

PERCHLORATE ON EARTH AND MARS, FORMATION PROCESSES, FATE, IMPLICATIONS FOR ASTROBIOLOGY AND SUGGESTIONS FOR FUTURE WORK. Max Coleman, NASA Astrobiology Institute and Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, M/S 183-301, Pasadena CA 91101. max.coleman@jpl.nasa.gov.

Introduction: The discovery of perchlorate (ClO_4) by the Phoenix mission [1] has posed many questions about its origin and possible effects on the other components of martian surface soils and sediments. This paper reviews the ClO_4 geochemical cycle on Earth and discusses whether these are applicable to Mars and suggests future work to elucidate the issues raised. Much of the research so far has been driven by forensic needs, firstly terrorist bombs but later environmental differentiation of manufactured and natural perchlorate. Most advances used stable isotope approaches that inform all aspects of the subject.

ClO_4 on Earth: The largest concentration of ClO_4 is associated with another oxyanion salt, nitrate, in the Atacama Desert [1]. Its concentration varies between 0.1% and 1% in deposits but local values as high 2 to 3% occur. However, it also occurs at low concentrations in potassium-rich evaporite deposits [2], in vadose zones of soils or sands in the SW states of the USA [3], in atmospheric precipitation [4] and in seawater [5]. Clearly, because of their great solubility both nitrate and perchlorate only accumulate in the arid environments, but how do they get there?

Origin of terrestrial ClO_4 : Cl isotopic analysis of ClO_4 was developed in response to the need to characterize chlorate and ClO_4 in terrorist bombs [6] but it is most powerful coupled with its O triple isotope composition. Mass-independent fractionation of O ($\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ changed from the normal approx. 1:2 ratio) indicates its origin and formation process. The positive $\Delta^{17}\text{O}$ values for Atacama ClO_4 (and nitrate), are like those of ozone, indicate formation by UV induced reactions of oxygen in the troposphere and stratosphere [8] and possible reaction with seawater aerosol Cl. Accumulation in arid environments arises from particulate deposition, which may occur uniformly over the Earth but is not preserved, potentially implying a considerable flux. In contrast, manufactured ClO_4 , used extensively in propellants for solid-fuel rockets and also for air bags, fireworks and road flares, has isotope compositions showing only mass-dependent O values. Thus, there is a clear isotopic differentiation between natural and manufactured ClO_4 [10]; much of the latter disposed of carelessly, has led to major water resource pollution. Such environmental problems led to much research on microbial degradation of ClO_4 .

Microbial degradation of ClO_4 : Microbes that grow by reducing ClO_4 to chloride [11] occur in many

environments [12] (all are nitrate reducers too). Measuring the associated Cl [13,14] and O [15] isotope fractionations showed very large values used to determine the extent of microbial degradation of pollution. Also, isotopes showed that microbial reduction is currently active in degrading manufactured pollutant ClO_4 in the vadose zone of desert sands in Israel [16], a feasible Mars analog environment. A similar interpretation could be applied but less robustly to the Atacama.

ClO_4 on Mars: Although ClO_4 has been identified only by Phoenix, elemental analyses indicate almost ubiquitous presence of Cl and some or all of it may be perchlorate or other Cl oxyanions. It is unlikely that its mode of formation is like that on Earth, however, it could be formed by surface UV induced reactions with oxidants like iron oxides. It is possible other Cl oxyanions also could be produced. Chlorate, chlorite and hypochlorite react with and destroy organic matter while perchlorate is more stable but most are plausible electron acceptors for microbial respiration processes.

Future work: To address future Mars science needs, possible formation processes must be investigated together with biological and abioblogical degradation. In all cases it is essential to use isotopic characterization which has been the key to terrestrial understanding and can differentiate biological from inorganic equivalent products. A design for a feasible in situ isotope instrument already exists. All of these will be addressed in detail in the presentation.

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