



Atmospheric origins of perchlorate on Mars and in the Atacama

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[1] Isotopic studies indicate that natural perchlorate is produced on Earth in arid environments by the oxidation of chlorine species through pathways involving ozone or its photochemical products. With this analogy, we propose that the arid environment on Mars may have given rise to perchlorate through the action of atmospheric oxidants. A variety of hypothetical pathways can be proposed including photochemical reactions, electrostatic discharge, and gas-solid reactions. Because perchlorate-rich deposits in the Atacama desert are closest in abundance to perchlorate measured at NASA's Phoenix Lander site, we made a preliminary study of the means to produce Atacama perchlorate to help shed light on the origin of Martian perchlorate. We investigated gas phase pathways using a 1-D photochemical model. We found that perchlorate can be produced in sufficient quantities to explain the abundance of perchlorate in the Atacama from a proposed gas phase oxidation of chlorine volatiles to perchloric acid. The feasibility of gas phase production for the Atacama provides justification for future investigations of gas phase photochemistry as a possible source for Martian perchlorate.

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1. Introduction

[2] NASA's Phoenix Lander was equipped with a Wet Chemistry Laboratory (WCL) experiment comprising four wet chemistry cells [Kounaves *et al.*, 2009b]. In three of the four WCL cells, $\sim 1 \text{ cm}^3$ of Martian soil was mixed with 25 cm^3 of dilute leaching solution and a combination of ion-specific electrodes, electrical conductivity and cyclic voltammetry was used to identify a variety of soluble anions. Unfortunately, one cell out of the four failed to acquire a soil sample, although this provided a fortuitous experimental control. Of particular note was a Hofmeister series anion electrode sensor, which had sensitivity to nitrate and perchlorate (ClO_4^-) in a ratio of $\sim 1:10^3$. This sensor obtained such a large signal that no other explanation than a substantial concentration of perchlorate can be viable because if the signal were attributed to nitrate then the amount of nitrate would be unfeasible, greatly exceeding the soil sample mass. On this basis, perchlorate was identified

as a dominant soluble anion [Hecht *et al.*, 2009; Kounaves *et al.*, 2009a]. For an assumed soil sample mass $\sim 1 \text{ g}$, the WCL measurements imply a range of $\sim 0.5\text{--}0.6 \text{ wt } \% \text{ ClO}_4^-$ in the three soil samples [Hecht *et al.*, 2009]. The inferred presence of perchlorate is consistent with two additional measurements. First, a Ca^{2+} ion-specific electrode in each WCL cell suffered an offset consistent with a known interference when perchlorate is in solution. Second, evidence for perchlorate appeared in the Thermal Evolved Gas Analyzer (TEGA) where soil samples were heated and gas released was fed into a mass spectrometer. Mass 32, consistent with molecular oxygen (O_2), started to be produced at a temperature $\sim 325^\circ\text{C}$ with a peak at 465°C , which is expected for the thermal decomposition of alkali or alkaline earth perchlorates [Hecht *et al.*, 2009].

[3] On a molar basis, the WCL data suggest that perchlorate exceeds chlorine in the soil by about an order of magnitude, although the factor could be greater given that there was a leak into the WCL cells of a barium chloride reagent. In any case, most of the chlorine has been oxidized as far as possible because the chlorine within perchlorate has a maximal +7 oxidation number. From a thermodynamic perspective, this makes perchlorate a strong oxidizing agent but kinetically, perchlorate is very inert at typical planetary surface temperatures. The energetically stable tetrahedral structure of oxygen atoms in perchlorate around the central, electrophilic chlorine atom renders perchlorate unreactive [Brown and Gu, 2006]. Hence, perchlorate, once formed, is prone to persist in soil provided that liquid water does not flush the perchlorate away, given that perchlorate salts are generally highly soluble. In contrast, if an environment is very wet, perchlorate is liable to be leached out

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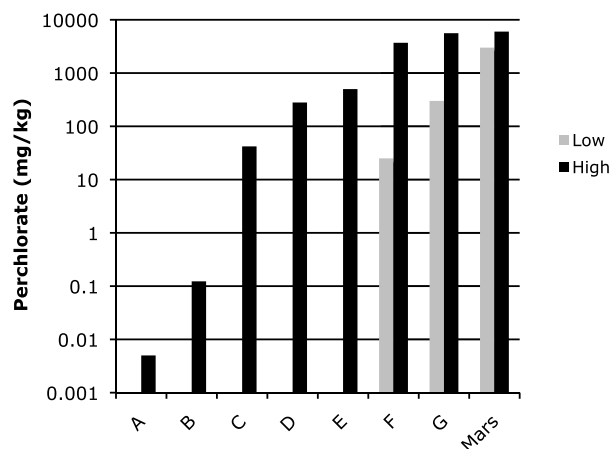


Figure 1. Perchlorate abundances in locations on Earth (A to G) compared with that deduced from the Phoenix Mars Lander. Where a range is reported, bounds are marked by high and low values. Location A, within sulfate aerosols in Earth stratosphere [Murphy and Thomson, 2000]; location B, carbonate of Mission Valley Formation, San Diego [Duncan et al., 2005]; location C, potash sylvinitic-rich ore, Saskatchewan; location D, Searles Lake evaporites, California [Orris et al., 2003]; location E, Bolivian playa evaporite crusts in the Andean Altiplano [Orris et al., 2003]; location F, Permo-Triassic sylvinitic-rich potash ore, Carlsbad, New Mexico [Orris et al., 2003]; location G, Atacama caliche blanco veins (best nitrate ore) [Ericksen, 1981].

of soil and end up diluted to trace concentrations in groundwater or rivers. In anaerobic conditions on Earth, the perchlorate is then microbially degraded back to chloride [Coates and Achenbach, 2004]. In short, perchlorate will accumulate in soil if its rate of deposition exceeds the rate of dissolution, and it will then persist if conditions remain free of perchlorate reduction. Thus, the oxidizing aridity of Mars, combined with perchlorate being an unreactive cul-de-sac of oxidation chemistry, probably explains the unusual abundance of perchlorate in Martian soil.

[4] Where the perchlorate came from is an important question. The answer could help us in understanding the general origin of the components of soil and, in turn, the overall geochemical evolution of Mars. Here, after briefly reviewing our knowledge of terrestrial perchlorate, we consider various chemical pathways for the formation of Martian perchlorate. In general, the chemistry suggests that the source was likely atmospheric, associated with the production of oxidants. If this is so, perchlorate will act as a tracer of past atmospheric chemistry. For example, perchlorate might track volcanic gas fluxes of chlorine. Consequently, the measurement of perchlorate might be a valuable consideration for future missions to Mars to drill polar ice [Hecht, 2006] or return samples [MEPAG, 2008].

[5] Because the chemical pathways to produce natural perchlorate on Earth are currently unknown, we investigate the formation of perchlorate in the Atacama desert, where the abundance of perchlorate is the best analog to Mars. By

looking at the Atacama, we may gain some insight into possible atmospheric formation mechanisms on Mars.

2. Occurrence and Origin of Natural Perchlorate on Earth

[6] Before considering the origin of perchlorate on Mars, it is appropriate to start with what is known about perchlorate on Earth. Most terrestrial perchlorate is produced artificially for uses such as rocket propellants and fireworks [Trumpolt et al., 2005]. In contrast, natural perchlorate is rare and is found only in the driest places, such as unusually arid deserts and the stratosphere. Figure 1 shows reported concentrations of various natural sources of perchlorate compared with the abundance range from the three soils sampled by WCL at the Phoenix site. Natural terrestrial perchlorate occurs at Mars-like levels only in the Atacama, where peak perchlorate concentrations reach ~ 0.6 wt % in veins of white-colored nitrate ore known as caliche blanco [Ericksen, 1981]. In general, average nitrate ores from the Atacama have perchlorate concentrations ~ 0.03 wt % [Michalski et al., 2004]. At lower abundances than on Mars, perchlorate is reported from deserts of West Texas [Dasgupta et al., 2005] and Bolivian playas [Orris et al., 2003], as well as in carbonates of the upper Eocene Mission Valley Formation of San Diego [Duncan et al., 2005] and sylvinitic (KCl) ore in central Canada and Permo-Triassic New Mexico [Orris et al., 2003]. In terms of perchlorate abundance, the Atacama clearly provides the best match, but we note that the average perchlorate:chloride ratio in Atacama nitrate ores of ~ 0.002 [Grossling and Ericksen, 1971] is markedly different compared to Mars. In the Atacama, chloride has potentially large sources including marine aerosols or leaching from highly permeable rhyolitic ash flow tuffs produced by Andean volcanism [Ericksen, 1981].

[7] Key insights into the origin of natural perchlorate on Earth have come from isotopic analysis [Bao and Gu, 2004; Duncan et al., 2005]. Through such investigation, perchlorate in the Atacama can be definitively attributed to an atmospheric source. The specific evidence is that significant nonmass-dependent (NMD) fractionation occurs in the oxygen isotopes of ClO_4^- . In most processes, isotopes undergo mass-dependent fractionation (MDF) in proportion to the difference in mass between the isotopes. In the case of oxygen isotopes measured with respect to ^{16}O , the mass of ^{17}O relative to ^{16}O is half that of ^{18}O relative to ^{16}O , so usual isotopic fractionation gives a straight-line relationship defined by $\delta^{17}\text{O} \sim 0.5\delta^{18}\text{O}$. (A more precise determination of the mass-dependent line is $\delta^{17}\text{O} = 0.52\delta^{18}\text{O}$). Deviations from this straight-line relationship are termed NMD or “mass-independent fractionation” and are measured as the deviation off the straight line, which is represented by the notation $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52\delta^{18}\text{O}$ (reviewed by Farquhar and Johnston [2008] and Thiemens [2006]). In the terrestrial atmosphere, the oxygen atoms in ozone (O_3) are known to possess an unusual degree of NMD isotopic fractionation. Consequently, the NMD isotopic fractionation of oxygen in perchlorate is attributed to the photochemical reaction of ozone or its products (such as O or OH) with volatile chlorine species in which perchlorate is formed that inherits its NMD oxygen isotope signature from O_3 . A factor of four difference between the $\Delta^{17}\text{O}$ of perchlorate (4.2–9.6‰)

and O₃ (30–40‰) suggests that O₃ or its products contributes one oxygen atom in four to perchlorate [Bao and Gu, 2004]. Chlorine isotopes are also unusual. Atacama ClO₄⁻ has a δ³⁷Cl of -14.5 to -9.2‰, which is the lowest δ³⁷Cl of any common substance on Earth and consistent with atmospheric fractionation [Böhlke et al., 2005].

