

POSSIBLE ATMOSPHERIC ORIGINS OF PERCHLORATE ON MARS. D. C. Catling^{1,2}, M. W. Claire³, R. C. Quinn⁴, K. J. Zahnle⁵, B. C. Clark⁶, S. Kounaves⁷, M. H. Hecht⁸. ¹Dept. Earth Sciences, University of Bristol, Bristol, United Kingdom. ²Earth and Space Sciences/Astrobiology Program, University of Washington, Box 351310, Seattle WA 98195 (dcatling@u.washington.edu). ³Dept. Astronomy/Astrobiology Program, University of Washington, Seattle WA 98195. ⁴SETI Institute/NASA Ames Research Center, Moffett Field, CA 94035. ⁵NASA Ames Research Center, Moffett Field, CA 94035. ⁶Space Exploration Systems, Lockheed Martin, Denver, CO 80201. ⁷Dept. of Chemistry, Tufts University, Medford, MA 02035. ⁸JPL/Caltech, Pasadena, CA 91109.

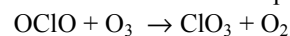
Introduction: The wet chemistry experiment on NASA's Phoenix lander had cells where $\sim 1 \text{ cm}^3$ of Martian soil was mixed with 25 cm^3 of dilute leaching solution and electrochemical measurements were made to identify a variety of soluble ions. Surprisingly, perchlorate (ClO_4^-) was measured as a dominant anion [1]. For an assumed soil sample mass $\sim 1 \text{ g}$, the soluble perchlorate concentration converts to $\sim 1 \text{ wt}\%$ in the soil [1].

These data suggest that most of the chlorine in the soil at the Phoenix site has been oxidized to perchlorate, in which chlorine attains a maximal +7 oxidation number. From a thermodynamic perspective, perchlorate is a strong oxidizing agent but kinetically, perchlorate is very inert at typical planetary surface temperatures. The tetrahedral coordination of oxygen atoms in perchlorate is an energetically stable geometry around the central, electrophilic chlorine atom and renders perchlorate unreactive. Hence, perchlorate, once formed, is prone to persist in soil provided that it is in a dry environment where liquid water cannot wash it away, given that perchlorate salts are generally highly soluble. (If an environment is wet, perchlorate is liable to accumulate in ground water). Thus, the aridity of Mars, combined with perchlorate being an unreactive, dead-end of oxidation chemistry, probably explains why Phoenix discovered relatively abundant perchlorate. Here, we consider the origin of Martian perchlorate and suggest that a likely source is atmospheric, associated with the production of oxidants. If this is so, perchlorate will act as a tracer of past atmospheric chemistry (and possibly volcanic gas fluxes), which could be important in future missions such as sample return or polar ice drilling.

Occurrence and origin of natural perchlorate on Earth: In considering the origin of perchlorate on Mars, it is appropriate to start with what we know about perchlorate on Earth. Most terrestrial perchlorate is manmade for uses such as fireworks and rocket propellants. In contrast, natural perchlorate is rare and is found only in the driest places: unusually arid deserts and the stratosphere. Natural perchlorate occurs in the Atacama at levels of 0.03 to 0.6wt% [2] and is also reported from deserts of West Texas [3] and Bolivian

playas [4]. Perchlorate is also found in carbonates of the upper Eocene Mission Valley Formation of San Diego [5] and sylvinite (KCl) ore in central Canada and Permo-Triassic New Mexico [4].

Isotopic analysis allows Atacama perchlorate to be definitively attributed to an atmospheric source. Non-mass dependent (NMD) fractionation occurs in the oxygen isotopes of ClO_4^- . This is ascribed to the photochemical reaction of ozone with volatile chlorine species because perchlorate inherits its distinctive NMD oxygen isotope signature from O_3 . Specifically, the $\Delta^{17}\text{O}$ of perchlorate (4.2-9.6‰) compared to O_3 (30-40‰) suggests that O_3 contributes one oxygen atom in four to perchlorate [6]. Atacama ClO_4^- also has $\delta^{37}\text{Cl}$ of -14.5 to -9.2‰, which is the lowest $\delta^{37}\text{Cl}$ of any common substance on Earth and consistent with atmospheric fractionation [7]. The photochemistry to produce atmospheric ClO_4^- is not fully known. However, once chlorine oxides are generated from chlorine inputs to the atmosphere, reactions initiated by O_3 can produce perchloric acid (HClO_4), which can deposit onto the surface. For example, one possible scheme is



In the Atacama, a variety of Cl sources have been discussed: Volcanic HCl from the Andes, aeolian chlorides where heterogeneous reactions liberate chlorine volatiles, or methyl chloride from marine sources.

Perchloric acid (HClO_4) is a stable end-product of atmospheric chemistry due to its resistance to photolysis [8]. Consequently, HClO_4 also occurs in the dry environment of Earth's stratosphere at abundances of 0.5-5 ppt in sulfate aerosols [9].

