PERCHLORATE ORIGINS IN THE ATACAMA AND ON MARS.

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Introduction: Perchlorate comprises ~0.3-0.6wt% of the soil at the site of NASA's Phoenix Mars Lander [1, 2]. Also, on a molar basis, ClO_4^- exceeds Cl^- by about an order of magnitude. But what's its origin?

Hypothetical ways to produce Martian perchlorate include photochemistry, electrostatic discharge, and gas-solid reactions [3]. We propose that the Martian environment especially favors perchlorate production associated with atmospheric oxidants. If so, ClO_4^- could act as a tracer of past volcanic chlorine and its measurement might be fruitful in returned samples [4] or polar deposits drillcores [5]. However, even on Earth, the exact pathway to produce natural perchlorate is unknown. Consequently, we examine perchlorate formation in the Atacama desert to shed light on Mars because perchlorate levels are comparable to those on Mars only in the Atacama [6]. Isotopic studies indicate that such perchlorate is produced by oxidation involving atmospheric ozone [7-9]. Such pathways terminate in perchloric acid ($HClO_4$) [10], which can dry deposit.

Pathways to perchlorate: For the terrestrial atmosphere, [10] suggested the pathway:

$$Cl + O_3 + M \rightarrow ClO_3 + M \quad (1)$$

$$ClO_3 + OH + M \rightarrow HClO_4 + M \quad (2)$$

OH reacts with many species, so (2) relies on enough available ClO_3. OClO can also generate ClO_3 via [11]:

$$OClO + O_3 \rightarrow ClO_3 + O_2 \quad (3)$$

$$OClO + O + M \rightarrow ClO_3 + M \quad (4)$$

where OClO derives from gas-ice interaction [12] or gas phase chemistry. [13] made another proposal with weakly bound $ClO.O_2$ and $ClO.O_3$ intermediates:

$$ClO + O_2 + M \rightarrow ClO.O_2 + M \quad (5)$$

$$ClO.O_2 + O_3 \rightarrow ClO.O_3 + O_2 \quad (6)$$

$$ClO.O_3 + HO_2 \rightarrow HOClO_3 + O_2 \quad (7)$$

But $ClO.O_3$ is hypothetical while the stability of $ClO.O_2$ remains questionable [14, 15]. A third model postulates heterogeneous chemistry [16]:

$$ClO \xrightarrow{H_2SO_4} HClO_4 + HCl + \text{products} \quad (8)$$

However, measurements have shown that ClO uptake on sulfuric acid is insignificantly slow [17].

Method: We examined an Atacama-like atmosphere with a 1-D photochemical model [18, 19]. A flux of HCl was distributed throughout the troposphere to represent a Cl source from volcanism. Model runs had no rainfall and an Atacama-like tropospheric RH.

Results: Fig. 1 shows deposition fluxes as a function of HCl input. ClO_3 is produced predominantly via (1) and also via (3) and (4); then $HClO_4$ is produced via (2). Fluxes needed to generate the mass of Atacama salts over the ~10^7 year age of the deposits are ~10^8 molecules-NO_3/cm^2/s and ~10^5 molecules-ClO_4/cm^2/s [3]. Modeled nitrate fluxes compare favorably (Fig. 1). A match for the required perchlorate flux occurs at HCl fluxes 50-60 times higher than estimates of the globally-averaged HCl flux to the atmosphere, ~0.5×10^9 molecules-HCl/cm^2/s [20]. But a much higher local flux is reasonable given the proximity of the Atacama to Andean volcanoes.

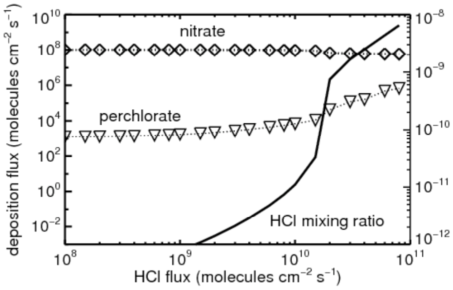

***Fig. 1**. HCl fluxes (x-axis) result in HCl mixing ratios (solid line) mapped to the R.H. y-axis. Deposition fluxes map to the L.H. y-axis.*

Conclusion. We find that the gas phase formation of perchlorate proposed by [10] is feasible for explaining Atacama perchlorate, noting dependence on the uncertain rate of (1). Work is underway with a Mars version of the photochemical model.

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