[8] Despite the inference that natural perchlorate is formed atmospherically, the photochemical pathway is presently unknown and remains speculative [Bao and Gu, 2004; Kang et al., 2008; Roberts, 2009]. Chlorine oxides are readily generated from chlorine inputs to the atmosphere, and reaction pathways that include O₃ can produce perchloric acid (HClO₄). Perchloric acid is a condensed phase and a stable end product of atmospheric chemistry due to its resistance to photolysis [Simonaitis and Heicklen, 1975]. Presently, tropospheric measurements of perchloric acid are lacking, but HClO₄ has been quantified in the dry environment of Earth's stratosphere at abundances of 0.5–5 ppt in sulfate aerosols [Murphy and Thomson, 2000]. In an atmosphere devoid of rain, perchloric acid will undergo dry deposition onto the surface below. In this regard, it is useful to think of sulfuric acid and nitric acid as analogs to perchloric acid, because both sulfuric and nitric acids are the terminal condensed phases that result from the photochemical oxidation of sulfur- or nitrogen-bearing gases.

[9] Although there is good evidence that the Atacama perchlorate derives from atmospheric chlorine, the origin of this chlorine is not yet fully known or quantified. A variety of chlorine sources have been discussed including volcanic HCl from the Andes, aeolian chlorides where heterogeneous reactions liberate chlorine volatiles, or biogenic methyl chloride from distal marine sources [Bao and Gu, 2004; Ericksen, 1981].

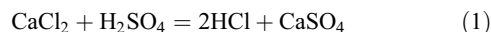
3. Possible Origins of Perchlorate on Mars

[10] Using terrestrial perchlorate as an analog, we might reasonably suggest that perchlorate forms on Mars through oxidizing chemistry in the desiccating environment. A well-known source of oxidizing power on Mars today is the atmosphere where photochemistry generates a variety of oxidizing species [Huntten, 1979]. Photochemical models show that fluxes of H₂O₂ and O₃ dominate the oxidizing fluxes to the surface and are roughly equivalent in terms of their oxidizing power [Zahnle et al., 2008]. Other oxidants include, for example, OH, HO₂, O and O⁻. Meanwhile ultraviolet action on minerals can produce superoxide free radicals (O₂⁻), further providing an environment conducive to oxidation [Yen et al., 2000].

[11] Perchlorate could form in a cold, oxidizing environment and such conditions have probably existed over much of Martian history, including times when active volcanism emitted chlorine-bearing volatiles. Evidence from aqueous alteration minerals and fluvially eroded geological features suggests that different climate regimes and atmospheric conditions occurred during the Noachian before ~3.7 Ga and the Hesperian era, which terminated ~2.9–3.3 Ga [Carr, 1996, 2006; Hartmann and Neukum, 2001]. A largely cold, dry climate since then is consistent with a combination of evidence and theory that suggests that much of Mars' atmosphere would have been lost by the end of the

Hesperian [Catling, 2009]. But volcanism has occurred since then. First, lava flows with few or no impact craters show that volcanism has been active in the past tens of millions of years [Hartmann et al., 1999; Neukum et al., 2004]. Second, with the sole exception of the 4.5 Ga ALH84001 Martian meteorite, the crystallization ages of all the other Martian meteorites are relatively young, ranging from 1.3 Ga for Chassigny and the nakhlites, to 180 Ma for peridotitic shergottites and 165–475 Ma for basaltic shergottites [Nyquist et al., 2001]. These radiometric ages unequivocally indicate active volcanism in the Amazonia era (since 2.9–3.3 Ga). Thus, for hundreds of millions of years during which Mars has likely been predominantly cold and dry, perchlorate may have accumulated on the surface as a result of photochemical reactions when volcanic emissions occurred. If wet climates on early Mars were intermittent, as some suggest [Segura et al., 2002], perchlorate may also have formed then but it would have been mobilized in the soil whenever liquid water was available.

[12] The schematic diagram of Figure 2 summarizes oxidative processes that might hypothetically generate perchlorate on Mars and in the Atacama. In Figure 2a, some pathways for Mars are likely unimportant relative to others and some pathways might not function at all. The range of hypothetical processes is succinctly classified in Table 1, a subset of which is relevant only to the Atacama. Overall, there are two possibilities for chlorine sources that might lead to perchlorates: first, chlorine-containing gases released into the atmosphere that take part in gas phase reactions; second, chlorides in minerals (aerosol or surface soil particles) that participate in heterogeneous reactions. In volcanic gases, HCl would have been abundant in the past on Mars [Wänke and Dreibus, 1994]. Given that acidic, near-surface aqueous environments have been suggested for Mars [Hurowitz et al., 2006], another way that HCl could have been generated on Mars is via acid displacement reactions with chloride salts, e.g.,



[13] However, if the perchlorate chlorine solely derived from volcanism, principally as HCl, the required flux turns out to be reasonably modest and plausible. Estimates for the terrestrial HCl emission flux range $\sim(3.3 \text{ to } 465) \times 10^{10}$ mol HCl yr⁻¹, which includes the water soluble fraction removed during ascent of volcanic plumes [Halmer et al., 2002]. It should also be noted that volcanic fluxes are very variable over time [Hammer et al., 1997]. On the basis of estimates of relative volcanic outgassing between Earth and Mars [Greeley and Schneid, 1991; Tanaka, 1988], it is reasonable to consider a past volcanic flux on Mars $\sim 10^8$ mol HCl yr⁻¹, of order $\sim 10^2$ times smaller than the modern Earth's. Mass balance shows that such a volcanic source acting over ~ 10 Myr could produce ~ 1 wt % Mg(ClO₄)₂ in 10 cm of soil (with density ~ 1 g cm⁻³) over the entire surface of Mars if we assume that all the chlorine is converted to perchlorate. Because this is a modest volcanic flux over a modest time scale, a volcanic chlorine source is credible for perchlorate on Mars.

[14] Chlorine might also be sourced from aerosols. On Earth, OH radicals react at the deliquesced water-gas

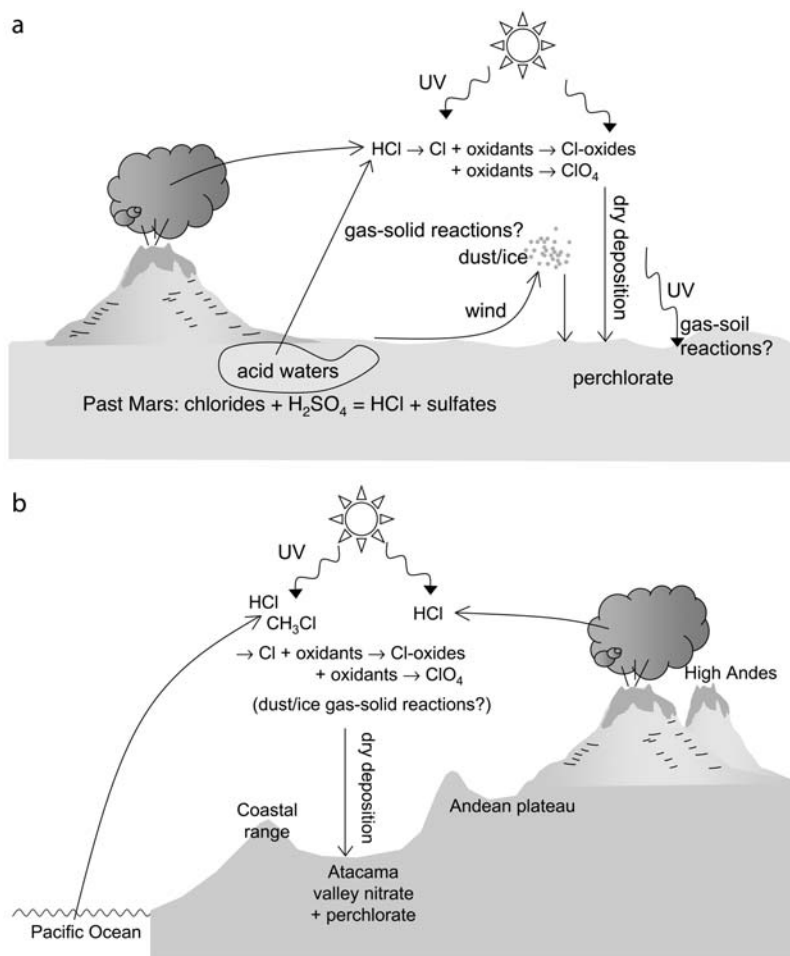
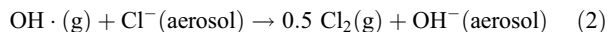


Figure 2. (a) Schematic diagram illustrating possible chemical pathways to produce perchlorate on Mars. (b) Schematic showing the case of the perchlorate-rich deposits in the arid Atacama desert of northern Chile.

interface of sea salt particles to release chlorine via [Knipping *et al.*, 2000]



[15] However, films of liquid water on the aerosol are essential for this reaction to be kinetically viable. If any similar reactions took place on Mars, Cl₂ would rapidly photolyze to reactive chlorine atoms, potentially available for oxidation to perchlorate.

[16] If ozone is specifically required to create Martian perchlorate (as inferred for terrestrial perchlorate from isotope measurements), perchlorate formation might be enhanced in polar environments due to the marked variation of ozone with latitude. Observations by ultraviolet spec-

trometers on Mariner 9 and Mars Express show that ozone is most abundant in the spring-winter circumpolar regions [Barth *et al.*, 1973; Perrier *et al.*, 2006]. The ozone levels in the tropics increase during aphelion possibly due to heterogeneous loss of odd hydrogen species onto water ice cloud particles [Lefevre *et al.*, 2008] but are still lower than the levels reached in polar regions.

