



The formation of sulfate, nitrate and perchlorate salts in the martian atmosphere[☆]



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ABSTRACT

In extremely arid regions on Earth, such as the Atacama Desert, nitrate, sulfate and perchlorate salts form in the atmosphere and accumulate on the surface from dry deposition according to diagnostic evidence in their oxygen isotopes. Salts of similar oxyanions should have formed in the atmosphere of Mars because of comparable photochemical reactions. We use a 1-D photochemical model to calculate the deposition rates of sulfate, nitrogen oxyanions, and perchlorate from Mars' atmosphere, given a plausible range of volcanic fluxes of sulfur- and chlorine-containing gases in the past. To calculate integrated fluxes over time, we assume that throughout the last 3 byr (the Amazonian eon), the typical background atmosphere would have been similar to today's cold and dry environment. If the soil has been mixed by impact perturbations to a characteristic depth of ~2 m during this time, given a time-average volcanic flux 0.1% of the modern terrestrial volcanic flux, the model suggests that the soil would have accumulated 1.0–1.7 wt.% SO_4^{2-} and 0.2–0.4 wt.% N in the form of pernitrate (peroxynitrate) or nitrate. The calculated sulfate concentration is consistent with *in situ* observations of soils from rovers and landers and orbital gamma ray spectroscopy. However, nitrates or pernitrates are yet to be detected. The modeled formation of perchlorate via purely gas-phase oxidation of volcanically-derived chlorine is insufficient by orders of magnitude to explain 0.4–0.6 wt.% ClO_4^- measured by NASA's Phoenix Lander. The far smaller amount of ozone in the martian atmosphere compared to the terrestrial atmosphere and the colder, drier conditions are the cause of lower rates of gas phase oxidation of chlorine volatiles to perchloric acid. Our calculations imply that non-gas-phase processes not included in the photochemical model, such as heterogeneous reactions, are likely important for the formation of perchlorate and are yet to be identified.

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1. Introduction

The elemental composition of the martian soil was first determined by X-ray fluorescence spectroscopy on the Viking Landers (VLs), which measured absolute concentrations (Clark et al., 1977). Concentrations of elements in what was called the “average deep soil” at the VLs only summed to ~89%. The missing ~11% was attributed to bound water (H_2O , $-\text{OH}$), carbonates, nitrates, phosphates and oxides, given that some light elements (H, C, N, O plus Li, B, and F) were undetectable while other elements were obscured (Na, P, Cr and Mn) (Clark et al., 1982). How the elements were bound into salts was uncertain, although Mg and S were

correlated in duricrust soils, which was interpreted as a cement of magnesium sulfate (Clark, 1993).

Some of the “missing components” in VL soil analyses have since been detected. Orbital thermal infrared spectroscopy showed that 2–5 wt.% carbonates are present in the global dust (Bandfield et al., 2003), while thermal evolved gas analysis in soils at the site of the Phoenix Lander revealed 3–6 wt.% carbonate (Boynton et al., 2009; Sutter et al., 2012). Additionally, thermal evolved gas analysis in soils at the Rocknest location in Gale Crater was consistent with the presence of 1–2% fine-grained siderite and/or magnesite (Leshin et al., 2013). Orbital gamma-spectroscopy have also revealed 1.5–7.5 wt.% water-equivalent hydrogen near the martian surface (Boynton et al., 2007), and the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) detected evolved H_2O consistent with ~1.5–3 wt.% H_2O in sand grains at the Rocknest location (Leshin et al., 2013).

The Wet Chemistry Laboratory (WCL) on the Phoenix Lander provided *in situ* measurements of the composition of soluble salts in the martian soil. Soluble sulfate was present at 1.3 ± 0.5 wt.%

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(Kounaves et al., 2010b), along with cations of sodium, potassium, calcium and magnesium. The most surprising result was the presence of perchlorate (ClO_4^-) at an inferred concentration in the soil of ~ 0.5 wt.% (Hecht et al., 2009; Kounaves et al., 2010a). The dominance of $\text{Mg}(\text{ClO}_4)_2$ is consistent with simulations of evaporation and freezing at the Phoenix landing site (Marion et al., 2010); however, further analysis of data from the WCL suggests that $\text{Ca}(\text{ClO}_4)_2$ may be the dominant form of perchlorate (Kounaves et al., 2012). The perchlorate-sensitive electrode in the WCL experiment was also sensitive to nitrate, but it was 1000 times more sensitive to perchlorate. Thus, the methodology precluded the detection of nitrate because the signal would have required a mass of nitrate that exceeded the mass of the sample (Hecht et al., 2009). Recently, the MSL mission has also confirmed the presence of perchlorate using pyrolysis as part of the SAM experiment (Steininger et al., 2013). Specifically, pyrolysis showed release of chloromethane and O_2 from heated soil samples at the Rocknest location, which is consistent with the decomposition of perchlorate (Sutter et al., 2013). If all of the evolved O_2 was released from perchlorate, then the samples contained a comparable amount of perchlorate to the samples at the Phoenix landing site (Leshin et al., 2013). Furthermore, reanalysis of the Viking thermal volatilization experiments suggest $\leq 1.6\%$ perchlorate at both Viking 1 and Viking 2 landing sites (Navarro-Gonzalez et al., 2010); however, this has been subject to some debate (Biemann and Bada, 2011). Native perchlorate has also recently been measured in the martian meteorite EETA79001, albeit at a level < 1 ppm by mass (Kounaves et al., 2014). Given the various locations of possible detection, perchlorate appears to be ubiquitous on the martian surface.