Possible origins of perchlorate on Mars:

Terrestrial perchlorate is a useful analog and suggests that perchlorate forms and persists on Mars because of oxidizing chemistry and a desiccating environment. A well known source of oxidizing power on Mars is the atmosphere, where photochemistry generates a variety of oxidizing species [10]. Fluxes of H_2O_2 and O_3 are calculated to dominate the oxidizing fluxes to the surface, where the respective fluxes of these two species are roughly equivalent in terms of oxidizing power [11]. Other oxidants include OH, HO_2 , O and O^- .

Meanwhile ultraviolet action on minerals can produce free radicals, further providing an environment conducive to oxidation.

Table 1 summarizes broad classes of oxidative processes that could generate perchlorate on Mars. We also identify two possibilities for chlorine sources that lead to perchlorates: chlorine-containing gases released into the atmosphere that take part in gas phase reactions or chlorides in minerals (aerosol or surface soil particles) that participate in heterogeneous reactions. Volatile chlorine must have occurred in the past on Mars as volcanic HCl and also could have been generated by acid displacement reactions with salts in acidic, near-surface aqueous environments (e.g., $\text{CaCl}_2 + \text{H}_2\text{SO}_4 = 2\text{HCl} + \text{CaSO}_4$). If the Cl derives from volcanism, the required flux turns out to be quite modest. A source of $\sim 10^8$ mol HCl yr^{-1} over ~ 1 Myr could produce ~ 1 wt% $\text{Mg}(\text{ClO}_4)_2$ in 10 cm of soil (with density $\sim 1\text{g cm}^{-3}$) over $\sim 10\%$ of Mars' surface. On Earth, the volcanic HCl/SO₂ ratio is 1/20 and the SO₂ flux is $\sim 5 \times 10^{11}$ mol yr^{-1} , so Earth releases $\sim 2 \times 10^{10}$ mol HCl yr^{-1} . Hence Mars needs to generate only 0.5% of the terrestrial volcanic HCl flux for 1 Myr to generate our distribution scenario above. Chlorine gas may also be sourced from aerosols. On Earth, OH radicals react at the deliquesced water-gas interface of seasalt particles to release chlorine ($\text{OH} \cdot (\text{g}) + \text{Cl}^- (\text{aerosol}) \rightarrow 0.5\text{Cl}_2(\text{g}) + \text{OH}^- (\text{aerosol})$) but the liquid phase seems essential [12]. If any similar reactions took place on Mars, Cl₂ would rapidly photolyze to reactive chlorine atoms.

If ozone is specifically required to create Martian perchlorate, as it is on Earth, perchlorate formation might be enhanced in polar environments due to the meridional distribution of ozone. Observations by ultraviolet spectrometers on Mariner 9 and Mars Express show that ozone is most abundant in the spring-winter circumpolar regions but non-detectable or barely detectable in the tropics during all seasons [13, 14].

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 volatile chlorine species but labwork under Mars-like conditions is required to confirm that such pathways exist and to assess their efficiency. A role for ice as a reaction surface for adsorbed species cannot be excluded since it is an effective adsorber. This may favor perchlorate at colder, high latitudes. 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 [15]. However, although the production of terrestrial perchlorate from chloride aerosols with electrostatic discharge has been demonstrated [3], the $\text{ClO}_4^-/\text{Cl}^-$ ratios are very small ($<1\%$), whereas the Phoenix soil data require perchlo-

rate to far exceed chloride. Either more efficient oxidation pathways (such as gas phase reactions) are implied or multiple events over geologic time with high cumulative efficiency would be required.

Flux Constraints: An atmospheric origin of perchlorate sets an upper limit on the perchlorate production rate. Mars' overall oxidation flux is set by the rate that hydrogen escapes to space. Theory and evidence (discussed in [11]) suggests that hydrogen escapes from Mars close to the diffusion-limited rate of $\sim 3.7 \times 10^8$ H atoms $\text{cm}^{-2} \text{s}^{-1}$. This translates to a net oxidation flux of 4.8×10^{-9} mol O₂ $\text{cm}^{-2} (\text{Earth yr})^{-1}$. If we assume that all the perchlorate is in the form of $\text{Mg}(\text{ClO}_4)_2$, and all oxidation is used to make perchlorate, we obtain an upper limit on perchlorate production as $< 1.2 \times 10^{-9}$ mol $\text{cm}^{-2} \text{yr}^{-1}$. This upper limit sets a minimum age constraint on the perchlorate at the Phoenix site. If we assume 1%wt Mg-perchlorate mixed to ~ 5 cm depth of soil above ice, the perchlorate at the Phoenix site cannot be younger than ~ 0.2 Myr.

Table 1: Possible mechanisms to produce perchlorate on Mars. In all cases, the ultimate source of oxidation is atmospheric.

Mechanism	Chlorine source
Gas phase photochemical reactions with oxidants such as O ₃	- Volcanic HCl - HCl liberated from acid displacement reactions - Cl atoms liberated from aerosol chloride
Electrostatic discharge	- Aerosol or surface soil chlorides - Volatile species as above
Gas-solid reactions with oxidants	- Aerosol or surface soil chlorides

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