[17] Dry, gas-solid reactions of UV-activated chlorides with oxidizing atmospheric species at the ground or on aerosol surfaces may be alternative ways to produce perchlorate without invoking volatile chlorine species; however, laboratory studies under Mars-like conditions are required to confirm that such pathways exist and to assess their efficiency. Some experiments show that O₃ does not react directly with dry NaCl but will if thin films of water

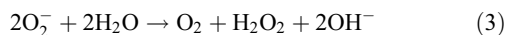
Table 1. Possible Mechanisms to Produce Perchlorate on Mars or the Atacama^a

Mechanism	Chlorine Source
Photochemical reactions with oxidants such as O ₃	(1) Volcanic HCl (plus CH ₃ Cl for the Atacama) (2) HCl liberated from acid displacement reactions (3) Cl atoms liberated from aerosol chloride
Electrostatic discharge	(1) Aerosol or surface soil chlorides (2) Volatile species as above
Gas-solid reactions with oxidants	Aerosol surfaces or soil chlorides on the ground

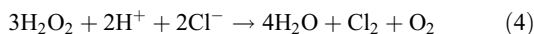
^aIn all cases, the ultimate source of oxidation is atmospheric.

are involved [Alebic-Juretic et al., 1997; Oum et al., 1998]. On the other hand, other experiments in high levels of ozone ($\sim 1\%$ versus ~ 10 ppbv typically in Earth's troposphere) produced a small molar yield of 0.025–0.4% conversion of chloride-coated sand to perchlorate [Kang et al., 2008]. Trace amounts of perchlorate have also been produced when dry chloride salts were exposed in the presence of titanium dioxide (TiO_2) and nitrate to ultraviolet radiation [Miller et al., 2004]. Both TiO_2 and nitrate are thought to catalyze the formation of the hydroxyl radical from adsorbed water under UV irradiation.

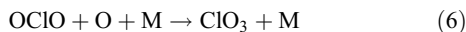
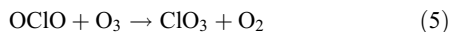
[18] Superoxide free radicals (O_2^-) are also generated by the action of ultraviolet light on mineral surfaces [Yen et al., 2000]. Ignoring possible reactions with organic molecules, superoxide is relatively stable in dry conditions, which why Yen et al. [2000] hypothesized its existence on Mars today, so it seems unlikely that it would generate perchlorate through dry reaction with chlorides, although lab experiments are needed for verification. In water, superoxide dismutates into hydrogen peroxide (H_2O_2):



[19] Experiments show that H_2O_2 fails to produce perchlorate from lower oxidation states of chlorine. Boiling 15 cm^3 of 30% H_2O_2 solution with 1g of dissolved sodium chlorate produces no perchlorate in alkaline conditions, whereas in acid conditions, chlorides oxidize and gas evolved [Mack, 1917] via reactions such as



[20] A role for water ice as a reaction surface for adsorbed species may be a possible path to perchlorate chemistry. ClO radicals are readily produced by atmospheric oxidation of chlorine volatiles, and ClO can interact on ice to produce OClO when the ice sublimates [McKeachie et al., 2004]. Chlorine dioxide (the OClO molecule is not to be confused with Cl-O-O, which is the chlorine peroxy radical, unfortunately also sometimes called “chlorine dioxide”) is a possible source of perchlorate because it can react with O_3 or O to make chlorine trioxide [Wayne et al., 1995]:



[21] Here “M” is any molecule, usually the most abundant one. In turn, ClO_3 can react with OH to make perchloric acid. An involvement of water ice might favor perchlorate at colder, high latitudes on Mars.

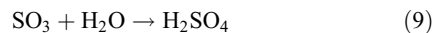
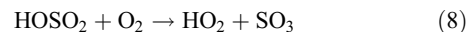
[22] Finally, electrostatic discharge can act as an oxidant for chloride-bearing aerosols. Electrostatic discharges are believed to occur in Martian dust storms and dust devils because of triboelectric charging of dust and low barometric pressure [Atreya et al., 2006]. However, although the production of terrestrial perchlorate from chloride aerosols with electrostatic discharge has been demonstrated [Dasgupta et al., 2005], the $\text{ClO}_4^-:\text{Cl}^-$ ratios are very small (<0.01), whereas the Phoenix soil data require $\text{ClO}_4^-:\text{Cl}^-$

ratios around 3 orders of magnitude greater, i.e., ratios of a factor of ~ 10 or more. Either more efficient oxidation pathways (such as gas phase reactions) are implied or a vast number of electrostatic events over geologic time with high cumulative efficiency would be required.

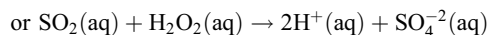
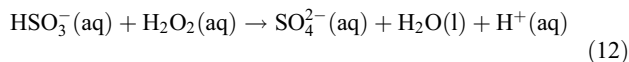
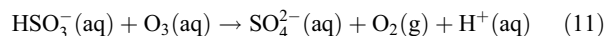
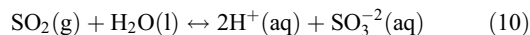
4. Atmospheric Pathways to Produce Perchlorate

[23] In the rest of this paper, we focus on examining the viability of one of the possible processes to produce perchlorate, namely gas phase reactions ending in condensed phase perchlorate. In principle, the chemistry is amenable to investigation through photochemical models by using the large body of chlorine photochemical knowledge that has accumulated from the extensive study of Earth's stratospheric ozone depletion and tropospheric halogens [von Glasow and Crutzen, 2006]. However, since the chemical pathway to produce atmospheric perchlorate on Earth is still unknown, we concentrate on examining the origin of terrestrial perchlorate in the Atacama rather than on Mars for a number of reasons. The Atacama provides the best analog for Martian perchlorate based on abundance (Figure 1) and has the advantage that we have measurements of the relative amounts of sulfate, nitrate and perchlorate. The bulk of these salts in some parts of the Atacama are inferred to have atmospheric sources on the basis of NMD fractionation in the oxygen isotopes [Michalski et al., 2004]. Also, we have knowledge of the background concentration of trace chlorine and nitrogen species in the Earth's atmosphere, which makes the Atacama more amenable to study than Mars. Consequently, consideration of Atacama salts allows verification of a model of photochemical production of perchlorate and tests of proposed pathways of atmospheric chemistry.

[24] We mentioned above that the photochemical production of sulfate and nitrate might bear some analogy to that of perchlorate. In the gas phase, sulfate can be produced as follows [Seinfeld and Pandis, 1998]:



[25] However, no NMD isotope fractionation of oxygen (as found in the sulfate) is created in this gas phase sequence because OH, O_2 , H_2O and SO_2 have $\Delta^{17}\text{O} \sim 0\%$. Instead, an aqueous phase process has been suggested in which SO_2 dissolves to form sulfurous acid and is then oxidized by either O_3 or H_2O_2 :

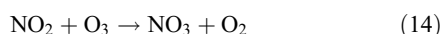


[26] Ozone and, to a much lesser extent, H_2O_2 are carriers of $\Delta^{17}\text{O}$ anomalies that can be transferred to the sulfate [Savarino *et al.*, 2000]. The branching ratio of reaction (11) to (12) depends on the concentration of reactants and the pH, where acidity favors oxidation by H_2O_2 [Xing and Chameides, 1991].

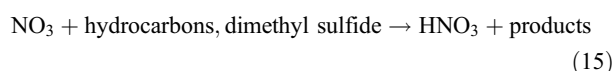
[27] Nitrate in the form of nitric acid can be atmospherically produced in three ways. First, NO_2 can react with OH (in exact analogy to (7)):



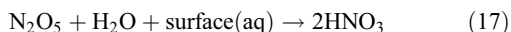
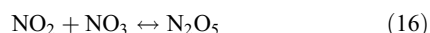
Alternatively, NO_2 can react with ozone to make NO_3 :



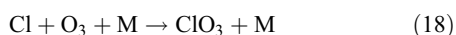
The above can be followed by two possible pathways: either



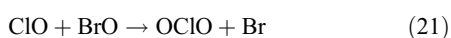
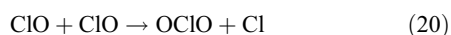
or



[28] In contrast with the production of sulfate or nitrate, the pathways to perchlorate are uncertain [Roberts, 2009]. In Earth's atmosphere, Simonaitis and Heicklen [1975] suggested that perchloric acid might be a sink in the stratosphere to account for "missing chlorine" in the chlorine budget. The key steps were the production of chlorine trioxide and its oxidation by OH:



[29] Because OH reacts with a number of species in the atmosphere, the final step can only be efficient if there is enough available ClO_3 . An alternative to reaction (18) is that ClO_3 can form from chlorine dioxide, OClO. Chlorine dioxide can make chlorine trioxide via reactions (5) and (6). However, a difficulty is the small rate constant for reaction (5) of OClO with O_3 and the susceptibility of OClO to photolysis to O and ClO, which makes it less important during the daytime [Birks *et al.*, 1977]. In a minor pathway, chlorine perchlorate (ClOClO_3) can also form from the three-body $\text{ClO}_3 + \text{ClO} + \text{M}$ reaction [Barton *et al.*, 1984; Croce *et al.*, 2008; Schell-Sorokin *et al.*, 1982]. In turn, chlorine perchlorate could, in principle, react with metal chlorides to form perchlorates. The OClO itself could derive from gas-ice interaction as mentioned earlier, while in homogeneous chemistry the commonly known source is from XO radicals, where "X" is Cl or Br:

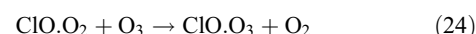
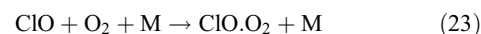


[30] Reactions (20) and (21) vie with others; notably (20) competes with a trimolecular reaction to form the ClO dimer, $(\text{ClO})_2$ [Finlayson-Pitts *et al.*, 2000, p.679]. Ab initio quantum chemistry calculations by Zhu and Lin [2003] show that a three-body reaction can also produce OClO:



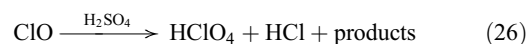
Combined with equations (5), (6), and (19), OClO presents a pathway to form perchloric acid.

[31] Prasad and Lee [1994] proposed a second model to make perchloric acid in which weakly bound $\text{ClO}\cdot\text{O}_2$ and $\text{ClO}\cdot\text{O}_3$ could be formed as reaction intermediates:



However, the existence of $\text{ClO}\cdot\text{O}_3$ is hypothetical while the stability of $\text{ClO}\cdot\text{O}_2$ remains an open question [Rauk *et al.*, 1993; Shindell, 1997].

