

Correspondence

Perchlorate Isotope Forensics

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Perchlorate has been detected recently in a variety of soils, waters, plants, and food products at levels that may be detrimental to human health. These discoveries have generated considerable interest in perchlorate source identification. In this study, comprehensive stable isotope analyses (³⁷Cl/³⁵Cl and ¹⁸O/¹⁷O/¹⁶O) of perchlorate from known synthetic and natural sources reveal systematic differences in isotopic characteristics that are related to the formation mechanisms. In addition, isotopic analyses of perchlorate extracted from groundwater and surface water demonstrate the feasibility of identifying perchlorate sources in contaminated environments on the basis of this technique. Both natural and synthetic sources of perchlorate have been identified in water samples from some perchlorate occurrences in the United States by the isotopic method.

Perchlorate (ClO₄⁻) has been detected recently in groundwater, surface water, soils, plants, and food products at concentrations exceeding microgram-per-liter levels in many areas of the United States.^{1–5} Because of the potential for small amounts of perchlorate to affect thyroid function by interfering with iodide uptake,⁶ its widespread distribution in the environment has generated considerable interest in techniques to distinguish natural and syn-

thetic perchlorate sources.^{7,8} Synthetic (manufactured) perchlorate is an important constituent of explosives, rocket propellants, roadside flares, fireworks, matches, automobile airbags, and a variety of other military and commercial products. The manufacture, use, or disposal of these products is thought to be responsible for many local occurrences of perchlorate contamination in the environment.⁹ However, perchlorate also has been detected in precipitation at sub-microgram-per-liter levels,¹⁰ it has been reported in some natural potassium-rich salt deposits,¹¹ and it is a well-known natural constituent of the nitrate-rich salt deposits in the Atacama Desert of Chile.¹² Imported Chilean nitrate (mainly NaNO₃) was used extensively as nitrogen fertilizer for agriculture during the early 1900s, and it is still imported to the U.S. for use on cotton, tobacco, citrus, and some vegetable crops.¹³ Concentrations of perchlorate in Chilean nitrate fertilizer are reported to range from ~1 to 8 g/kg, with concentrations near the low end of that range being more common in recent years.^{13,14} A metric ton of imported material could yield as much as 40 to 340 million gallons of water with 6 μg/L of perchlorate, which is the current California Public Health Goal for perchlorate in drinking water.¹⁵ More than 477 000 metric tons of Chilean nitrate fertilizer were used in California between 1923 and 1998.¹⁶

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On the basis of these observations, perchlorate may be present in the environment from various combinations of (a) artificial production and artificial distribution (e.g., military and commercial uses), (b) natural production and artificial distribution (e.g., application of imported Chilean nitrate fertilizer), or (c) natural production and natural distribution (e.g., local atmospheric deposition concentrated by evapotranspiration). Understanding the relative importance and distribution of these different sources is important for evaluating exposure risks, determining liability, and optimizing perchlorate remediation efforts. In this paper, we show that some of the different perchlorate sources can be distinguished by comprehensive stable isotopic analyses of chlorine ($^{37}\text{Cl}/^{35}\text{Cl}$) and oxygen ($^{18}\text{O}/^{17}\text{O}/^{16}\text{O}$), and we demonstrate the application of this technology for environmental perchlorate isotope forensics in representative water samples with different perchlorate sources.

EXPERIMENTAL SECTION

The isotope ratios of Cl and O are expressed as deviations from reference values:

$$\delta^{37}\text{Cl} = [({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{sample}}/({}^{37}\text{Cl}/{}^{35}\text{Cl})_{\text{reference}} - 1] \quad (1)$$

$$\delta^{18}\text{O} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{reference}} - 1] \quad (2)$$

$$\delta^{17}\text{O} = [({}^{17}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{17}\text{O}/{}^{16}\text{O})_{\text{reference}} - 1] \quad (3)$$

Variations in $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ caused by most physical–chemical processes on Earth are related systematically by the relative differences in the isotopic masses,

$$(1 + \delta^{17}\text{O}) = (1 + \delta^{18}\text{O})^\lambda \quad (4)$$

with $\lambda \approx 0.51$ – 0.53 ; however, deviations from mass-dependent variation may be large in some materials, including atmospheric ClO_4^- and NO_3^- . Major departures from mass-dependent O-isotope variation in this paper are described by¹⁷

$$\Delta^{17}\text{O} = [(1 + \delta^{17}\text{O})/(1 + \delta^{18}\text{O})^{0.525}] - 1 \quad (5)$$

Values of $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ are reported in parts per thousand (‰).

