al. [2013]* analyzed the effects of GCR irradiation on Ca(ClO₄)₂ and found that hypochlorite (ClO⁻) and OClO could be produced in the Martian soils. OClO would return to the atmosphere, creating a recycling mechanism for HClO₄ production, while unstable ClO⁻ would likely be converted into hypochlorous acid (HOCl) under aqueous settings and participate in the Cl/HCl recycling, or chloride ion (Cl⁻), impacting the Cl⁻/ClO₄⁻ ratio.

Recent experiments [Turner *et al.*, 2016] demonstrate that the decomposition of hydrated perchlorate by energetic electrons from GCR irradiation would produce chlorate anions (ClO_3^-), which could form perchloric acid from the mechanism in this study.

As mentioned above, the irradiation of the Martian surface by UV [Schuttlefield *et al.*, 2011; Carrier and Kounaves, 2015] or by GCRs (this study) may produce the requisite perchlorate on the Martian surface. However, they may not be the only radiation source of chlorine oxides in the Mars environment. Solar cosmic rays (SCRs) are a source of radiation whose dosage can exceed that of GCRs during periods of low obliquity on Mars [Pavlov *et al.*, 2012], when the total atmospheric pressure would drop to 0.2–0.3 mbar [Armstrong *et al.*, 2004]. Periods of low atmospheric pressure would likely make up about 10% of the Martian history. Furthermore, the SCR dosage in these periods of low pressure would drop off by 2 orders of magnitude below the top 2–3 cm of the Martian surface [Pavlov *et al.*, 2012], making SCRs a likely minor radiation source. GCRs can also provide ionizing radiation on Martian dust, which contains comparable amounts of chlorine [Morris *et al.*, 2006]. This dust can act as a potential additional source of chlorine oxides in the Martian atmosphere. In addition to GCRs, solar energetic particles (SEPs) provide significant ionizing radiation, which acts on the dust in the atmosphere [Norman *et al.*, 2014]. Events producing SEPs are sporadic, and SEPs have little effect below the surface, but the energy provided by such an event can be a source of radiolysis on atmospheric dust particles over the course of Martian history.

6. Conclusions

In summary, we have investigated the formation of perchloric acid initiated by radiolysis of the Martian surface by galactic cosmic rays. The injection of chlorine oxides into the atmosphere can proceed through the interaction of secondary electrons from the radiolysis process with the Martian surface, followed by the sublimation of the chlorine volatiles into the atmosphere. We conclude that the injection of one such chlorine oxide into the atmosphere, OClO, with a flux as low as 3.2×10^7 molecules $\text{cm}^{-2} \text{s}^{-1}$ integrated over the Amazonian period and an accumulation depth of 30 cm can produce the requisite amount of HClO_4 to account for the observed perchlorate abundance in the Martian surface.

Although there are many uncertainties regarding the details, this study demonstrates that the radiolysis mechanism presents a viable mechanism for the formation of the necessary chlorine oxides and a reasonable alternative to other hypotheses considered. GCRs act as an available energy source over the entire planet at all times throughout Martian history, and climatological changes brought on by obliquity evolution make radiolysis a feasible process globally. As a result, the proposed mechanism can inject more chlorine into the atmosphere than the volcanism mechanism proposed by Catling *et al.*/Smith *et al.*

We also find that the injection of OClO into the atmosphere presents chemical pathways that are more efficient in forming higher-order chlorine oxides than the volcanic mechanism, as the chemical mechanism of association; attaching O atoms and OH molecules to chlorine dioxide largely circumvents much of the efficient Cl/HCl recycling mechanism that inhibits the growth of chlorine compounds in the Martian atmosphere. This mechanism may provide an explanation for the larger perchlorate/chloride ratio observed on Mars as compared to the Earth, which may be an indication of differing perchlorate formation mechanisms for those two examples. Additional lab studies are required to determine the precise yields and nature of chlorine oxides from surface radiolysis and the possibility of production of perchloric acid and eventually, perchlorates directly in the surface.

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