[32] Finally, a third proposal is that heterogeneous chemistry on sulfate particles generates perchlorate [Martin *et al.*, 1979], written schematically as



This unspecific mechanism appeared to be consistent with trace amounts of perchlorate found in stratospheric sulfuric acid particles [Jaegle *et al.*, 1996]. However, subsequent measurements showed that the ClO uptake on sulfuric acid is insignificantly slow [Abbatt, 1996].

5. Photochemical Model

[33] To investigate the chlorine chemistry of the Atacama atmosphere, we used a one-dimensional (vertical grid) photochemical model. The model is derived from a Fortran code developed by Kasting [e.g., Kasting, 1979; Kasting and Donahue, 1980; Kasting *et al.*, 1984, 1989]. Although this code was originally built for studying paleoatmospheres, modified versions of the program have been applied to the modern atmosphere and validated for contemporary cases [Kasting and Singh, 1986; Taubman and Kasting, 1995], including studies of modern chlorine-bearing species [Singh and Kasting, 1988]. In recent work, our version of the 1-D photochemical model has been used for investigating the chemical evolution of the Earth's atmosphere [Zahnle *et al.*, 2006] and studies of the past and present Martian atmosphere [Zahnle *et al.*, 2008]. However, in those studies, chlorine chemistry was not incorporated. Consequently, the principal effort in using the photochemical model to examine perchlorate fluxes in the Atacama was to include a comprehensive set of chlorine reactions with the most up-to-date reaction rate and photolysis parameters in a version of the code for the modern terrestrial atmosphere.

[34] The version of the model reported here includes 83 chemical species that participate in 360 chemical reactions. The model solves a time-dependent coupled transport-chemistry equation:

$$\frac{\partial f_i}{\partial t} = \frac{P_i}{N} - L_i f_i - \frac{1}{N} \frac{\partial}{\partial z} (b_{ia} f_i (H_a^{-1} - H_i^{-1})) + \frac{1}{N} \frac{\partial}{\partial z} \left((b_{ia} + KN) \frac{\partial f_i}{\partial z} \right) + \frac{1}{N} \frac{\partial}{\partial z} (v_{FALL} N_i) \quad (27)$$

where f_i is the mixing ratio of the species i , P is the chemical production (molecules $\text{cm}^3 \text{s}^{-1}$), L is the chemical loss (molecules s^{-1}), N is atmospheric number density (molecules cm^{-3}), b_{ia} is the binary diffusion coefficient between species i and the background atmosphere a , H_a and H_i are the scale heights of the background atmosphere and of species i , and K is an eddy diffusion coefficient. The variable v_{FALL} is a (positive downward) fall velocity that applies only to particulate species. Because molecular diffusion (the terms involving b_{ia}) is only implemented for atomic and molecular hydrogen (H and H_2) and $v_{FALL} = 0$ for nonparticle species, equation (27) only involves the first, second, and fourth right-hand terms for most species. The profile of the eddy diffusion coefficient is an average determined by *Massie and Hunten* [1981] for gas species based on observational data. The model is run forward in time by a first-order reverse Euler solver to obtain a steady state solution for an average sun angle of 50° .

[35] Chlorine reactions and their rate constants (along with additional NO_x and hydrocarbon reactions not in previous model iterations) that were used in the model are listed in Table 2 based on the best currently available compilations. At the lower boundary, deposition velocities (cm s^{-1}) were imposed for HCl (0.2), Cl (1.0), ClO (0.5), HOCl (0.5), ClONO_2 (0.5), $\text{CH}_3\text{O}_2\text{NO}_2$ (0.5), CH_3OOH (0.2), and HClO_4 (0.2). These values follow those used in a 1-D photochemical model of *Segura et al.* [2005] (although the deposition velocity values are not actually recorded in Segura et al.'s paper). Also CH_3Cl was set at a constant mixing ratio of 600 pptv consistent with observations [*Graedel and Keene*, 1995]. The remaining lower boundary conditions and all upper boundary conditions for the newly added species were specified as zero flux, except for a driving flux of chlorine species.

[36] To drive the model, fluxes of chlorine species into the atmosphere must be considered. The total natural flux of chlorine species to the global terrestrial atmosphere derives from three principal sources: HCl released from surface reactions of sea spray particles, HCl from volcanism, and methyl chloride (CH_3Cl) produced by marine algae in the oceans and soil biota on land. The largest flux of HCl is considered to result from acid displacement reactions on sea spray particles with atmospheric acids (H_2SO_4 and HNO_3). (We note that other reactions produce different Cl-bearing species: photochemical reactions with sea salt leads to BrCl or Cl_2 release (equation (2)), while surface reactions promote the release of nitryl chloride (ClONO_2) [*von Glasow and Crutzen*, 2006]). The global flux of HCl from sea salt is uncertain, with various estimates of $\sim 1.0 \text{ Tmol HCl yr}^{-1}$ [*Meszaros*, 1992], $1.4 \pm 0.6 \text{ Tmol HCl yr}^{-1}$ [*Graedel and Keene*, 1995] and $0.21 \text{ Tmol HCl yr}^{-1}$ [*Erickson et al.*,

1999]. The estimated CH_3Cl source flux is $\sim 0.04 \text{ Tmol yr}^{-1}$ [*Keene et al.*, 1999], while the volcanic HCl source has recently been estimated as $0.12 \pm 0.3 \text{ Tmol HCl yr}^{-1}$ [*Pyle and Mather*, 2009]. For the purpose of this paper, we simplified matters by assuming that the global flux of HCl dominates chlorine inputs and so we ignored variations in CH_3Cl fluxes, such that the CH_3Cl flux was constant and that needed to maintain a typical 600 pptv mixing ratio at ground level. In our investigations, we varied the HCl source flux to see how perchlorate formation responded and we distributed HCl throughout the troposphere to represent the combined source from volcanism and the biosphere. This makes the conservative assumption that the Andean volcanism near to the Atacama does not directly inject HCl into the stratosphere.

[37] Given that parts of the Atacama that have large perchlorate accumulations are hyperarid, all model runs were “dry,” without any rainfall. The model troposphere was set dry with a relative humidity arbitrarily fixed to 15%, which is the consistent with the range of values in the Atacama troposphere of around 10–20% [*Giovanelli et al.*, 2001]. The dry atmosphere allowed sulfate, nitrate and perchlorate to undergo dry deposition so that we could quantify these dry production fluxes and compare them with estimates of those needed to create the Atacama salts.

6. Results From a Photochemical Model of Atacama Perchlorate Production

[38] To validate the chlorine chemistry in the model, we examined the vertical profiles of chlorine-bearing species and compared them with observations and other models. Recent Earth-observing satellites have measured atmospheric chlorine-bearing species over the globe, with reliable data in the stratosphere. For comparison with our model, we used vertical profiles of the mixing ratios of HCl and ClO retrieved by the Microwave Limb Sounder (MLS) on NASA's Aura satellite [*Waters et al.*, 2006]. For representative profiles, we used version 2.2 MLS archived profiles collected in the year 2006 that fell within a latitude-longitude box encompassing the Atacama nitrate deposits, $69.5\text{--}70^\circ\text{W}$, $19.5\text{--}26^\circ\text{S}$ [*Erickson*, 1981]. Although HOCl is also retrieved, the limited data over the Atacama was found to be very noisy and not useful. Instead, we used zonal average data compiled by *Zander et al.* [1992] for HOCl; these are for 30°N , but given approximate zonal symmetry they provide a rough guide for likely HOCl values above the Atacama. MLS HCl and ClO data were quality controlled according to the recommendations for the values of status and quality flags in archived data files [*Froidevaux et al.*, 2008; *Santee et al.*, 2008]. We sampled over the recommended reliable altitude range for HCl and ClO, given that data confidence is poor at low and high pressures, and we ignored any retrieved profiles that were flagged as being possibly affected by clouds or that had more than 50% of bad data values. The Aura satellite has a sun-synchronous orbit, so our average profiles are derived from averaging day and night profiles obtained at $\sim 0130 \text{ LT}$ and $\sim 1400 \text{ LT}$.

[39] Chlorine species in the contemporary atmosphere are affected by anthropogenic emissions [*Russell et al.*, 1996], which is different from the historical case when perchlorate