Purified ClO_4^- salts of Na, K, Rb, and Cs were prepared for isotopic analysis by conversion to CO, O₂, and CH₃Cl, as described below. The ClO_4^- was extracted from mixed salt solutions in the laboratory and in the field by using highly selective bifunctional anion-exchange resin columns.¹⁸ Groundwater samples were collected from existing wells using submersible pumps. The water was passed through glass columns containing ion-exchange resin (Purolite A530E) at flow rates ranging from 0.3 to 0.9 L/min until at least 10 mg of ClO_4^- was collected. Columns from the field were placed on ice and shipped to the laboratory for extraction and purification of the ClO_4^- . The ClO_4^- was eluted from ion exchange columns with a solution of FeCl₃ and HCl, then precipitated by addition of KCl, RbCl, or CsCl to form KClO₄,

RbClO₄, or CsClO₄,^{19,20} which was purified by gentle rinsing with H₂O. The purity of the salts was verified by micro-Raman spectroscopy or by ion chromatography (>99% ClO_4^-). Tests of the ion exchange extraction and purification procedures using reagents with known isotopic compositions indicated that no measurable isotope fractionation was associated with the procedures used to produce the ClO_4^- salts. These tests included isotopic analyses of ClO_4^- reagent before and after being dissolved, extracted, precipitated, and purified.

For $\delta^{18}\text{O}$ determinations, ClO_4^- salts were reacted with glassy C at 1325 °C to produce CO, which was transferred in a He carrier through a molecular-sieve gas chromatograph to a Finnigan Delta Plus XP isotope-ratio mass spectrometer and analyzed in continuous-flow mode by monitoring peaks at m/z 28 and 30.²¹ Values of $\delta^{18}\text{O}$ are given with respect to Vienna Standard Mean Ocean Water ($\delta^{18}\text{O}_{\text{VSMOW}} \equiv 0.0\text{‰}$), and they were normalized with respect to VSMOW and SLAP by analyzing reference materials NBS-127 sulfate ($\delta^{18}\text{O} = +8.6\text{‰}$), IAEA-N3 nitrate ($\delta^{18}\text{O} = +25.6\text{‰}$), and USGS34 nitrate ($\delta^{18}\text{O} = -27.9\text{‰}$).²¹ Yields of O (as CO) from the ClO_4^- and NO_3^- reagents and samples typically were within $\pm 2\%$. Average reproducibilities of normalized $\delta^{18}\text{O}$ values were approximately $\pm 0.2\text{‰}$ (1σ).

For $\Delta^{17}\text{O}$ determinations, ClO_4^- salts were decomposed at 650 °C in evacuated quartz glass tubes to produce O₂, which was expanded into a liquid N₂ trap under vacuum and then admitted to a Finnigan Delta Plus XP isotope-ratio mass spectrometer and analyzed in dual-inlet mode by measurements at m/z 32, 33, and 34. Yields of O (as O₂) from ClO_4^- reagents and samples typically were within $\pm 5\%$. A representative KClO₄ reagent designated USGS37 was assumed to have a $\Delta^{17}\text{O}$ value of 0.00‰, and the values for other samples were calculated from $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ measurements relative to USGS37 by using eq 5. This procedure yielded an average $\Delta^{17}\text{O}$ value of $0.00 \pm 0.06\text{‰}$ for all analyzed ClO_4^- reagents, consistent with derivation of the O from H₂O during ClO_4^- synthesis, and it yielded an average $\Delta^{17}\text{O}$ value of $-0.45 \pm 0.09\text{‰}$ for tank O₂ from air.²² Average reproducibilities of normalized $\Delta^{17}\text{O}$ values were approximately $\pm 0.1\text{‰}$ (1σ).

