Environ. Sci. Technol. **2004**, 38, 5073−5077

Natural Perchlorate Has a Unique Oxygen Isotope Signature

HUIMING BAO*

Department of Geology & Geophysics, E235 Howe-Russell Geoscience Complex, Louisiana State University, Baton Rouge, Louisiana 70803

BAOHUA GU

Environmental Sciences Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee 37381

Perchlorate is known to be a minor component of the hyperarid Atacama Desert salts, and its origin has long been a subject of speculation. Here we report the first measurement of the triple-oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) for both man-made perchlorate from commercial sources and natural perchlorate extracted from Atacama soils. We found that the $\delta^{18}O$ values (i.e., normalized $^{18}O/^{16}O$ ratios) of man-made perchlorate were at −18.4 ± 1.2‰, whereas natural perchlorate has a variable $\delta^{18}O$ value, ranging from −4.5‰ to −24.8‰. The $\delta^{18}O$ and $\delta^{17}O$ values followed the bulk Earth's oxygen isotope fractionation line for man-made perchlorate, but all Atacama perchlorates deviated from this line, with a distinctly large and positive ^{17}O anomaly ranging from +4.2‰ to +9.6‰. These findings provide a tool for the identification and forensics of perchlorate contamination in the environment. Additionally, they confirm an early speculation that the oxidation of volatile chlorine by O_3 and the formation of $HClO_4$ can be a sink (albeit a minor one) for atmospheric chlorine.

Introduction

Man-made perchlorate (ClO_4^-) salt has been widely used as the primary oxidizer in the solid propellant for rockets and missiles, and improper disposal of perchlorate-containing materials has resulted in a significant new threat to groundwater and drinking water supplies (*1−3*). Millions of people are potentially exposed to perchlorate contamination in the United States, although the Environmental Protection Agency has yet to set a maximum concentration level (MCL) for drinking water.

In addition to man-made sources, natural perchlorate was found as a minor component in salt deposits in the hyperarid Atacama Desert over 100 years ago (*4*). George Ericksen at the U.S. Geological Survey (USGS) verified the presence of natural perchlorate in Chilean nitrates in early 1980s (*5*, *6*). He and colleagues also reported a trace of perchlorate in the "blister" caliche of a nitrate deposit in southeastern California (*7*). However, the origin of natural perchlorate remains a subject of speculation. Erickson cited Simonaitis and Heicklen's (*8*) hypothesis and proposed that natural perchlorate could be formed by the photochemical oxidation of volatile sea-salt chlorine (Cl) by ozone in the troposphere or at soil surface (*5*). Unfortunately, this mechanism has never been validated, partly because of the difficulties encountered in extracting and analyzing trace quantities of perchlorate from soil deposits that contain large quantities of nitrate and other salt impurities.

The presence of natural or atmospheric perchlorate in the environment obviously has far-reaching ramifications, ranging from public health issues to huge liabilities that could be imposed by agricultural and environmental cleanup needs. Controversy exists with respect to perchlorate contamination in those cases in which the sources of perchlorate contamination are not readily identifiable. For example, questions were raised about traces of perchlorate contamination in some commercial fertilizers, although such contamination was later found to be associated with nitrate deposits imported from Chile (*9−11*). Recent studies also suggest that some potash minerals obtained from the western United States, Canada, and Bolivia contain perchlorate (*12*), although additional studies and confirmation of these findings are necessary.

Perchlorate is a nonlabile oxyanion. Once formed, its oxygen atoms will not exchange with those in the ambient environment, and it thus retains the oxygen isotopic signatures of its sources (*13*). The measurement of oxygen isotope composition can, therefore, provide clues to the origin and subsequent alteration of perchlorate in the environment. Oxygen isotope composition is defined as

$$\delta^{18}O = (R^{18}_{sample}/R^{18}_{standard} - 1) \times 1000‰ \quad (1)$$

or

$$\delta^{17}O = (R^{17}_{sample}/R^{17}_{standard} - 1) \times 1000‰ \quad (2)$$

in which R is the abundance ratio of $^{18}O/^{16}O$ or $^{17}O/^{16}O$. International standard for oxygen isotope composition is V−SMOW (Vienna-Standard Mean Ocean Water), which, by definition, has $\delta^{18}O = \delta^{17}O = 0‰$. For most oxygen-bearing compounds on Earth, there is a highly correlated relationship between their $\delta^{18}O$ and $\delta^{17}O$ values,