Table 2. Chlorine, NO_x, and Hydrocarbon Reactions Added to the Model

Reactants		Products	Rate ^a	Reference ^b
<i>Two- and Three-Body Reactions</i>				
O(³ P) + HCl	→	OH + Cl	$1.00 \times 10^{-11} e^{-3300/T}$	JPL-06
OH + HCl	→	H ₂ O + Cl	$2.60 \times 10^{-12} e^{-350/T}$	JPL-06
O(¹ D) + HCl	→	O(³ P) + HCl	1.50×10^{-11}	JPL-06
O(¹ D) + HCl	→	OH + Cl	9.75×10^{-11}	JPL-06
O(¹ D) + HCl	→	H + ClO	3.75×10^{-11}	JPL-06
Cl + H ₂	→	HCl + H	$3.05 \times 10^{-11} e^{-2270/T}$	JPL-06
Cl + H ₂ O ₂	→	HCl + HO ₂	$1.10 \times 10^{-11} e^{-980/T}$	JPL-06
Cl + CH ₄	→	HCl + CH ₃	$7.30 \times 10^{-12} e^{-1280/T}$	JPL-06
Cl + H ₂ CO	→	HCl + HCO	$8.10 \times 10^{-11} e^{-30/T}$	JPL-06
Cl + C ₂ H ₆	→	HCl + C ₂ H ₅	$7.20 \times 10^{-11} e^{-70/T}$	JPL-06
Cl + H ₂ S	→	HCl + HS	$3.70 \times 10^{-11} e^{210/T}$	JPL-06
SO + OClO	→	SO ₂ + ClO	1.90×10^{-12}	JPL-06
ClO + SO	→	Cl + SO ₂	2.80×10^{-11}	JPL-06
O(³ P) + ClO	→	Cl + O ₂	$2.80 \times 10^{-11} e^{85/T}$	JPL-06
O(³ P) + HOCl	→	OH + ClO	1.70×10^{-13}	JPL-06
OH + ClO	→	Cl + HO ₂	$7.40 \times 10^{-12} e^{270/T}$	JPL-06
OH + ClO	→	HCl + O ₂	$6.00 \times 10^{-13} e^{230/T}$	JPL-06
OH + HOCl	→	H ₂ O + ClO	$3.00 \times 10^{-12} e^{-500/T}$	JPL-06
HO ₂ + Cl	→	HCl + O ₂	$1.80 \times 10^{-11} e^{170/T}$	JPL-06
HO ₂ + Cl	→	OH + ClO	$4.10 \times 10^{-11} e^{-450/T}$	JPL-06
HO ₂ + ClO	→	HOCl + O ₂	$2.70 \times 10^{-12} e^{220/T}$	JPL-06
O(¹ D) + Cl ₂	→	ClO + Cl	2.025×10^{-10}	JPL-06
O(¹ D) + Cl ₂	→	Cl ₂ + O(³ P)	6.75×10^{-11}	JPL-06
OH + Cl ₂	→	HOCl + Cl	$1.40 \times 10^{-12} e^{-900/T}$	JPL-06
Cl + HOCl	→	Cl ₂ + OH	$1.25 \times 10^{-12} e^{-130/T}$	JPL-06 ^c
Cl + HOCl	→	HCl + ClO	$1.25 \times 10^{-12} e^{-130/T}$	JPL-06 ^c
O(³ P) + OClO	→	ClO + O ₂	$2.40 \times 10^{-12} e^{-960/T}$	JPL-06
OH + OClO	→	HOCl + O ₂	$4.50 \times 10^{-13} e^{800/T}$	JPL-06
ClO + ClO + M	→	Cl ₂ O ₂	$2.0 \times 10^{-12} (300/T)^{2.4}$	JPL-06 ^d
			$1.6 \times 10^{-32} (300/T)^{4.5} M$	JPL-06 ^c
Cl ₂ O ₂ + M	→	ClO + ClO	$7.90 \times 10^{15} e^{-8820/T} F_c = 0.45$	IUPAC-07 ^f
			$3.70 \times 10^{-7} e^{-7690/T} M$	IUPAC-07 ^c
Cl + O ₂ + M	→	ClOO	$1.4 \times 10^{-33} (300/T)^{3.90} M$	IUPAC-07 ^c
ClOO + M	→	Cl + O ₂	$2.8 \times 10^{-10} e^{-1820/T}$	IUPAC-07
O + ClO + M	→	OCIO	$4.33 \times 10^{-11} e^{43/T} \times T^{-0.03}$	Zhu and Lin [2003] ^d
			$8.6 \times 10^{-21} e^{-420/T} \times T^{-4.1}$	Zhu and Lin [2003] ^c
Cl + OClO	→	ClO + ClO	$3.40 \times 10^{-11} e^{160/T}$	JPL-06
Cl + ClOO	→	Cl ₂ + O ₂	2.3×10^{-10}	JPL-06
Cl + ClOO	→	ClO + ClO	1.2×10^{-11}	JPL-06
ClO + O ₃	→	ClOO + O ₂	$1.0 \times 10^{-12} e^{-3600/T}$	JPL-06
ClO + O ₃	→	OCIO + O ₂	$1.0 \times 10^{-12} e^{-4000/T}$	JPL-06
ClO + ClO	→	Cl ₂ + O ₂	$1.00 \times 10^{-12} e^{-1590/T}$	JPL-06
ClO + ClO	→	ClOO + Cl	$3.00 \times 10^{-11} e^{-2450/T}$	JPL-06
ClO + ClO	→	OCIO + Cl	$3.5 \times 10^{-13} e^{-1370/T}$	JPL-06
ClO + CH ₃ O ₂	→	ClOO + CH ₃ O	$3.3 \times 10^{-12} e^{-115/T}$	JPL-06 ^g
Cl + CH ₃ O ₂	→	HCl + CH ₂ O ₂	8.0×10^{-11}	JPL-06 ^c
Cl + CH ₃ O ₂	→	ClO + CH ₃ O	8.0×10^{-11}	JPL-06 ^c
OH + CH ₃ Cl	→	CH ₂ Cl + H ₂ O	$2.4 \times 10^{-12} e^{-1250/T}$	JPL-06 ^h
Cl + CH ₃ Cl	→	CH ₂ Cl + HCl	$2.17 \times 10^{-11} e^{-1130/T}$	JPL-06 ^h
CH ₂ Cl + O ₂ + M	→	CH ₂ ClO ₂	$2.9 \times 10^{-12} (300/T)^{1.20}$	JPL-06 ^{d,h}
			$1.9 \times 10^{-30} (300/T)^{3.20} M$	JPL-06 ^{e,h}
CH ₂ ClO ₂ + NO	→	CH ₂ ClO + NO ₂	$7.0 \times 10^{-12} e^{300/T}$	JPL-06 ^h
CH ₂ ClO + O ₂	→	CHClO + HO ₂	6.0×10^{-14}	JPL-06 ^h
Cl + CH ₃ OH	→	CH ₂ OH + HCl	5.50×10^{-11}	JPL-06
ClO + CH ₃ O ₂	→	ClOO + CH ₃ O	$1.65 \times 10^{-12} e^{-115/T}$	JPL-06 ^c
ClO + CH ₃ O ₂	→	CH ₃ OCl + O ₂	$1.65 \times 10^{-12} e^{-115/T}$	JPL-06 ^c
OH + CH ₃ OCl	→	HOCl + CH ₃ O	$2.50 \times 10^{-12} e^{-370/T}$	JPL-06 ^g
Cl + Cl ₂ O ₂	→	Cl ₂ + ClOO	1.0×10^{-10}	JPL-06 ^g
O(³ P) + Cl ₂ O	→	ClO + ClO	$2.7 \times 10^{-11} e^{-530/T}$	IUPAC-07
Cl + Cl ₂ O	→	Cl ₂ + ClO	$6.2 \times 10^{-11} e^{130/T}$	IUPAC-07
Cl + O ₃	→	ClO + O ₂	$2.30 \times 10^{-11} e^{-200/T}$	JPL-06
Cl + O ₃ + M	→	ClO ₃	$1.00 \times 10^{-31} M$	Simonaitis and Heicklen [1975] ⁱ
O(³ P) + OClO + M	→	ClO ₃	8.3×10^{-12}	JPL-06 ^d
			$2.90 \times 10^{-31} (300/T)^{3.1} M$	JPL-06 ^c
O ₃ + OClO	→	ClO ₃ + O ₂	$2.1 \times 10^{-12} e^{-4700/T}$	JPL-06
ClO + ClO ₃	→	ClOO + OCLO	$1.85 \times 10^{-18} e^{-2417/T} \times T^{2.28}$	Xu and Lin [2003]
ClO + ClO ₃	→	OCIO + OCLO	$1.42 \times 10^{-18} e^{-2870/T} \times T^{2.11}$	Xu and Lin [2003]
ClO + ClO ₃ + M	→	Cl ₂ O ₄	$1.43 \times 10^{-10} e^{-82/T} T^{0.094}$	Xu and Lin [2003] ^d
			$8.62 \times 10^{15} e^{-1826/T} T^{-9.75} M$	Xu and Lin [2003] ^c
OH + ClO ₃	→	HClO ₄	6.67×10^{-13}	Simonaitis and Heicklen [1975] ⁱ
OH + ClO ₃ + M	→	HClO ₄	$3.2 \times 10^{-10} T^{0.07} e^{-25/T}$	Zhu and Lin [2001] ^{d,j}
			$1.94 \times 10^{36} T^{-15.3} e^{-5542/T} M$	Zhu and Lin [2001] ^{e,j}

Table 2. (continued)

