Natural Perchlorate Has a Unique Oxygen Isotope Signature

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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 $-18.4 \pm 1.2\%$ whereas natural perchlorate has a variable $\delta^{18}$O value, ranging from $-4.5\%$ to $-24.8\%$. The $\delta^{17}$O and $\delta^{18}$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 ($\text{ClO}_4^-$) 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 Simonsen 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

$$\delta^{18}O = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000\%$$  \hspace{1cm} (1)

or

$$\delta^{17}O = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000\%$$  \hspace{1cm} (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,

$$\delta^{17}O \approx 0.52 \times \delta^{18}O$$  \hspace{1cm} (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

$$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$$  \hspace{1cm} (4)

or in a logarithmic format (15)

$$\Delta^{17}O = \delta^{17}O - 1000 \times \left[ (1 + \delta^{18}O/1000)^{0.52} - 1 \right]$$  \hspace{1cm} (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

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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 $\text{SO}_3^{2-}$ by atmospheric $\text{O}_3$ is a mass-dependent chemical reaction. But the reaction results in the transfer of $\text{SO}_4^{2-}$ (19), a phenomenon being widely recognized in nature (20).

If perchlorate of atmospheric origin involves $\text{O}_3$, 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 perchlorate 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 on any exchange. The $\Delta^{17}$O anomaly 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 $\text{O}_3$ 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 $[\text{ClO}_4^-]$ range from 0 to ~250 ppm, and there is no correlation between $[\text{NO}_3^-]$ or $[\text{Cl}^-]$ with $[\text{ClO}_4^-]$ 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% $\text{SO}_4^{2-}$, 6.2% $\text{Cl}^-$, and 5.0% $\text{NO}_3^-$, 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.

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 $\text{O}_3$ 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 $\text{O}_3$ 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. $\text{O}_3$ 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 $\text{O}_3$ was collected in a sieved sample tube submerged in liquid N$_2$. $\text{O}_3$ 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 $\Delta^{18}$O values were found to be consistent within 0.1%. This small deviation of $\Delta^{18}$O values is due to the covariation of $\Delta^{17}$O and $\Delta^{18}$O values during the analytical procedures. Similarly, the effect of lower yield only affects the $\Delta^{17}$O and $\Delta^{18}$O value but not the $\Delta^{18}$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-
Recently, small amounts of perchlorate were observed in sulfate aerosols in the stratosphere (27). Our measured $\Delta^{17}O$ 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$_3$Cl 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 ($\sim-18.4\%$) for man-made perchlorates suggest that the $\Delta^{17}O$ of perchlorate is roughly $\sim10\%$ lighter than that of the water (assuming it is meteoric water) from which it formed via electrolysis. We also know that atmospheric O$_3$ has a well-defined $\Delta^{18}O$ value at $-23.5\%$ (28) and that O$_3$ has a less well-defined $\Delta^{17}O$ value at $\sim100\%$ (16, 17). Another piece of information is the $\Delta^{13}O$ values for Atacama perchlorate (ranging from +4.2 to +9.6%). Since atmospheric O$_3$ has a $\Delta^{13}O$ value ranging from 30% and 40% (17, 29), we conclude that up to one O 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 4) is insignificant for perchlorate observed in mid-latitudes since the ClO$_3$ is formed either by the photolysis of ClO$_2$ or from OCIO + O, both of which require OCIO that is only present in the polar springtime (30). Our $\Delta^{13}O$ 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$_2$ (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 $\sim-165\%$ 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.

$$\text{ClO}_3 + \text{HO}_2 \rightarrow \text{HClO}_4 + \text{O}_2$$

where ClO$_3$-O$_3$ is formed by reactions between ClO$_2$ and O$_3$. However, the existence of ClO$_3$-O$_2$ or ClO$_2$-O$_3$ has yet to be confirmed. On the other hand, if ClO has already inherited an O$_2$ signature (which is likely), the final perchlorate would have at least two O atoms derived from O$_3$ and a $\Delta^{13}O$ value...
at least as high as \( \sim 18\% \). 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):

\[ \text{ClO} (\text{on } \text{H}_2\text{SO}_4 \text{ aerosol}) \rightarrow \text{HClO} + \text{products} \]  

(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 \( \Delta^{18} \)O values and a rather linear array on a \( \Delta^{17} \)O\( - \)\( \Delta^{18} \)O diagram for our Atacama perchlorate data (Figure 2). It suggests that there was probably a mixing of different natural perchlorate endmembers 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 \( \delta^{17} \)O and \( \delta^{18} \)O values could be used to distinguish the origin of perchlorate. In particular, the \( \delta^{18} \)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 \( \delta^{18} \)O anomaly. However, as demonstrated by our data, man-made and natural perchlorates overlap in their \( \delta^{17} \)O values. Thus, using \( \delta^{17} \)O value as a tool to distinguish man-made perchlorate from atmospheric perchlorate will not be as effective as the \( \Delta^{18} \)O parameter. Chemical reactions and biodegradation of perchlorate are mass-dependent processes and may change values of both \( \delta^{17} \)O and \( \delta^{18} \)O. However, the \( \Delta^{18} \)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 \( \Delta^{18} \)O value of perchlorate in a reservoir.

The \( \delta^{17} \)O and \( \delta^{18} \)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 16O or 32Cl) will be preferentially reduced than those of heavier isotopomers (e.g., containing 18O or 35Cl). Recently, chlorine stable isotope composition (\( \delta^{35} \)Cl/\( \delta^{37} \)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.

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