For $\delta^{37}\text{Cl}$ determinations, ClO_4^- salts were decomposed at 650 °C in evacuated borosilicate glass tubes to produce Cl⁻ salts, which were dissolved, converted to AgCl, and reacted with CH₃I to produce CH₃Cl.²³ The CH₃Cl was purified cryogenically (or by gas chromatography) and then admitted to a Finnigan Delta Plus isotope-ratio mass spectrometer and analyzed in dual-inlet mode (or in continuous-flow mode using He carrier gas) by measurements at m/z 50 and 52. Derived values of $\delta^{37}\text{Cl}$ were calibrated against Standard Mean Ocean Chloride ($\delta^{37}\text{Cl}_{\text{SMOC}} \equiv 0.0\text{‰}$).²⁴ Average reproducibilities of $\delta^{37}\text{Cl}$ values were approximately $\pm 0.3\text{‰}$ (1σ).

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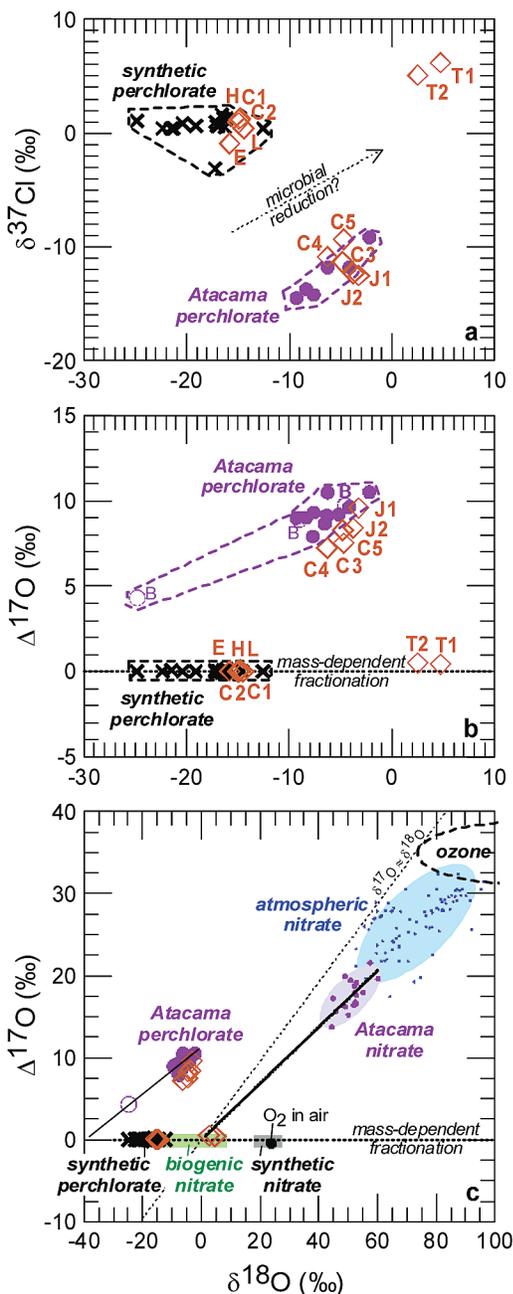


Figure 1. Cl and O isotope data for perchlorate (a, b, c) and nitrate (c). $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values are referenced to 0‰ for SMOC, VSMOW, and synthetic perchlorate, respectively (see text). Open circles (B) indicate additional perchlorate O-isotopic data from Bao and Gu.²⁰ Nitrate isotope data are from Michalski et al.²⁵ Labeled data points (diamonds) indicate a surface-water sample from Las Vegas Wash, Nevada (L); and groundwater samples from Edwards Air Force Base, California (E); Henderson, Nevada (H); southern California (C1–C5); northern New Jersey (J1, J2); and west Texas (T1, T2).