Reactants		Products	Rate ^a	Reference ^b
OH + ClO ₃	→	HO ₂ + OClO	$2.1 \times 10^{-10} T^{0.09} e^{-18/T}$	Zhu and Lin [2001] ^j
ClO + NO	→	NO ₂ + Cl	$6.40 \times 10^{-12} e^{290/T}$	JPL-06
NO + Cl ₂ O ₂	→	Cl ₂ O + NO ₂	1.0×10^{-15}	Ingham et al. [2005]
Cl + NO ₃	→	ClO + NO ₂	2.4×10^{-11}	JPL-06
NO ₃ + ClO	→	ClOO + NO ₂	4.7×10^{-13}	JPL-06
NO + OClO	→	NO ₂ + ClO	$2.50 \times 10^{-12} e^{-600/T}$	JPL-06
Cl + CH ₃ ONO ₂	→	CH ₂ ONO ₂ + HCl	$1.30 \times 10^{-11} e^{-1200/T}$	JPL-06 ^g
Cl + NO ₂ + M	→	ClONO	$1.0 \times 10^{-10} (300/T)^{1.00}$	JPL-06 ^d
O(³ P) + ClONO ₂	→	O ₂ + ClONO	$2.9 \times 10^{-12} e^{-800/T}$	JPL-06 ^g
OH + ClONO ₂	→	HOCl + NO ₃	$6.0 \times 10^{-13} e^{-330/T}$	JPL-06 ^c
OH + ClONO ₂	→	ClO + HNO ₃	$6.0 \times 10^{-13} e^{-330/T}$	JPL-06 ^c
Cl + ClONO ₂	→	Cl ₂ + NO ₃	$6.5 \times 10^{-12} e^{135/T}$	JPL-06
ClO + NO ₂ + M	→	ClONO ₂	$1.5 \times 10^{-11} (300/T)^{1.90}$	JPL-06 ^d
			$1.8 \times 10^{-31} (300/T)^{3.40} M$	JPL-06 ^c
Cl + NO	→	ClNO	$7.6 \times 10^{-32} (300/T)^{1.80} M$	JPL-06 ^c
Cl + ClNO	→	NO + Cl ₂	$5.8 \times 10^{-11} e^{100/T}$	JPL-06
Cl + NO ₂ + M	→	ClNO ₂	$1.0 \times 10^{-10} (300/T)^{1.00}$	JPL-06 ^d
			$1.8 \times 10^{-31} (300/T)^{2.00} M$	JPL-06 ^c
OH + ClNO ₂	→	HOCl + NO ₂	$2.4 \times 10^{-12} e^{-1250/T}$	JPL-06
Cl + HO ₂ NO ₂	→	ClO + HNO ₃	1.0×10^{-13}	JPL-06 ^g
O(³ P) + NO ₃	→	O ₂ + NO ₂	1.00×10^{-11}	JPL-06
HO ₂ + NO ₃	→	OH + NO ₂ + O ₂	3.50×10^{-12}	JPL-06
NO + NO ₃	→	NO ₂ + NO ₂	$1.50 \times 10^{-11} e^{170/T}$	JPL-06
O(³ P) + NO ₂ + M	→	NO ₃	$2.2 \times 10^{-11} (300/T)^{0.70}$	JPL-06 ^d
			$2.5 \times 10^{-31} (300/T)^{1.80} M$	JPL-06 ^c
OH + NO ₃	→	HO ₂ + NO ₂	2.20×10^{-11}	JPL-06
N + NO ₂	→	N ₂ O + O(³ P)	$5.80 \times 10^{-12} e^{220/T}$	JPL-06
O(¹ D) + N ₂ + M	→	N ₂ O	$2.80 \times 10^{-36} (300/T)^{0.9} M$	JPL-06 ^c
O(¹ D) + N ₂ O	→	N ₂ + O ₂	$4.70 \times 10^{-11} e^{20/T}$	JPL-06
O(¹ D) + N ₂ O	→	NO + NO	$6.70 \times 10^{-11} e^{20/T}$	JPL-06
N + HO ₂	→	NO + OH	2.2×10^{-11}	Brune et al. [1983]
O(³ P) + N ₂ O ₅	→	NO ₂ + NO ₂ + O ₂	3.0×10^{-16}	JPL-97
NO ₂ + NO ₃ + M	→	N ₂ O ₅	$1.4 \times 10^{-12} (300/T)^{0.7}$	JPL-06 ^d
			$2.0 \times 10^{-30} (300/T)^{4.4} M$	JPL-06 ^c
N ₂ O ₅ + M	→	NO ₃ + NO ₂	$7.90 \times 10^{15} e^{-8820/T}, F_c = 0.45$	IUPAC-04 ^f
			$3.70 \times 10^{-7} e^{-7690/T} M$	IUPAC-04 ^c
NO ₂ + NO ₃	→	NO + NO ₂ + O ₂	$4.5 \times 10^{-14} e^{-1260/T}$	JPL-06 ^g
NO ₂ + O ₃	→	NO ₃ + O ₂	$1.2 \times 10^{-13} e^{-2450/T}$	JPL-06
NO ₃ + NO ₃	→	NO ₂ + NO ₂ + O ₂	$8.5 \times 10^{-13} e^{-2450/T}$	JPL-06
HO ₂ + NO ₂ + M	→	HO ₂ NO ₂	$2.9 \times 10^{-12} (300/T)^{1.1}$	JPL-06 ^d
			$2.0 \times 10^{-31} (300/T)^{3.4} M$	JPL-06 ^c
HO ₂ NO ₂ + M	→	HO ₂ + NO ₂	$4.80 \times 10^{15} e^{-11170/T}, F_c = 0.6$	IUPAC-04 ^f
			$4.10 \times 10^{-5} e^{-10650/T} M$	IUPAC-04 ^c
O(³ P) + HO ₂ NO ₂	→	OH + NO ₂ + O ₂	$7.80 \times 10^{-11} e^{-3400/T}$	JPL-06
OH + HO ₂ NO ₂	→	H ₂ O + NO ₂ + O ₂	$1.90 \times 10^{-12} e^{270/T}$	IUPAC-04
NO + CH ₃ O	→	HNO + H ₂ CO	$2.3 \times 10^{-12} (300/T)^{0.7}$	IUPAC-06
NO ₂ + CH ₃ O	→	H ₂ CO + HNO ₂	$9.60 \times 10^{-12} e^{-1150/T}$	IUPAC-06
NO + CH ₃ O + M	→	CH ₃ ONO	$3.30 \times 10^{-11} (300/T)^{0.6}$	IUPAC-06 ^d
			$1.40 \times 10^{-29} (300/T)^{3.8} M$	IUPAC-06 ^c
CH ₃ ONO + M	→	CH ₃ O + NO	$1.06 \times 10^{15} e^{-18041/T}$	Fernandez-Ramos et al. [1998] ^k
NO ₂ + CH ₃ O + M	→	CH ₃ ONO ₂	$2.10 \times 10^{-11}, F_c = 0.44$	IUPAC-06 ^f
			$8.10 \times 10^{-29} (300/T)^{4.5} M$	IUPAC-06 ^c
O ₃ + CH ₃ ONO	→	CH ₃ ONO ₂ + O ₂	$6.76 \times 10^{-13} e^{-5315/T}$	Hastie et al. [1976]
OH + CH ₃ ONO ₂	→	CH ₂ ONO ₂ + H ₂ O	$4.00 \times 10^{-13} e^{-845/T}$	IUPAC-06
CH ₂ ONO ₂ + O ₂	→	H ₂ CO + NO ₂ + O ₂	1.00×10^{-10}	estimated ^g
NO ₂ + CH ₃ O ₂ + M	→	CH ₃ O ₂ NO ₂	$1.80 \times 10^{-11}, F_c = 0.36$	IUPAC-06 ^f
			$2.50 \times 10^{-30} (300/T)^{5.5} M$	IUPAC-06 ^c
CH ₃ O ₂ NO ₂ + M	→	CH ₃ O ₂ + NO ₂	$1.10 \times 10^{16} e^{-10560/T}, F_c = 0.6$	IUPAC-06 ^f
			$9.00 \times 10^{-5} e^{-9690/T} M$	IUPAC-06 ^c
CH ₃ O ₂ + CH ₃ O ₂	→	CH ₃ O + CH ₃ O + O ₂	$7.40 \times 10^{-13} e^{-520/T}$	IUPAC-06
CH ₃ O ₂ + CH ₃ O ₂	→	H ₂ CO + CH ₃ OH + O ₂	$1.03 \times 10^{-13} e^{365/T}$	IUPAC-06
CH ₃ + O ₂ + M	→	CH ₃ O ₂	$1.20 \times 10^{-12} (300/T)^{-1.1}$	JPL-06 ^d
			$4.00 \times 10^{-31} (300/T)^{3.6} M$	JPL-06 ^c
CH ₂ O ₂ + M	→	CO + H ₂ O	6×10^4	IUPAC-06 ^k
HO ₂ + CH ₃ O ₂	→	CH ₃ OOH + O ₂	$3.80 \times 10^{-13} e^{780/T}$	IUPAC-06
CH ₂ OOH + M	→	OH + H ₂ CO	5.0×10^4	Vaghjiani and Ravishankara [1989] ^k
CH ₃ O + O ₂	→	H ₂ CO + HO ₂	$7.2 \times 10^{-14} e^{-1080/T}$	IUPAC-06
NO + CH ₃ O ₂	→	CH ₃ O + NO ₂	$2.80 \times 10^{-12} e^{300/T}$	JPL-06
O(³ P) + HNO ₃	→	OH + NO ₃	3.0×10^{-17}	JPL-06
HO ₂ + NO ₂	→	HNO ₂ + O ₂	5.00×10^{-16}	JPL-06
O(¹ D) + CH ₄	→	CH ₃ O + H	3.0×10^{-11}	JPL-06

Table 2. (continued)

Reactants		Products	Rate ^a	Reference ^b
OH + CH ₃ OOH	→	CH ₂ OOH + H ₂ O	$2.12 \times 10^{-12} e^{190/T}$	IUPAC-06
OH + CH ₃ OOH	→	CH ₃ O ₂ + H ₂ O	$3.18 \times 10^{-12} e^{190/T}$	IUPAC-06
OH + CH ₃ OH	→	CH ₂ OH + H ₂ O	$2.42 \times 10^{-12} e^{-345/T}$	IUPAC-06
OH + CH ₃ OH	→	CH ₃ O + H ₂ O	$4.28 \times 10^{-13} e^{-345/T}$	IUPAC-06
CH ₂ OH + O ₂	→	H ₂ CO + HO ₂	9.70×10^{-12}	IUPAC-06
<i>Photolysis Reactions¹</i>				
NO ₃ + hν	→	NO + O ₂	1.20×10^{-2}	JPL-06
NO ₃ + hν	→	NO ₂ + O(³ P)	1.50×10^{-2}	JPL-06
N ₂ O + hν	→	N ₂ + O(¹ D)	5.47×10^{-7}	JPL-06
HO ₂ NO ₂ + hν	→	HO ₂ + NO ₂	2.05×10^{-4}	JPL-06
HO ₂ NO ₂ + hν	→	OH + NO ₃	5.51×10^{-5}	JPL-06
N ₂ O ₅ + hν	→	NO ₃ + NO ₂	3.02×10^{-4}	JPL-06
CH ₃ OOH + hν	→	CH ₃ O + OH	2.86×10^{-5}	JPL-06
CH ₃ O ₂ NO ₂ + hν	→	CH ₃ O ₂ + NO ₂	2.16×10^{-4}	IUPAC-06
HCl + hν	→	H + Cl	4.50×10^{-3}	JPL-06
ClO + hν	→	O(¹ D) + Cl	7.17×10^{-4}	JPL-06
ClO + hν	→	O(³ P) + Cl	2.40×10^{-3}	JPL-06
HOCl + hν	→	OH + Cl	3.03×10^{-4}	JPL-06
Cl ₂ + hν	→	Cl + Cl	1.99×10^{-3}	JPL-06
ClOO + hν	→	ClO + O(³ P)	4.94×10^{-3}	JPL-06
OCIO + hν	→	ClO + O(³ P)	6.23×10^{-2}	JPL-06
ClONO + hν	→	Cl + NO ₂	4.74×10^{-3}	JPL-06
ClONO ₂ + hν	→	Cl + NO ₃	2.36×10^{-4}	JPL-06
ClONO ₂ + hν	→	ClO + NO ₂	1.46×10^{-4}	JPL-06
ClNO ₂ + hν	→	Cl + NO ₂	9.40×10^{-4}	JPL-06
ClNO + hν	→	Cl + NO	3.55×10^{-3}	JPL-06
CHClO + hν	→	HCO + Cl	1.71×10^{-5}	JPL-06 ^h
CH ₃ Cl + hν	→	Cl + CH ₃	1.14×10^{-6}	JPL-06
CH ₃ OCl + hν	→	CH ₃ O + Cl	1.20×10^{-4}	JPL-06
Cl ₂ O ₂ + hν	→	Cl + ClOO	3.32×10^{-3}	JPL-06
Cl ₂ O ₂ + hν	→	ClO + ClO	1.16×10^{-4}	JPL-06
Cl ₂ O + hν	→	Cl + ClO	2.13×10^{-3}	JPL-06
ClO ₃ + hν	→	ClO + O ₂	1.03×10^{-1}	JPL-06
Cl ₂ O ₄ + hν	→	ClOO + OCIO	2.45×10^{-4}	JPL-06

^aTwo-body rates [cm³s⁻¹]; three-body rates [cm⁶s⁻¹]; photolysis rates [s⁻¹].