$$\delta^{17}O \approx 0.52 \times \delta^{18}O \quad (3)$$

due to the fact that most oxygen isotope fractionation processes (physical, chemical, or biological) are mass-dependent (i.e., thermodynamic or kinetic isotope fractionation) (*14*). In other words, no independent information can be obtained from the $\delta^{17}O$ if $\delta^{18}O$ value has been measured. However, exceptions arise in reactions under non-Boltzmann conditions such as photochemical reactions, in which the $\delta^{18}O$ and $\delta^{17}O$ may not follow the mass-dependent fractionation relationship (eq 3). A parameter has been developed to measure the deviation of the $\delta^{17}O$ value from the mass-dependent relationship or terrestrial fractionation line (eq 3). This deviation, measured by $\Delta^{17}O$ (or ^{17}O anomaly), is calculated as

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \quad (4)$$

or in a logarithmic format (*15*)

$$\Delta^{17}O = \delta^{17}O - 1000 \times [(1 + \delta^{18}O/1000)^{0.52} - 1] \quad (5)$$

It has been well-known that atmospheric O_3 has a high $\delta^{18}O$ value as well as a highly positive $\Delta^{17}O$ value (*16*, *17*). The precise mechanism that contributes to the unique O_3 isotopic signatures has been elusive, and a recently proposed RRKM (Rice, Ramsperger, Kassel, Marcus)-based theory is gaining

---

* Corresponding author phone: (225)578-3419 (office), −3413 (lab); e-mail: bao@lsu.edu.

10.1021/es049516z CCC: $27.50

popularity (*18*). The bearing of an anomalous ^{17}O signal, however, does not necessarily mean that the chemical reaction that produced the compound has to be mass-independent. For example, aqueous oxidation of SO_3^{2-} by atmospheric O_3 is a mass-dependent chemical reaction. But the reaction results in the transfer of O_3's anomalous signal to the product SO_4^{2-} (*19*), a phenomenon being widely recognized in nature (*20*).

If perchlorate of atmospheric origin involves O_3, either by a mass-independent oxygen isotope fractionation process or by an isotope transfer process, a positive $\Delta^{17}O$ value would be expected for the perchlorate. On the other hand, man-made perchlorate is produced by electrolysis of aqueous chlorate solution (*21*). Its oxygen is derived from the water used for production. We can thus anticipate that the $\delta^{18}O$ value of man-made perchlorate could change with the processes or the water used. We, however, do not expect to see any ^{17}O anomaly (i.e., $\Delta^{17}O = 0$) in man-made perchlorates, since the electrolysis process is entirely mass-dependent: any change in the $\delta^{18}O$ value would have a corresponding change in its $\delta^{17}O$ value. Therefore, the present study was designed to test the hypothesis that natural or atmospheric perchlorate has a ^{17}O anomaly whereas man-made perchlorate does not. Innovative techniques such as selective ion-exchange and tetrachloroferrate displacement were utilized for perchlorate extraction and recovery. A modified thermal-decomposition method was developed to generate O_2 from perchlorate for both $\delta^{18}O$ and $\delta^{17}O$ measurements. We report that natural perchlorate indeed carries a unique ^{17}O signature, a very robust parameter that can be used to distinguish between man-made and natural sources of perchlorate.

Experimental Methods

Perchlorate in Atacama Soils. The central Atacama Desert is the driest portion of the desert in northern Chile and generally consists of three geographic zones: the Coastal Zone, the Central Depression, and the Preandean Ranges. Among these, the Central Depression (or the Central Valley) is the driest. It has essentially no precipitation (<2 mm per year) and is devoid of plants and normal hydrological processes (*5*, *22*). We previously measured 5 different soil samples from the Central Depression and adjacent area; we found that the $[ClO_4^-]$ ranges from 0 to ~250 ppm, and there is no correlation between $[NO_3^-]$ or $[Cl^-]$ with $[ClO_4^-]$ in these soils (data not shown). In this study we analyzed seven samples collected from the Central Depression, but only three of them yielded sufficient quantities of perchlorate for isotope measurement.

