Evidence of martian perchlorate, chlorate, and nitrate in Mars meteorite EETA79001: implications for oxidants and organics

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Abstract

The results from the Viking mission in the mid 1970's provided evidence that the martian surface contained oxidants responsible for destroying organic compounds. In 2008 the Phoenix Wet Chemistry Lab (WCL) found perchlorate (ClO₄⁻) in three soil samples at concentrations from 0.5 to 0.7 wt%. The detection of chloromethane (CH₃Cl) and dichloromethane (CH₂Cl₂) by the Viking pyrolysis gas chromatograph-mass spectrometer (GC-MS) may have been a result of ClO₄⁻ at that site oxidizing either terrestrial organic contaminants or, if present, indigenous organics. Recently, the Sample Analysis at Mars (SAM) instrument on the Mars Science Laboratory (MSL) Curiosity directly measured the presence of CH₃Cl, CH₂Cl₂ and, along with measurements of HCl and oxygen, indirectly indicate the presence of ClO₄⁻. However, except for Phoenix, no other direct measurement of the ClO₄⁻ anion in martian soil or rock has been made. We report here ion chromatographic (IC) and isotopic analyses of a unique sawdust portion of the martian meteorite EETA79001 that show the presence by mass of 0.6 ± 0.1 ppm ClO₄⁻, 1.4 ± 0.1 ppm ClO₃⁻, and 16 ± 0.2 ppm NO₃⁻ at a quantity and location within the meteorite that is difficult to reconcile with terrestrial contamination. The sawdust sample consists of basaltic material with a minor salt-rich inclusion in a mass ratio of ~300:1, thus the salts may be 300 times more concentrated within the inclusion than the whole sample. The molar ratios of NO₃⁻ : ClO₄⁻ and Cl⁻ : ClO₄⁻, are very different for EETA79001 at ~ 40:1 and 15:1, respectively, than the Antarctic soils and ice near where the meteorite was recovered at ~ 10,000:1 and 5000:1, respectively. In addition, the isotope ratios for EETA79001 with δ¹⁵N = -10.48 ± 0.32 ‰ and δ¹⁸O = +102.80 ± 0.14 ‰ are significantly different from that of the nearby Miller Range blue ice with δ¹⁵N = +102.80 ± 0.14 ‰ and δ¹⁸O = +43.11 ± 0.64 ‰. This difference is notable, because if the meteorite had been contaminated with nitrate from the blue ice, the δ¹⁵N values should be the same. More importantly, the δ¹⁵N is similar to the uncontaminated Tissint Mars meteorite with δ¹⁵N = -4.5 ‰. These findings suggest a martian origin of the ClO₄⁻, ClO₃⁻ and NO₃⁻ in EETA79001, and in conjunction with previous discoveries, support the hypothesis that they are present and ubiquitous on Mars. The presence of ClO₃⁻ in EETA79001 suggests the accompanying presence of other highly oxidizing oxychlorines such as ClO₂⁻ or ClO⁻, produced both by UV oxidation of Cl⁻ and γ- and x-ray radiolysis of ClO₄⁻. Since such intermediary species may contribute to oxidation of organic compounds, only highly refractory and/or well-protected organics are likely to survive. The global presence of ClO₄⁻, ClO₃⁻, and NO₃⁻, has broad implications for the planet-wide water cycle, formation of brines, human habitability, organics, and life.