^bJPL-97,-06, see publications by Sander et al.; IUPAC-04, -06, -07, see publications by Atkinson et al.

^cBranching ratio uncertain; we split measured rate for net reaction evenly between the two channels.

^dHigh density limit (k_{∞}) for three-body reaction [cm³s⁻¹].

^eLow density limit for three-body reaction, where M is background density [cm⁻³].

^fHigh density limit (k_{∞}) for three-body reaction [cm³s⁻¹], along with F_c factor used in IUPAC three-body reaction rates.

^gProducts assumed.

^hThis pathway stems from biogenic methyl chloride (CH₃Cl), and so is likely not relevant for Mars.

ⁱThese estimated rates were lowered by a factor of 30 from those in the work of *Simonaitis and Heicklen* [1975]. See paper text for justification and sensitivity analysis.

^jRates extrapolated below lower limits of 300 K and used only as described in text.

^kFirst-order reaction rate [s⁻¹].

^lPhotolysis rates are evaluated at the top of the atmosphere subject for a 50° slant path, and reduced by a factor of two to account for the diurnal cycle. Absorption cross sections were obtained from the MPI-Mainz-UV-VIS Spectral Atlas of Gaseous Molecules at <http://www.atmosphere.mpg.de/enid/2295>.

accumulated in the Atacama. In particular, the major reservoir species in the stratosphere, HCl, has accumulated man-made chlorine. At the top of the stratosphere, HCl increased from ~2.8 ppbv to ~3.5 ppbv from 1993 to 2006 [*Froidevaux et al.*, 2008; *Russell et al.*, 1996]. We are interested in preanthropogenic times so we ignore chlorine-bearing human emissions in our model. In order to match the observed upper stratosphere HCl of 3.5 ppb in 2006 we would have to use an HCl flux of 8×10^9 molecules HCl cm⁻² s⁻¹ that is biased high relative to natural fluxes (up to 5.5×10^9 molecules HCl cm⁻² s⁻¹, globally) since it compensates for lack of human emissions. For subsequent runs, we used a flux of 5×10^9 molecules HCl cm⁻² s⁻¹, which produces upper stratosphere HCl levels that are systematically lower by ~0.7 ppb than 2006 observations.

[40] Although our reaction rates in the model are taken from reviewed compilations, such as Jet Propulsion Laboratory [*Sander et al.*, 2006] or the International Union and

Pure and Applied Chemistry (IUPAC) recommendations [*Atkinson et al.*, 2004, 2006, 2007, 2008], two important reaction rates concerned with perchlorate production are highly uncertain and the observational data was used to help constrain them. *Simonaitis and Heicklen* [1975] estimated a rate for reaction (18) based on old laboratory data that is open to interpretation [*Norrish and Neville*, 1934] and they guessed a rate for reaction (19) by analogy with the reactions of OH with NO₂, NO, or CO. If we used these rates in our model, our modeled stratospheric profile of HCl (the major reservoir) was significantly different from observations both in magnitude and shape (Figure 3a). We therefore concluded that the rates of reaction estimated by *Simonaitis and Heicklen* [1975] were too high. We used observational profiles of HCl, ClO and HOCl as constraints on these poorly known reaction rates. By lowering the reaction rates of (18) and (19) by a factor of 30, the model provided a reasonable match to the data within observa-

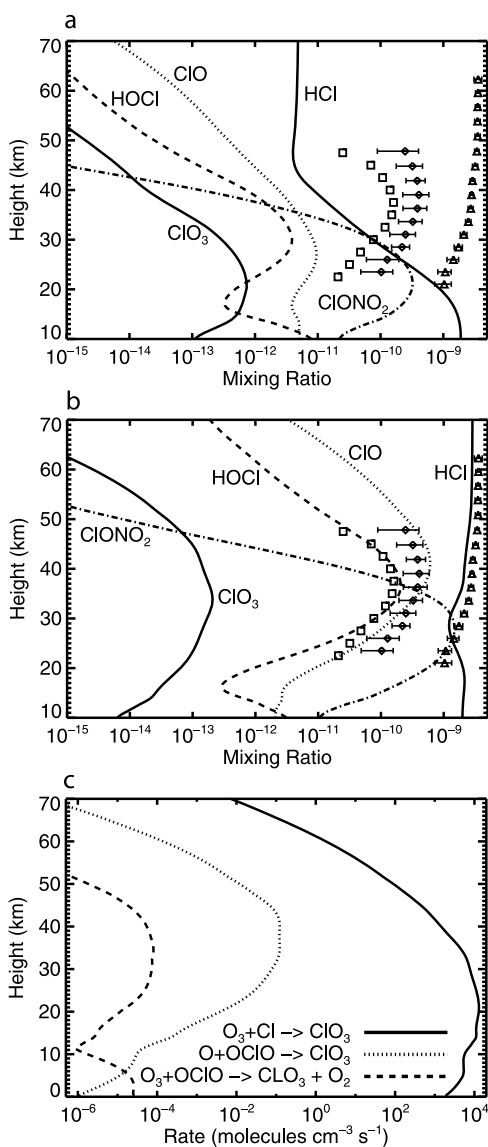


Figure 3. (a) Modeled mixing ratios of chlorine species as a function of altitude using the nominal reaction rates of *Simonaitis and Hecklen* [1975] for reactions (18) and (19). The modeled profiles do not compare favorably with measured profiles of HCl and ClO over the Atacama because the Simonaitis and Hecklen reaction rates are too fast for removing chlorine into ClO_3 and perchlorate. (b) Modeled mixing ratios of chlorine species as a function of altitude using values of reaction rates for reactions (18) and (19) lowered by a factor of 30 to match observations. HCl profiles are expected to be lower, as discussed in the text because we do not include anthropogenic emissions of CFCs. (c) Production rates as a function of altitude of the chlorine trioxide precursor to perchlorate for the model atmosphere in Figure 3b.

tional uncertainty (Figure 3b) and produced trace quantities of ClO_3 and HClO_4 . Although otherwise arbitrary, we adopted these rates for our ‘standard model’. With these rates, the overall model profiles also compare favorably in shape and magnitude with nominal profiles of chlorine-bearing species (HCl, ClONO_2 , HOCl, Cl, and ClO) from

other models, as reproduced in textbooks [see, e.g., *Brasseur and Solomon*, 1986, p.280].

[41] We next examined the pathway by which perchlorate is produced in our ‘standard model’ and the magnitude of the production flux. In the model, volatile Cl is oxidized first to ClO_3 via equations (5), (6), and (18), and then to perchloric acid, HClO_4 , via equation (19). The model predicts upper limits on perchlorate production because HClO_4 is assumed to be stable and unreactive once formed and is lost only through deposition at the lower boundary. Because reaction (19) is the means to produce perchloric acid, the perchloric acid production profile tracks the ClO_3 profile and so depends on the reactions producing ClO_3 . The dominant production of ClO_3 is from reaction (18), $\text{Cl} + \text{O}_3 + \text{M}$. The maximum production rate follows a Cl mixing ratio profile that peaks in the lower stratosphere (Figure 3c). At 15 km altitude, the production rate of ClO_3 from reaction (18) is $\sim 10^4$ molecules $\text{cm}^{-3} \text{s}^{-1}$. Although the two body reaction $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ is faster at all heights than the three body reaction, there is enough Cl and O_3 that both reactions occur, allowing generation of ClO_3 . In the troposphere, where there are lower amounts of reactants, the rate of production of ClO_3 is only $\sim 10^3$ molecules $\text{cm}^{-3} \text{s}^{-1}$. Reaction (6), $\text{OCIO} + \text{O} + \text{M}$ is the next largest producer of ClO_3 , but its maximum rate, which also occurs at ~ 30 km altitude, is only $\sim 10^{-1}$ molecules $\text{cm}^{-3} \text{s}^{-1}$. Clearly, the modeled deposition flux of perchlorate is sensitive to the rates of reactions (18) and (19) proposed by *Simonaitis and Hecklen* [1975].

[42] The rate of reaction (19) has also been assessed through calculations of *Zhu and Lin* [2001], albeit focused on the case of perchlorate combustion, so that the rate for temperatures below 300 K is an extrapolation. If the perchloric acid formation rate of *Zhu and Lin* [2001] is used along with one thirtieth of the *Simonaitis and Hecklen* [1975] estimated rate for reaction (18), the model calculates unrealistic profiles of major chlorine species, very similar to Figure 3a, because too much chlorine is extracted into perchlorate. If the multiplicative factor for the reaction rate of (18) is lowered to 2×10^{-34} (~ 4 orders of magnitude below the *Simonaitis and Hecklen* [1975] rate), stratospheric profiles of Cl-bearing species match observations, similar to Figure 3b, although ClO_3 concentrations are lower and peak at $\sim 10^{-15}$ rather than $\sim 10^{-13}$ mixing ratio. Given our assumption of no other sources and sinks, the perchlorate deposition flux depends on the ClO_3 concentration and the HClO_4 formation rate, as discussed above. The *Zhu and Lin* [2001] rate for HClO_4 formation is a factor of ~ 20 larger at 300 K than that estimated by *Simonaitis and Hecklen* [1975], so lower ClO_3 concentrations along with a high rate of HClO_4 formation produces similar overall perchlorate deposition fluxes to the ‘standard model’ described above. Clearly, laboratory studies are needed to help constrain the key uncertain rates of reactions (18) and (19).