Extraction and Purification of Perchlorate from Soils. Each soil sample was crushed before being soaked in doubly deionized water. The Atacama soils are extremely rich in salts; the concentrations of anions such as sulfate, nitrate, and chloride are several orders of magnitude higher than that of perchlorate. For example, sample AT24-1 has 7.4% SO_4^{2-}, 6.2% Cl^-, and 5.0% NO_3^-, as measured by ion chromatography (IC). We used a highly selective bifunctional anion-exchange resin to extract and concentrate perchlorate from the soil extract (*3*). This process involves the initial sorption of perchlorate onto a packed resin column by pumping the extract solution through the column. Usually >90% of the perchlorate was adsorbed, depending on individual samples and salt concentrations. The sorbed perchlorate in the resin column was then recovered by displacement with tetrachloroferrate ions formed in a solution of ferric chloride and HCl, as reported previously (*23*). Over 99% of the sorbed perchlorate could be recovered and was usually concentrated in the first few bed volumes of the $FeCl_3$ and HCl effluent solution. After neutralization and additional concentrations, when necessary, using a Speed-Vac concentration system, the concentrated sample was mixed with additional KCl or CsCl to give a final concentration of ~0.2−0.4 M K or Cs. Because of their relatively low solubility, $KClO_4$ or $CsClO_4$ form precipitates or pure crystalline phases over time and can thus be recovered.

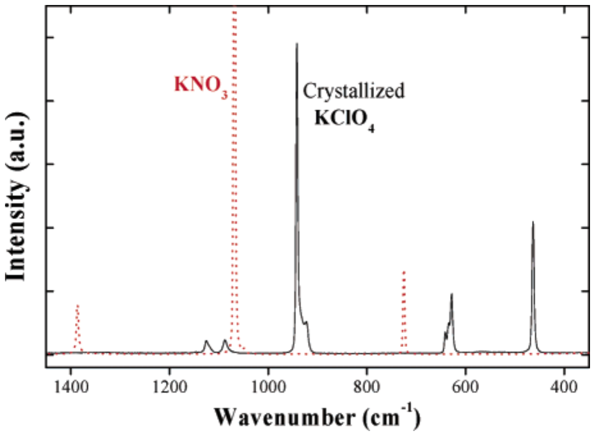

FIGURE 1. Raman spectroscopy spectrum (solid line) of a final perchlorate sample purified from a soil sample from the central Atacama Desert, Chile. The dashed line is a reference spectrum for nitrate. It demonstrates the successful separation of perchlorate and nitrate from a mixture.

The purity of recovered $KClO_4$ or $CsClO_4$ was validated by Raman spectroscopic analysis at Oak Ridge National Laboratory (Figure 1) and by IC (ICS-90) at Louisiana State University (Table 1). Both methods show that the final perchlorate crystals are pure and free of nitrate or other oxygen-bearing impurities. Achieving the highest purity of the recovered perchlorates is essential, because any other oxygen-bearing compounds in the final precipitates could mask the oxygen isotope analysis during the thermal decomposition method outlined below. Preventing nitrate contamination is especially important because the Atacama nitrate is known to have a large $\Delta^{17}O$ value (*24*).

Measurement of Both $\delta^{18}O$ and $\delta^{17}O$ Values for Perchlorate. Hoering et al. (*13*) was the first to try a thermal decomposition method to generate O_2 to measure the $\delta^{18}O$ for chlorate and perchlorate salts. They used isotopically labeled water to study the oxygen exchange kinetics of various oxyanions of chlorine. Since O_2 is required for simultaneous measurement of $\delta^{18}O$ and $\delta^{17}O$ values, a thermal decomposition (pyrolysis) approach is thus adopted in our experiment. Approximately 1 mg of perchlorate crystals was preloaded and sealed in a silver capsule, which was subsequently loaded into a cone-shaped coil made of platinum wire (0.5 mm) in a vacuum flask. O_2 is generated when platinum wire is heated to a dark-red color by adjusting electric current. The generated gases were passed through 2 to 3 liquid-N_2 traps, and O_2 was collected in a sieved sample tube submerged in liquid N_2. O_2 was analyzed directly on a Finnigan MAT 253 using a dual-inlet interface. For duplicate samples that went through the same pyrolysis procedure, the difference in $\delta^{18}O$ was found to be less than 1.0‰. A larger error would result if the yield was low. The duplicate $\Delta^{17}O$ values were found to be consistent within 0.1‰. This small deviation of $\Delta^{17}O$ values is due to the covariation of $\delta^{18}O$ and $\delta^{17}O$ values during the analytical procedures. Similarly, the effect of lower yield only affects the $\delta^{18}O$ and $\delta^{17}O$ value but not the $\Delta^{17}O$ value. All reported oxygen isotope compositions are calibrated against V−SMOW, the international standard for oxygen isotope composition.