Alpha-proton X-ray fluorescence on landers and rovers after the VIs has led to the inference of a global soil unit (Blake et al., 2013; Bruckner et al., 2003; Morris et al., 2010; Rieder et al., 2004; Yen et al., 2013, 2005). Soils can have components derived from local rocks but these are imprinted upon a global-scale soil that has characteristic ratios of the concentration of certain elements (Mg, Al, K, Ca and Fe) relative to silicon and also a positive correlation of Cl and S. Given the lander and rover detections of perchlorate, the Cl in this global soil may well be in the form of perchlorate.

Salts are relevant to the habitability of Mars. First, perchlorate reduction is a metabolism used by some terrestrial bacteria in anaerobic conditions (Coates and Achenbach, 2004). If such organisms exist (or did exist) on Mars, then they could gain energy by reducing perchlorate and oxidizing an electron donor such as organic carbon or ferrous iron. This would require organic molecules to be present on Mars. Indigenous organic molecules have yet to be confirmed on Mars; however the presence of perchlorate itself may have inhibited the detection of organics on Mars in pyrolysis experiments (Navarro-Gonzalez et al., 2010). Second, perchlorate salts are highly deliquescent and significantly lower the freezing point of liquid water (Gough et al., 2011). The eutectic point of $\text{Mg}(\text{ClO}_4)_2$ is -57°C (Stillman and Grimm, 2011), while that of $\text{Ca}(\text{ClO}_4)_2$ is -75°C (Pestova et al., 2005). Given typical soil salt concentrations, small amounts of water (~ 0.02 g H_2O per g soil) would permit a water activity sufficient for terrestrial life to be viable (Kounaves et al., 2010b). Third, if all organisms require fixed nitrogen in proteins and nucleic acids, as they do on Earth, then the discovery of nitrogen oxyanions on Mars would be significant as well.

Perchlorate may be advantageous to microorganisms, but its impact on human exploration is more complicated. Perchlorate may be harmful because it is potentially toxic to humans if ingested (Urbansky, 2002). On the other hand, perchlorate could be useful for future exploration of Mars. It is kinetically stable at typical planetary surface temperatures, but at high temperatures perchlorate is a powerful oxidant suitable for rocket propulsion

(Trumpolt et al., 2005). So perchlorate could be utilized as an *in situ* fuel resource for sample return missions and in the eventual human exploration of Mars.

On Earth, one source of sulfate, nitrate, and perchlorate salts is atmospheric deposition. The salts can build up in extremely arid environments, such as the Atacama Desert in Chile (Catling et al., 2010; Ericksen, 1983) and the Antarctic Dry Valleys (Kounaves et al., 2010c). Given the oxic arid environment of Mars, it is possible that the same salts, or similar ones, have formed in the atmosphere. This work estimates the photochemical formation and deposition rates of martian oxyanions, and evaluates the plausibility of atmospheric chemistry as an important source of salts in the global martian soil.

This study builds upon the work of Catling et al. (2010), which used a one-dimensional photochemical model to investigate the formation of salts in the terrestrial atmosphere over the Atacama Desert. Using purely gas-phase pathways, Catling et al. (2010) reproduced measured profiles of chlorine species in the terrestrial atmosphere and estimated deposition rates of both perchlorate and nitrate that were consistent with Atacama soil measurements. Several profound differences, however, alter the photochemistry of Mars relative to Earth, including atmospheric composition, density, and temperature. Our results reveal how these differences impact the formation of atmospheric salts on Mars as compared to Earth.

2. Background: atmospheric perchlorates, sulfates, and nitrates on Earth versus Mars

Perchlorates, sulfates, and nitrates are formed in the atmosphere on Earth and by analogy may have formed in the atmosphere of Mars. In this section, we consider how terrestrial pathways of salt formation inform possible mechanisms on Mars.

2.1. Perchlorate formation

Perchlorate salts produced synthetically on Earth can be distinguished from those produced naturally in the atmosphere by virtue of their oxygen and chlorine isotope ratios. Synthetic formation creates perchlorate with ordinary mass-dependent oxygen isotope fractionation (i.e. oxygen isotopes are distributed according to the linear relationship, $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$). Conversely, naturally occurring perchlorate typically contains mass-independently fractionated oxygen isotopes, a deviation defined as $\Delta^{17}\text{O}$, where $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$. The known source for $\Delta^{17}\text{O}$ occurs during ozone formation, leading to stratospheric ozone with 30–40‰ (Thiemens, 2006). Perchlorate that contains $\Delta^{17}\text{O}$ thus preserves a telltale signature of a naturally occurring formation pathway involving stratospheric photochemistry. Natural perchlorate has been discovered in locations across the globe, including the Atacama Desert (Bao and Gu, 2004), the Antarctic Dry Valleys (Kounaves et al., 2010c), and the American southwest (Jackson et al., 2010; Rajagopalan et al., 2006). The Mojave Desert in California and Atacama Desert in Chile have the highest $\Delta^{17}\text{O}$ values. In perchlorate samples from the Mojave Desert, $\Delta^{17}\text{O} = 8.6\text{--}18.4\text{‰}$ (Jackson et al., 2010), and in samples from the Atacama Desert, $\Delta^{17}\text{O} = 4.2\text{--}9.6\text{‰}$ (Bao and Gu, 2004). The occurrence of radioactive ^{36}Cl (produced by cosmic rays acting on atmospheric ^{36}Ar) relative to ^{37}Cl (Sturchio et al., 2009) further confirms a stratospheric source for the chlorine in natural terrestrial perchlorate.

A gas phase pathway for producing perchlorate is through the reaction of halogens with ozone. Simonaitis and Hecklen (1975) proposed that perchloric acid, HClO_4 , forms by:



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