RESULTS AND DISCUSSION

Results of perchlorate isotopic analyses are summarized and compared with similar analyses of nitrate in Figure 1a–c. $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ are measures of mass-dependent fractionation of Cl and O isotopes by normal physical, chemical, or biological processes. $\Delta^{17}\text{O}$ is largely a measure of anomalous (“mass-independent”) O-isotope variation that may be attributed to photochemical oxidation reactions involving atmospheric ozone, which has an

unusually high concentration of ^{17}O ,^{20,25} although minor variations also occur as a result of other terrestrial fractionation processes.²⁶ The association between nitrate and perchlorate is potentially important because (1) both compounds are produced in the atmosphere, and both are abundant in the Atacama Desert salt deposits and derivative fertilizers; (2) both compounds are susceptible to microbial reduction in anaerobic conditions but tend to be persistent in aerobic conditions;^{3,27} and (3) groundwaters with elevated perchlorate concentrations commonly also contain nitrate, which can inhibit perchlorate reduction in some situations.^{10,28,29}

Synthetic Perchlorate. Synthetic perchlorate is produced by a series of electrolytic oxidation reactions beginning with aqueous chloride. The efficiency of this process is relatively high for the Cl component, but less than half of the water O is incorporated in the perchlorate. The measured $\delta^{37}\text{Cl}$ values of synthetic perchlorates range from -3.1 to $+1.6$ ‰, with an average of $+0.6 \pm 1.1$ ($n = 16$), similar to typical Cl source values (0 ± 2 ‰³⁰). These data indicate that there is some measurable product variability, but there is not large systematic isotopic fractionation during perchlorate synthesis. The $\delta^{18}\text{O}$ values of synthetic perchlorates range from -24.8 to -12.5 ‰ and are about 0–20‰ lower than expected values in water supplies near manufacturing plants. In one specific case, the $\delta^{18}\text{O}$ value of synthetic perchlorate was ~ 7 ‰ lower than that of the local water supply. These data indicate moderate amounts of O-isotopic fractionation during synthesis and are qualitatively consistent with the incomplete electrolytic conversion and incorporation of the water O. There is no measurable variation in the $\Delta^{17}\text{O}$ values of the synthetic perchlorates ($\Delta^{17}\text{O} = 0.00 \pm 0.06$, $n = 16$).

Natural Perchlorate. As noted previously, the best-known natural perchlorate occurrences are associated with nitrate ore deposits in the Atacama Desert of Chile. Nitrate and perchlorate in those deposits have positive $\Delta^{17}\text{O}$ values, indicating that they were produced largely by photochemical reactions involving atmospheric ozone and accumulated in the desert soils from atmospheric deposition over long periods of time.^{20,25} The $\delta^{37}\text{Cl}$ values of perchlorate extracted from Atacama nitrate ore and from Chilean nitrate fertilizer products range from -14.5 to -9.2 ‰. These are the lowest $\delta^{37}\text{Cl}$ values reported for any common substance on Earth³⁰ and indicate large Cl isotope fractionations associated with perchlorate formation in the atmosphere. The $\delta^{18}\text{O}$ values of the Atacama perchlorates analyzed in this study range from -9.3 to -2.2 ‰, and the $\Delta^{17}\text{O}$ values range from $+7.9$ to $+10.5$ ‰. Bao and Gu²⁰ report a positive correlation between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ that may indicate isotopic variation in the natural source(s) (Figure 1b). It is possible that there is a similar relation between $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$ (Figure 1a), although some mass-

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dependent fractionation also may be indicated. There is no evidence in the current study or previous studies^{20,25} for any systematic alteration of the isotopic characteristics of the Atacama nitrate or perchlorate during the mining and processing of the ore for sale as fertilizer. Although the isotopic characteristics of the Atacama perchlorate are thought to reflect atmospheric processes in its formation, it is not known if these characteristics are representative of atmospheric perchlorate in general.