Results and Discussion

Man-made perchlorate from various sources was analyzed, including reagent perchlorate obtained from Allied Chemi-

TABLE 1. Multiple Oxygen Isotope Compositions of Perchlorate from Various Man-Made and Natural Sources[a]

sample	$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$	yield	$[NO_3^-]$ content
		Man-Made Perchlorate			
$KClO_4$ (Allied Chemicals)	−19.9	−10.5	−0.06	85%	not measured
$KClO_4$ (Aldrich)	−17.8	−9.5	−0.12	88%	not measured
$NaClO_4$ (EM-Science)	−17.3	−9.1	−0.06	84%	not measured
$NaClO_4$ (Fisher Scientific)	−19.5	−10.4	−0.20	85%	not measured
$AgClO_4$ (Aldrich)	−17.3	−9.1	−0.10	81%	not measured
		Atacama Perchlorate			
AT24-1-$CsClO_4$	−4.6	7.2	9.6	97%	0.02%
AT74-1-$CsClO_4$	−4.5	7.2	9.6	100%	not measured
AT75-1-$KClO_4$	−24.8	−8.7	4.2	102%	0.01%
$CsClO_4$ (Hoffman Nitrate)	−9.0	4.1	8.8	87%	0.00%

[a] The nitrate content of the extracted natural perchlorate crystals was measured by ion chromatography.

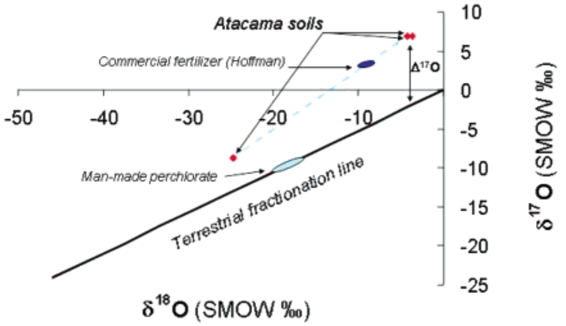

FIGURE 2. A $\delta^{18}O-\delta^{17}O$ plot for perchlorate from various man-made or natural sources including five reagent perchlorate salts, three different soils from the Central Depression of the central Atacama Desert, and a commercial nitrate fertilizer derived from Chilean salt deposits. Terrestrial fractionation line follows the mass-dependent fractionation relationship $\delta^{17}O = 0.52 \times \delta^{18}O$. The $\Delta^{17}O$ is the measure of the vertical deviation from this line (see text for detail).

cals, EM-Science, Aldrich, and Fisher Scientific, showing a narrow range of $\delta^{18}O$ value (from −17.3 to −19.9‰), with an average value of −18.4 ± 1.2‰. No ^{17}O anomaly was found for any of the man-made perchlorate ($\Delta^{17}O = -0.10 \pm 0.06$‰) (Table 1). However, perchlorates extracted from three different Atacama soils have $\delta^{18}O$ values ranging from −4.5‰ to −24.8‰ and $\Delta^{17}O$ values ranging from +9.6‰ to +4.2‰, respectively. Perchlorate extracted from a commercial fertilizer (Hoffman Nitrate) that is derived from the Atacama salt deposit (*10*) also possesses a positive $\Delta^{17}O$ value (+8.8‰). Interestingly, all four Atacama perchlorate data fall in a linear array in a $\delta^{18}O-\delta^{17}O$ diagram (dashed line in Figure 2).

