



Changes in Cl and O isotope compositions of perchlorate to measure extent of microbial reduction, but still identify the fingerprint of the original values

Max Coleman (1), Randall Mielke (1) and John D. Coates (2)

(1) Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, MS 183-301, Pasadena, California 91109-8099, USA, (2) Department of Plant and Microbial Biology, 271 Koshland Hall, University of California Berkeley, Berkeley, CA 94720, USA.
(max.coleman@jpl.nasa.gov)

1. Introduction

Perchlorate, as the ammonium, sodium or potassium salt is a key chemical component of various missile solid propellants, fireworks, flares and air-bag inflators. It is toxic and operates by interfering with uptake of iodide by the thyroid gland. It has been detected as a contaminant in water in more than 20 states in the USA. Natural bioremediation can occur by microbial perchlorate reduction but it is necessary to monitor how effectively the process is operating. Systematic changes in perchlorate stable isotope compositions as a result of kinetic fractionation offer a way of performing this task if the process conforms to a Rayleigh distillation model. Our latest work reported here for the first time shows that not only do the stable isotope compositions of perchlorate chlorine change systematically during degradation but oxygen isotope values do so also. Despite these changes we show that it may still be possible to use isotope compositions to fingerprint sources of perchlorate pollution.

2. Experimental determination of isotopic fractionation accompanying reduction of perchlorate

We grew *Dechlorosoma suillum* strain PS using a culture medium similar to that of Bruce et al. (1999). We periodically checked optical density, as a measure of cell growth, and used small samples for chemical and isotopic analysis. Perchlorate samples were prepared for Cl isotope analysis using the method of Ader et al. (2001). Variations of the isotope ratio of ^{37}Cl to ^{35}Cl are reported relative to Standard Mean

Ocean Chloride (SMOC, Godon et al., 2004) in the standard δ notation. Halite (NaCl) is the primary chlorine source of most manufactured chlorine compounds and a large range of samples of all ages displays a narrow range of isotopic compositions near to 0‰, with most not more than 1‰ from that value. Manufacturing processes can cause isotopic fractionation that may increase that range by up to a factor of two.

In our previous work we showed that microbial reduction of perchlorate is accompanied by a very large isotopic fractionation. Chloride produced by this process is 15.8‰ more negative than the perchlorate (Coleman et al., 2003). The residual perchlorate is left isotopically more positive and becomes increasingly so as the extent of reduction increases. The isotopic fractionation factor can be calculated independently both from the residual perchlorate and from the chloride produced, using appropriate formulations of the Rayleigh equation. Both approaches give the same value for the fractionation factor, which is constant throughout the reduction process. Thus the isotopic evolution can be used to track the extent of microbial reduction, independent of other processes.

3. Isotopic tracking and characterization with combined Cl and O isotope measurements

Changes in isotopic composition would seem to negate the possibility of isotopically characterizing the source, however, in a two isotope system it is possible to do so. Where the two isotopes are both fractionated, degradation may follow a predictable path in two dimensional isotope space. We have now applied to oxygen isotope fractionation, the approach we had taken previously for chlorine. Of course in this case we can only analyze the residual perchlorate. We removed most other oxyanions present in the culture medium. We then measured oxygen isotope compositions of perchlorate using a continuous flow mass spectrometer with high temperature reduction to CO, and corrected for the isotopic compositions of the small amounts of other oxyanions in the samples. The initial results show a very large isotopic fractionation of oxygen isotopes that more than matches that displayed by chlorine. Our data show that the fractionation factor for oxygen removed from perchlorate is 29.9‰ (0.7‰, 2 x standard error) more negative than the original composition. The measured chlorine and oxygen isotope values of perchlorate co-vary and define a trajectory in isotope space as the reduction process proceeds. By using the chloride mass balance it is possible to extrapolate this trajectory back to the initial value for the original perchlorate and thus define its characteristic isotopic composition.

4. Conclusions

We have now proved the combined isotope approach can work in the laboratory and our tasks in the near future are to validate the method under a large range of environ-

mental conditions and to apply it a natural attenuation field site.

5. References

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