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Destruction of organics on Mars by oxychlorines: Evidence from Phoenix, Curiosity, and EETA79001

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Abstract

The Phoenix lander measured 0.6 wt% perchlorate (ClO_4^-) in the martian soil. The Curiosity rover has also found CH_3Cl, CH_2Cl_2 and ClO_4^-. New analyses of martian meteorite EETA79001 show the presence of ClO_4^-, and chlorite (ClO_3^-). The ubiquity of ClO_4^- and ClO_3^- points to the global presence of highly oxidizing oxychlorines (ClO_x^-) on Mars. Produced both by oxidation of Cl^- and radiolysis of ClO_4^-, the oxychlorines are very highly destructive to organics. Their global presence has broad implications for the presence and detection of organics and life on Mars.

1. Introduction

In 2008 the Phoenix Mars lander's wet chemistry lab (WCL) measured ~0.6 wt% perchlorate (ClO_4^-) in three soil samples [1,2]. This led to suggestions that detection of chloromethanes (CH_3Cl, CH_2Cl_2) by the Viking GC-MS was a result of ClO_4^- [3,4]. Initial results from SAM on NASA's Curiosity rover also indicate presence of chloromethanes and ClO_4^- [5,6]. These discoveries suggest that ClO_4^- is likely global on Mars and that oxychlorines (ClO_x^-) may be responsible for the oxidation of organics.

The EETA79001 meteorite, from Antarctica is one of the largest martian meteorites found. It is composed of a primary basaltic host of feldspathic pyroxenite with olivine megacrysts and a minor component of pyroxene (lithology-A); a courser-grained basalt free of olivine megacrysts (lithology-B); and several shock-melted glass pockets and veins (lithology-C). Present in several pockets in lithology-A, is a large inclusion of white material. There have been few analyses focused on the soluble ionic species, though some have shown the presence of NO_3^-, none have analysed for ClO_4^-. EETA79001 has never been analysed for any soluble salts.

We have recently performed ion chromatographic (IC) and N/O stable isotope analyses of EETA79001 that show the presence of ClO_4^-, ClO_3^-, and NO_3^-, with isotopic ratios are different from adjacent ice. The location and concentration of the salts within EETA79001 are difficult to reconcile with terrestrial contamination. The evidence is consistent with a martian origin for the ClO_x^- and NO_3^- in EETA79001.

2. Results

The EETA79001 sample consisted of sawdust from a cross-cut that included a ~1.5 cm diameter inclusion and a ~1 cm diameter deposit of white granular material, both in the center ~8 cm from the nearest surface. Analyses by IC found ~ 600 ppb ClO_4^-, 1.4 ppm ClO_3^-, and 16 ppm NO_3^-. Even though rocks on Antarctic ice can absorb enough sunlight and form water around their base, it seems unlikely such a highly soluble salts could accumulate in the interior of EETA79001 that landed on Earth only 12 kyrs ago. Similar levels of ClO_4^- found in nearby Antarctic University Valley soils are estimated to require accumulation periods of 1-8 Myr [7]. No significant ClO_4^- was detected in nearby ice similar to that in which EETA79001 would have rested in for ≤ 12kyrs.

Evidence for the martian origin of the ClO_x^- and NO_3^- in EETA79001 is provided by the NO_3^- isotopic ratios in combination with the ClO_4^-, NO_3^-, and Cl^- concentration ratios. For example, EETA79001 NO_3^- $\delta^{15}N$ values are similar to those for MDV soils while $\delta^{18}O$ is depleted by ~20‰ [8], contrary to what is expected from contamination by the ice EETA79001 was transported through and with $\delta^{15}N$ in the range of 100-350‰. Isotopic analysis of Miller Range blue ice, which is similar to the EET site ice, gave $\delta^{15}N$ = +103‰. It's difficult to reconcile NO_3^- in EETA7901 of $\delta^{15}N$ = -10‰ with nearby ice of $\delta^{15}N$ = +103‰.

Even though the present martian atmosphere has $\delta^{15}N \approx 625$‰ [9], NO_3^- in EETA79001 probably did not originate from current atmospheric N_2, but from that during the first 1-2 Gyr before ^{14}N was depleted. Recently, the Tissint meteorite gave N=12.7ppm with $\delta^{15}N$ = -4.5‰ [9]. Since Tissint was rapidly collected, contamination is unlikely. The similarity of $\delta^{15}N$ for both Tissint and EETA79001 is an indicator that the NO_3^- in EETA79001 is most likely of martian origin.

3. Discussion and Conclusions

Based on terrestrial observations/models, production of ClO_4^- on Mars occurs either photochemically in the upper atmosphere from volcanic HCl, or through gas-phase reactions of Cl^- containing aerosols with O_3 or H_2O_2, and deposited as perchloric acid ($HClO_4$). However, since current active chlorine chemistry is limited (HCl < 0.6 ppb), production of ClO_4^- was probably confined to past volcanic activity. Recent landed missions have identified ClO_4^- to be widespread on the martian surface, and Phoenix showed ClO_4^- to be homogeneous within the top 10 cm of the soil. Thus, either ClO_4^- is a remnant from early volcanic activity and globally distributed by dust storms, or is continually produced by oxidation of mineral chlorides, or both. The former would place constraints on its exposure to liquid water, since its solubility would relocate and concentrate it. The later production of ClO_4^- by oxidation of mineral chlorides, would explain its ubiquitous presence today. Such processes have been shown to be possible [11,12]. In any of the above mechanisms, the reactions will generate hypochlorite (ClO^-), chlorite (ClO_2^-), and chlorate (ClO_3^-). Confirmation of ClO_3^- by Curiosity and in EETA79001 are indicators that oxychlorines are present in the martian soil. In addition, ClO_4^- can also contribute to production of ClO_x^- by radiolytic decomposition [13]. The ClO_x species are highly reactive and would destroy organics in the soil, with only refractory or well protected organics surviving.

Figure 1 shows possible processes and pathways for the production of ClO_4^- and accompanying intermediaries. Highly oxidizing species such as ClO^- and ClO_2^- can be generated from stable Cl-minerals by action of UV and from ClO_4-minerals by action of cosmic γ and x-rays. This suggests that oxychlorines are in effect at "equilibrium" and always present. Thus, their ubiquity has broad implications for the presence and detection of organics and life on Mars.

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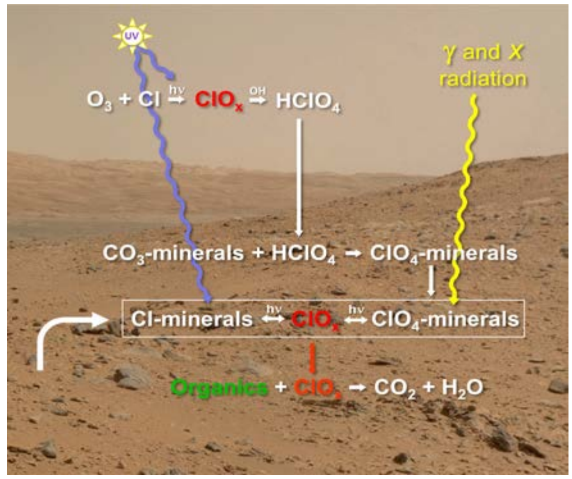

Figure 1: Processes and pathways for the production of perchlorate and accompanying intermediary oxychlorines.

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