These results appear to confirm an early speculation that the oxidation of volatile chlorine by O_3 and the formation of perchlorate could be a sink for atmospheric chlorine (*8*). The atmospheric chlorine budget is well characterized at this time, with dominate inputs from the ocean and biomass burning (*25*). In the troposphere, these reactive chlorine compounds are broken down by direct photolysis or by reacting with oxidants. A small amount of reactive Cl gets into the stratosphere and is involved in the ClO_x cycle, which can cause significant destruction of stratospheric O_3 through effective chain reactions (*26*). The predominant sink for the atmospheric chlorine is believed to be HCl. Simonaitis and Heicklen (*8*), however, speculated that the formation of $HClO_4$ could potentially be a sink for stratospheric Cl. This process may occur via the following reactions.

$$Cl + O_2 + O_3 \rightarrow ClO_3 + O_2 \qquad (6)$$

$$ClO_3 + OH \rightarrow HClO_4 \qquad (7)$$

Recently, small amounts of perchlorate were observed in sulfate aerosols in the stratosphere (*27*). Our measured ^{17}O anomalies for the Atacama perchlorate confirms that, albeit a minor sink, perchlorate formation via the O_3 oxidation of reactive chlorine deserves attention, especially in places such as the coast of northern Chile where the oceanic CH_3Cl emissions may be particularly high.

Detailed atmospheric reaction pathways or mechanisms that produce the Atacama perchlorate are not yet clear although the formation pathways ought to be constrained by the measured $\delta^{18}O$ and $\Delta^{17}O$ data. Three sources of oxygen atoms may contribute to the final atmospheric perchlorate: water (or OH radical), air O_2, and O_3. The measured $\delta^{18}O$ values (~ −18.4‰) for man-made perchlorates suggest that the $\delta^{18}O$ of perchlorate is roughly ~10‰ lighter than that of the water (assuming it is meteoric water) from which it formed via electrolysis. We also know that atmospheric O_2 has a well-defined $\delta^{18}O$ value at ~23.5‰ (*28*) and that O_3 has a less well-defined $\delta^{18}O$ value at ~100‰ (*16*, *17*). Another piece of information is the $\Delta^{17}O$ values for Atacama perchlorate (ranging from +4.2 to +9.6‰). Since atmospheric O_3 has a $\Delta^{17}O$ value ranging from 30‰ and 40‰ (*17*, *29*), we conclude that up to one O_3 atom is incorporated in the product perchlorate during the formation processes. With these constraints, we discuss three possible models for the formation of atmospheric perchlorate. As an approximation, temperature or kinetic isotope effect is not taken into consideration in the discussion.

Model 1: Jaegle et al. (*30*) argue that the pathway (eq 7) (*8*) is insignificant for perchlorate observed in mid-latitudes since the ClO_3 is formed either by the photolysis of Cl_2O_3 or from OClO + O, both of which require OClO that is only present in the polar spring time (*30*). Our $\Delta^{17}O$ data allow for no more than one of the O atoms in the final perchlorate to come from O_3. Since ClO_3 does not obtain O from water or HO_x (eq 6), a single OH would have to account for the negative $\delta^{18}O$ values for perchlorate. We estimate that the $\delta^{18}O$ for the involved OH would have to be as low as ~ −165‰ if eq 7 is the formation pathway (i.e., one O atom from O_3, two O atoms from O_2, and one O atom from OH). Interestingly, spectroscopic measurements and transport models suggest that −165‰ may well be within the range of $\delta^{18}O$ value for stratospheric water vapor (*31*−*33*).

Model 2: Prasad and Lee (*34*) proposed that perchlorate could form through the following reaction

$$ClO{\cdot}O_3 + HO_2 \rightarrow HClO_4 + O_2 \qquad (8)$$

where $ClO{\cdot}O_2$ is formed by reactions between $ClO{\cdot}O_2$ and O_3. However, the existence of $ClO{\cdot}O_2$ or $ClO{\cdot}O_3$ has yet to be confirmed. On the other hand, if ClO has already inherited an O_3 signature (which is likely), the final perchlorate would have at least two O atoms derived from O_3 and a $\Delta^{17}O$ value at least as high as ~18‰. This proposed pathway is apparently not supported by our $\Delta^{17}O$ data.

Model 3: Perchlorate is formed by heterogeneous reactions on the surface of sulfuric acid aerosol (*30*, *35*):

$$\mathrm{ClO\ (on\ H_2SO_4\ aerosol)} \rightarrow \mathrm{HClO_4} + \mathrm{products} \qquad (9)$$

This reaction path is poorly understood at this time and was suggested to be "an interesting possibility to consider under volcanic aerosol conditions" (*30*). Since no detailed pathway was given, our oxygen isotope data do not rule out this possibility.