[43] Figure 4 shows photochemical results for an Atacama atmosphere in terms of deposition fluxes of nitrate and perchlorate (molecules $\text{cm}^{-2} \text{s}^{-1}$) as a function of the input of chlorine volatiles for our ‘standard model.’ For the sake of this study, we assumed that the dominant input was in the form of HCl. As the HCl flux was ramped up, perchlorate fluxes changed as shown. To examine the sensitivity of the perchlorate deposition flux to the uncertain reaction rates of

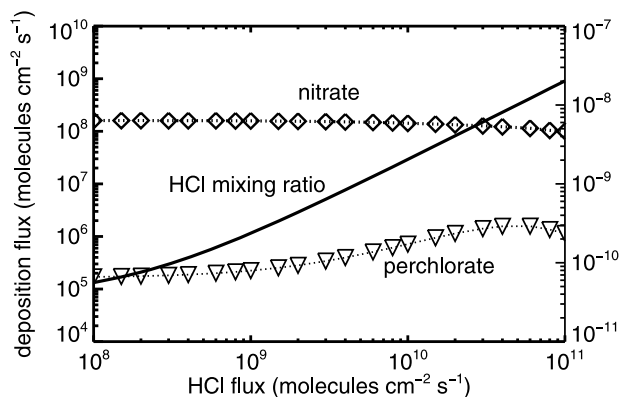


Figure 4. Photochemical results for a dry model atmosphere that is devoid of rainfall and assumed to be representative of the Atacama. Experiments were run changing only the net HCl flux (horizontal axis), resulting in the HCl mixing ratios (solid line) mapped to the right hand axis. Inverted triangles and diamonds indicate the model-predicted surface (dry) deposition fluxes for perchlorate and nitrate. Estimates for the current globally averaged HCl flux range from $(1.3\text{--}5.7) \times 10^9$ molecules $\text{HCl cm}^{-2} \text{s}^{-1}$ of which $\sim 0.5 \times 10^9$ molecules $\text{HCl cm}^{-2} \text{s}^{-1}$ is volcanic.

reactions (18) and (19), we ran the model for a nominal case with an HCl flux of 5×10^9 molecules $\text{HCl cm}^{-2} \text{s}^{-1}$, and changed the reaction rates by a factor of 30 in either direction from this nominal case. The results in Figure 5 show that if we take *Simonaitis and Hecklen's* [1975] rates for reactions (18) and (19), the deposition flux of perchlorate would become comparable to that of nitrate $\sim 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$, which is implausible and provides further justification for using lower reaction rates.

7. Discussion

[44] It is useful to estimate what typical deposition fluxes would be needed to produce the salt volumes and abundances in the Atacama and compare them with the fluxes calculated by the photochemical model. Economic resource estimates from *Ericksen* [1963] suggest that the total nitrate in high- and low-grade ore is $\sim 10^{11}$ kg as N [*Michalski et al.*, 2004], which is 4.43×10^{11} kg as nitrate. Using an average ratio in ores of perchlorate to nitrate of 0.0048 [*Grossling and Ericksen*, 1971], the total amount of perchlorate is therefore 2.1×10^9 kg. The age of hyperarid conditions in the Atacama ranges 6–15 million years [*Alpers and Brimhall*, 1988; *Hartley and Chong*, 2002], which generally relates to decreasing temperatures in eastern Pacific upwellings as the Antarctic ice cap became established, combined with secular global cooling. The age is consistent with recent measurements of cosmogenic nuclides (^{10}Be , ^{26}Al , ^{21}Ne) in surface boulders showing exposure ages from a few million to 14 million years [*Ewing et al.*, 2006] and comparison with other climate proxies that suggest the hyperarid environment commenced at 14.6 Ma [*Evenstar et al.*, 2009]. For our purposes, we require an approximate estimate, so we take a depositional area of 21,000 km^2 [*Ericksen*, 1983] and age $\sim 10^7$ years. This gives average fluxes required to account for the mass

of salts of $\sim 6.5 \times 10^7$ molecules $\text{NO}_3 \text{cm}^{-2} \text{s}^{-1}$ and $\sim 1.9 \times 10^5$ molecules $\text{ClO}_4 \text{cm}^{-2} \text{s}^{-1}$.

[45] The estimated required flux of nitrate compares favorably with the deposition flux (the sum of nitric acid (HNO_3) and minor hydroxy nitrate (HNO_4)) calculated by the photochemical model. Figure 4 reveals nitrate fluxes of $\sim 10^8$ molecules $\text{cm}^{-2} \text{s}^{-1}$ through the range of investigated HCl fluxes. The predicted perchlorate surface fluxes range from $10^5\text{--}10^6$ molecules $\text{cm}^{-2} \text{s}^{-1}$ for reasonable values of the HCl flux. The best match for the required Atacama perchlorate deposition occurs at HCl fluxes that are similar to the present best estimates of the globally averaged HCl flux to the atmosphere, including $\sim 0.5 \times 10^9$ molecules $\text{HCl cm}^{-2} \text{s}^{-1}$ from volcanoes [*Pyle and Mather*, 2009] and the flux derived from sea spray of $0.8\text{--}5.2 \times 10^9$ molecules $\text{HCl cm}^{-2} \text{s}^{-1}$ [*Graedel and Keene*, 1995; *Keene et al.*, 1999]. A higher local volcanic flux is possible given the proximity of the Atacama perchlorate-rich nitrate deposits to the Andean volcanoes.

[46] Bearing in mind the plausible correspondence between modeled and required deposition rates, we have shown in this preliminary study that the gas phase formation of perchlorate proposed by *Simonaitis and Hecklen* [1975] is a feasible mechanism to explain the perchlorate abundance of the Atacama desert. However, the process depends on the realism of the rates of reactions (18) and (19), which would greatly benefit from ab initio quantum chemistry calculations and lab work. More detailed analysis is warranted for comparing the alternative pathway (equations (23)–(25)) proposed by *Prasad and Lee* [1994] although this is subject to very considerable uncertainty regarding

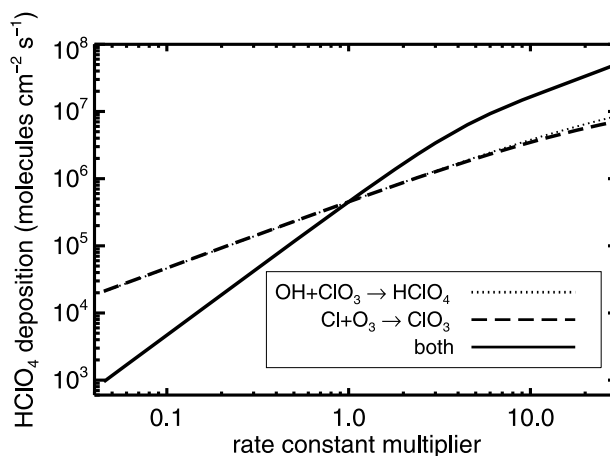


Figure 5. Sensitivity plot showing the perchlorate deposition flux (vertical axis) versus the rate of the poorly known three-body reactions: equation (18) leading to chlorine trioxide ($\text{Cl} + \text{O}_3 + \text{M} \rightarrow \text{ClO}_3 + \text{M}$) and (19) leading to perchloric acid. Arrhenius factors were varied from 1×10^{-31} and 6.67×10^{-13} for the reaction rates of (18) and (19), respectively, so that the rates at the far right (i.e., a multiplier of 30) use the rate constants given by *Simonaitis and Hecklen* [1975]. Sensitivity studies are shown for varying each rate while keeping the other constant and for covarying the rates. A nominal fixed HCl flux equivalent to 5×10^9 molecules $\text{HCl cm}^{-2} \text{s}^{-1}$ is assumed.

reaction rates and even the existence of certain proposed reaction intermediates.

[47] To extend our results to Martian conditions would require additional care. Many of the important pathways in the oxidation of chlorine involve pressure-dependent three-body reactions, whose overall rates will differ significantly in the tenuous Martian atmosphere. In general, such three-body reactions have rates that would tend to be increased by the lower atmospheric temperatures on Mars but decreased by the lower pressure. The penetration of UV light into the Martian atmosphere is significantly different than modeled here for several reasons. The top of atmosphere UV flux at Mars is lower than at Earth and varies considerably over the course of the year due to eccentric orbit; there is also a lack of a Martian ozone shield, which allows shortwave UV to penetrate deeper. These considerations, along with the fact the Mars is drier than the driest places on Earth limit direct extrapolation of our results to Mars. However, we have demonstrated that, in principle, perchlorate can be formed via gas phase photochemistry in amounts sufficient to explain the Atacama deposits. This provides strong justification for future investigations of gas phase photochemistry as a source for the Martian perchlorates. In addition, better estimates of reaction rates involving the chlorine trioxide precursor to perchlorate demands further laboratory and theoretical investigation.

8. Conclusions

[48] We conclude the following:

[49] 1. Terrestrial natural perchlorate is produced atmospherically in very arid environments from pathways involving the oxidation of chlorine species by ozone or oxygen-containing species (e.g., O or OH) derived from chemical reactions that include ozone. This makes it reasonable to propose that perchlorate on Mars may have originated as a consequence of the arid and oxidizing environment on Mars.

[50] 2. A variety of potential pathways can be proposed for Mars including photochemical reactions, electrostatic discharge, and gas-solid reactions, although the validity of some of these pathways remains unknown at present.

[51] 3. Perchlorate-rich deposits in the Atacama desert are closest in abundance to perchlorate in the soil at the Phoenix landing site and so an examination of the origin of Atacama perchlorate may help shed light on the source of Martian perchlorate.

[52] 4. We investigated gas phase pathways to produce the perchlorate in the Atacama using a 1-D photochemical model. We found that the proposed pathway of *Simonaitis and Heicklen* [1975] to produce perchloric acid from oxidation of chlorine volatiles can, in principle, produce perchlorate in sufficient quantities to explain the abundance of this salt in the Atacama.

[53] 5. Reaction rates proposed by *Simonaitis and Heicklen* [1975] for reactions producing chlorine trioxide and leading to perchloric acid were found to be too high because they greatly perturbed modeled chlorine-containing species such as stratospheric HCl away from observational profiles, whereas lowered reaction rates were found to be permissible. Consequently, further work on establishing these reaction rates would be highly desirable.

[54] 6. Overall, the feasibility of gas phase production in the Atacama atmosphere provides justification for future investigations of gas phase photochemistry as a source for Martian perchlorates.

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