

Use of Chlorine and Oxygen Isotopes to Define the Geochemical Cycle of Perchlorate on Mars (Including Possible Biological Processes). Max Coleman, NASA Astrobiology Institute and NASA Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109. max.coleman@jpl.nasa.gov

Introduction: Perchlorate was identified by the Wet Chemistry Laboratory instrument of the Phoenix mission [1]. Considerable effort has already been expended on characterizing the origin and geochemical cycle of perchlorate on Earth and thus can be applied to understanding that compound on Mars. Stable isotope characterization has played a major part in this work. This paper will describe the isotopic identification of the origins of terrestrial perchlorate, how stable isotopes might be used to recognize metabolic consumption of perchlorate and a possible approach for an in situ analytical instrument for isotopic analysis.

ClO₄ on Earth: The largest concentration of ClO₄ is associated with another oxyanion salt, nitrate, in the Atacama Desert [2]. Its concentration varies between 0.1% and 1% in deposits but local values as high as 2 to 3% occur. However, it also occurs at low concentrations in potassium-rich evaporite deposits [3], in vadose zones of soils or sands in the SW states of the USA [4], in atmospheric precipitation [5] and in seawater [6]. 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 ClO₄: Cl isotopic analysis of ClO₄ was developed in response to the need to characterize chlorate and ClO₄ in terrorist bombs [7] 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 ClO₄ (and nitrate), are like those of ozone, indicate formation by UV induced reactions of oxygen in the troposphere and stratosphere [8, 9] 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 ClO₄, 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 ClO₄ [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 ClO₄.

Microbial degradation of ClO₄: Microbes that grow by reducing ClO₄ to chloride [11] occur in many environments [12] (many are nitrate reducers too).

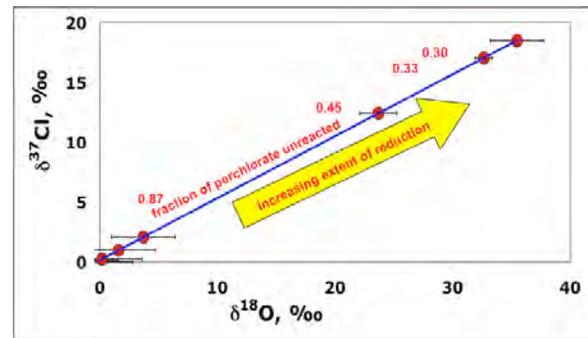


Figure 1. Isotopic changes with increasing extent of microbial reduction of perchlorate.

Measuring the associated Cl [13,14] and O [15] isotope fractionations showed very large values used to determine the extent of microbial degradation of perchlorate (Figure 1.)

Also, isotopes showed that microbial reduction is currently active in degrading manufactured perchlorate ClO₄ in the vadose zone of desert sands in Israel [16], a feasible Mars analog environment. This is an important finding since it shows that a potential energy source is being consumed in the presence of minimal amounts of water. A similar interpretation could be applied but less robustly to the Atacama.

ClO₄ on Mars: Although ClO₄ 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.

In situ stable isotopic analysis: All of this discussion would be academic of interest only if there were no feasible way to analyze Martian perchlorate without waiting for a maybe indefinitely-postponed Mars Sample Return Mission. We have developed a concept and started preliminary experiments on an in situ instrument for investigating stable isotope compositions of solids using laser sampling to allow spatially resolved

analysis for isotopic mapping. The outline of the instrument is shown in Figure 2.

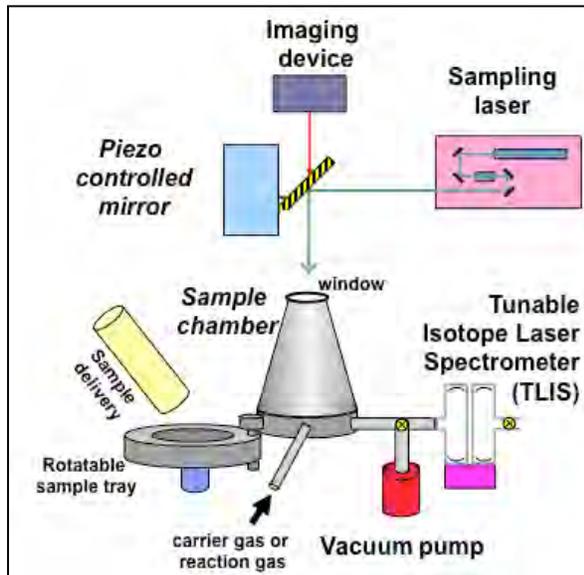


Figure 2. Outline of a stable isotope analysis in situ instrument with laser sampling to allow point analysis or isotopic mapping.

Conclusions: Study of terrestrial perchlorate has shown how use of stable isotopes can elucidate formation and degradation of perchlorate to help produce an understanding of the geochemical cycle of chlorine. On Earth biological processes form an essential part of the geochemical cycle of perchlorate. Similar approaches could be and should be applied to Mars.

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