Another intriguing observation is the variable $\Delta^{17}O$ values and a rather linear array on a $\delta^{18}O$-$\delta^{17}O$ diagram for our Atacama perchlorate data (Figure 2). It suggests that there was probably a mixing of different natural perchlorate end-members or there were unknown postformational alteration processes. Further investigation on this trend may reveal additional information on the reaction mechanisms associated with atmospheric perchlorate.

Results of this study have important implications in the identification or forensics of perchlorate contamination in the environment. Our data clearly indicate that unique oxygen isotope signatures exist, which differ between man-made and natural perchlorates. Accordingly, measurements of both $\delta^{18}O$ and $\delta^{17}O$ values could be used to distinguish the origin of perchlorate. In particular, the ^{17}O anomaly could provide unambiguously the presence of natural (as opposed to man-made) perchlorate in soil and groundwater because man-made perchlorate has no ^{17}O anomaly. However, as demonstrated by our data, man-made and natural perchlorates overlap in their $\delta^{18}O$ values. Thus, using $\delta^{18}O$ value as a tool to distinguish man-made perchlorate from atmospheric perchlorate will not be as effective as the $\Delta^{17}O$ parameter. Chemical reactions and biodegradation of perchlorate are mass-dependent processes and may change values of both $\delta^{18}O$ and $\delta^{17}O$. However, the $\Delta^{17}O$ of the original perchlorate will remain unchanged. In other words, only the addition of perchlorate with a different $\Delta^{17}O$ signal may change the $\Delta^{17}O$ value of perchlorate in a reservoir.

The $\delta^{18}O$ and $\delta^{17}O$ isotope compositions could also be used as an independent measure of the microbial degradation of perchlorate in soil and groundwater and therefore the effectiveness of bioremediation. Currently, biological treatment is one of the most actively pursued technologies being used to remove perchlorate from contaminated water or soil. Many bacteria are capable of dissimilatory perchlorate reduction anaerobically to produce final products of chloride (Cl^-) and O_2 (*36*, *37*). During this process, perchlorate anions of lighter isotopomers (e.g., containing ^{16}O or ^{35}Cl) will be preferentially reduced than those of heavier isotopomers (e.g., containing ^{17}O, ^{18}O, or ^{37}Cl). Recently, chlorine stable isotope composition ($^{37}Cl/^{35}Cl$) has been measured and shown large variations during microbial perchlorate reduction processes (*38*−*40*). A large kinetic isotope fractionation would indicate a biodegradation process, in contrast to a nonbiological loss process such as ion exchange. It is anticipated that a corresponding kinetic fractionation (but in a reduced magnitude) for oxygen isotopes will also be observed.

Acknowledgments

We thank the technical assistance of Margarita Khachaturyan, Kathryn Jenkins at LSU, and Yee-Kyoung Ku at ORNL. Financial support is provided by LSU Faculty Research Grant and ORNL Laboratory Directed Research and Development Fund. ORNL is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725.

Literature Cited

(1) Urbansky, E. T. Perchlorate chemistry: implications for analysis and remediation. *Bioremediation J.* **1998**, *2*, 81−95.

(2) Damian, P.; Pontius, F. W. From rockets to remediation: the perchlorate problem. *Environ. Protect.* **1999**, June issue, 24−31.

(3) Gu, B.; Brown, G. M.; Alexandratos, S. D.; Ober, R.; Dale, J. A.; Plant, S. Efficient treatment of perchlorate (ClO_4^-)-contaminated groundwater with bifunctional anion-exchange resins. *Environ. Sci. Res.* **2000**, *57*, 165−176.

(4) *Perchlorates-their properties, manufacture and uses*; Schumacher, J. C., Ed.; Reinhold Publishing Corporation: New York, 1960.

(5) Ericksen, G. E. Geology and origin of the Chilean nitrate deposits. U.S. Geological Survey Professional Paper P 1188, 1981.

(6) Ericksen, G. E. The Chilean nitrate deposits. *Am. Sci.* **1983**, *71*, 366−374.

(7) Ericksen, G. E.; Hosterman, J. W.; St. Amand, P. Chemistry, mineralogy and origin of the clay-hill nitrate deposits, Amargosa River valley, Death Valley region, California, U.S.A. *Chem. Geol.* **1988**, *67*, 85−102.

(8) Simonaitis, R.; Heicklen, J. Perchloric acid. Possible sink for stratospheric chlorine. *Planet Space Sci.* **1975**, *23*, 1567−1569.

(9) Hunter, W. J. Perchlorate is not a common contaminant of fertilizers. *J. Agron. Crop Sci.* **2001**, *187*, 203−206.

(10) Urbansky, E. T.; Brown, S. K.; Magnuson, M. L.; Kelty, C. A. Perchlorate levels in samples of sodium nitrate fertilizer derived from Chilean caliche. *Environ. Pollut.* **2001**, *112*, 299−302.

(11) Williams, T. L.; Martin, R. B.; Collette, T. W. Raman spectroscopic analysis of fertilizers and plant tissue for perchlorate. *Appl. Spectrosc.* **2001**, *55*, 967−983.

(12) Orris, G. J.; Harvey, G. J.; Tsui, D. T.; Eldrige, J. E. Preliminary Analysis for Perchlorate in Selected Natural Materials and Their Derivative Products. *USGS Open-File Report 03-314* 2003.

(13) Hoering, T. C.; Ishimori, F. T.; McDonald, H. O. Oxygen exchange between oxy-anions and water. II. Chlorite, chlorate, and perchlorate ions. *J. Am. Chem. Soc.* **1958**, *80*, 3876.

(14) Young, E. D.; Galy, A.; Nagahara, H. Kinetic and equilibrium mass-dependent isotope fractionation laws in nature and their geochemical and cosmochemical significance. *Geochim. Cosmochim. Acta* **2002**, *66*, 1095−1104.

(15) Miller, M. F. Isotopic fractionation and the quantification of O-17 anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. *Geochim. Cosmochim. Acta* **2002**, *66*, 1881−1889.

(16) Johnston, J. C.; Thiemens, M. H. The isotopic composition of tropospheric ozone in three environments. *J. Geophys. Res. [Atmos.]* **1997**, *102*, 25395−25404.

(17) Johnson, D. G.; Jucks, K. W.; Traub, W. A.; Chance, K. V. Isotopic composition of stratospheric ozone. *J. Geophys. Res. [Atmos.]* **2000**, *105*, 9025−9031.

(18) Gao, Y. Q.; Marcus, R. A. Strange and unconventional isotope effects in ozone formation. *Science* **2001**, *293*, 259−263.

(19) Savarino, J.; Lee, C. C. W.; Thiemens, M. H. Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth. *J. Geophys. Res. [Atmos.]* **2000**, *105*, 29079−29088.

(20) Bao, H.; Thiemens, M. H.; Farquhar, J.; Campbell, D. A.; Lee, C. C. W.; Heine, K.; Loope, D. B. Anomalous ^{17}O compositions in massive sulphate deposits on the Earth. *Nature* **2000**, *406*, 176−178.

(21) Grotheer, M. P.; Cook, E. H. Mechanism of electrolytic perchlorate production. *Electrochem. Technol.* **1968**, *6*, 221−224.

(22) Mikhailov, I. S. Exogenesis and soil formation in the Atacama region. *Eurasian Soil Sci.* **2000**, *33*, 1255−1262.

(23) Gu, B. H.; Brown, G. M.; Maya, L.; Lance, M. J.; Moyer, B. A. A. Regeneration of perchlorate (ClO_4^-)-loaded anion-exchange resins by a novel tetrachloroferrate ($FeCl_4^-$) displacement technique. *Environ. Sci. Technol.* **2001**, *35*, 3363−3368.

(24) Boehlke, J. K.; Mroczkowski, S. J.; Coplen, T. B. Oxygen isotopes in nitrate: New reference materials for 18O:17O:16O measurements and observations on nitrate-water equilibration. *Rapid Commun. Mass Spectrom.* **2003**, *17*, 1835−1846.

(25) Keene, W. C.; Khalil, M. A. K.; Erickson, D. J.; McCulloch, A.; Graedel, T. E.; Lobert, J. M.; Aucott, M. L.; Gong, S. L.; Harper, D. B.; Kleiman, G.; Midgley, P.; Moore, R. M.; Seuzaret, C.; Sturges, W. T.; Benkovitz, C. M.; Koropalov, V.; Barrie, L. A.; Li, Y. F. Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory. *J. Geophys. Res. [Atmos.]* **1999**, *104*, 8429−8440.

(26) Molina, M. J.; Rowland, F. S. Stratospheric sink for chlorofluoromethanes. Chlorine atom-catalyzed destruction of ozone. *Nature* **1974**, *249*, 810−812.

(27) Murphy, D. M.; Thomson, D. S. Halogen ions and NO+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere. *Geophys. Res. Lett.* **2000**, *27*, 3217−3220.

(28) Bender, M.; Sowers, T.; Labeyrie, L. The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core. *Global Biogeochem. Cycles* **1994**, *8*, 363−376.

(29) Lyons, J. R. Transfer of mass-independent fractionation in ozone to other oxygen-containing radicals in the atmosphere. *Geophys. Res. Lett.* **2001**, *28*, 3231−3234.

(30) Jaegle, L.; Yung, Y. L.; Toon, G. C.; Sen, B.; Blavier, J. F. Balloon observations of organic and inorganic chlorine in the stratosphere: The role of HClO4 production on sulfate aerosols. *Geophys. Res. Lett.* **1996**, *23*, 1749−1752.

(31) Johnson, D. G.; Jucks, K. W.; Traub, W. A.; Chance, K. V. Isotopic composition of stratospheric water vapor: Implications for transport. *J. Geophys. Res. [Atmos.]* **2001**, *106*, 12219−12226.

(32) Webster, C. R.; Heymsfield, A. J. Water isotope ratios D/H, $^{18}O/^{16}O$, $^{17}O/^{16}O$ in and out of clouds map dehydration pathways. *Science* **2003**, *302*, 1742−1746.

(33) Rinsland, C. P.; Gunson, M. R.; Foster, J. C.; Toth, R. A.; Farmer, C. B.; Zander, R. Stratospheric Profiles of Heavy-Water Vapor Isotopes and Ch3d from Analysis of the Atmos Spacelab-3 Infrared Solar Spectra. *J. Geophys. Res. [Atmos.]* **1991**, *96*, 1057−1068.

(34) Prasad, S. S.; Lee, T. J. Atmospheric Chemistry of the Reaction $ClO+O_2$ - - $ClO.O_2$ − Where It Stands, What Needs to Be Done, and Why. *J. Geophys. Res. [Atmos.]* **1994**, *99*, 8225−8230.

(35) Martin, L. R.; Wren, A. G.; Wun, M. Chlorine atom and chlorine oxide (ClO) wall reaction products. *Int. J. Chem. Kinet.* **1979**, *11*, 543−557.

(36) Coates, J. D.; Michaelidou, U.; Bruce, R. A.; O'Connor, S. M.; Crespi, J. N.; Achenbach, L. A. Ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. *Appl. Environ. Microbiol.* **1999**, *65*, 5234−5241.

(37) Coates, J. D.; Michaelidou, U.; O'Connor, S. M.; Bruce, R. A.; Achenbach, L. A. The diverse microbiology of (per)chlorate reduction. *Environ. Sci. Res.* **2000**, *57*, 257−270.

(38) Ader, M.; Coleman, M. L.; Doyle, S. P.; Stroud, M.; Wakelin, D. Methods for the stable isotopic analysis of chlorine in chlorate and perchlorate compounds. *Anal. Chem.* **2001**, *73*, 4946−4950.

(39) Coleman, M. L.; Ader, M.; Chaudhuri, S.; Coates, J. D. Microbial isotopic fractionation of perchlorate chlorine. *Appl. Environ. Microbiol.* **2003**, *69*, 4997−5000.

(40) Sturchio, N. C.; Hatzinger, P. B.; Arkins, M. D.; Suh, C.; Heraty, L. J. Chlorine Isotope Fractionation during Microbial Reduction of Perchlorate. *Environ. Sci. Technol.* **2003**, *37*, 3859−3863.

Received for review March 30, 2004. Revised manuscript received July 7, 2004. Accepted July 19, 2004.

ES049516Z