Perchlorate Extracted from Environmental Water Samples.

Having established distinctive isotopic signatures for some of the major perchlorate sources, we tested the environmental forensic application of these data by analyzing perchlorate extracted from representative water samples. Perchlorate in groundwater near a solid-fuel rocket testing location at the North Base site at Edwards Air Force Base, California (site E, with $\text{ClO}_4^- \sim 400 \mu\text{g/L}$) and from two wells at another southern California site involved in rocket testing (sites C1, C2, with $\text{ClO}_4^- \sim 65, 100 \mu\text{g/L}$) have isotopic signatures similar to those of synthetic sources (Figure 1a,b). These data are consistent with the interpretation that the groundwaters in these areas were contaminated with electrochemically manufactured perchlorate and that the isotopic characteristics of the source were preserved during transport in the subsurface.

Similar results were obtained for groundwater collected at the discharge end of a perchlorate plume downgradient from former perchlorate production facilities at Henderson, Nevada (site H, with $\text{ClO}_4^- \sim 20\,000 \mu\text{g/L}$) and for nearby surface water from Las Vegas Wash (site L, with $\text{ClO}_4^- \sim 200 \mu\text{g/L}$), a stream draining the area including the Henderson site. These data are consistent with the interpretation that the groundwater and streamwater were contaminated by the same or similar synthetic perchlorate sources. Other data indicate that discharge from Las Vegas Wash is a major source of perchlorate in Lake Mead and the lower Colorado River.³¹ Because lower Colorado River water is distributed widely for irrigation, groundwater recharge, and other uses, the isotopic characteristics of the Las Vegas Wash perchlorate may be useful for identifying this source of contamination in distant water bodies or agricultural products that have been affected by imported river water.

In contrast to the above sites, where local synthetic sources of perchlorate can be identified, there also are numerous occurrences of perchlorate in groundwater that cannot be explained readily as a result of local introduction of synthetic material. Near the contaminated rocket-testing site represented by C1 and C2 in southern California, three other groundwater samples (sites C3, C4, C5, with $\text{ClO}_4^- \sim 12, 10, 5 \mu\text{g/L}$) have relatively low values of $\delta^{37}\text{Cl}$ ($-11.3, -10.9, -9.3\%$), relatively high values of $\delta^{18}\text{O}$ ($-4.8, -6.3, -4.7\%$), and large positive values of $\Delta^{17}\text{O}$ ($+8.3, +7.3, +7.5\%$) (Figure 1a,b). These isotopic characteristics are similar to those of the natural Atacama perchlorates and indicate that the perchlorate in groundwater samples C3, C4, and C5 was not produced electrochemically. The isotopic signature of these samples could be consistent with at least two hypotheses for the origin of the perchlorate in the groundwater: (1) the perchlorate is from Chilean nitrate fertilizers that were used in the recharge areas of the samples, or (2) the perchlorate is from natural atmospheric perchlorate deposition, isotopically similar to that of the Atacama Desert, that was concentrated locally by evapotrans-

piration. Similar isotopic results were obtained for two groundwater samples from northern New Jersey (sites J1, J2, with $\text{ClO}_4^- \sim 25, 90 \mu\text{g/L}$), where concentration of perchlorate from atmospheric deposition by evapotranspiration is considered less likely, owing to the humid climate, and a Chilean nitrate source from fertilizer use, therefore, is suspected.

A major perchlorate occurrence of unknown origin has been reported in groundwater from the southern High Plains in west Texas.³² Beneath an area of at least $155\,000 \text{ km}^2$, perchlorate is almost ubiquitous in groundwater, with concentrations ranging from <0.1 to $50 \mu\text{g/L}$ in samples from wells used for public, private, and agricultural water supply. Samples from monitoring wells installed to evaluate vertical distribution indicate that perchlorate concentrations are highest (to more than $200 \mu\text{g/L}$) near the water table and decrease downward. Atmospheric deposition has been proposed as a likely source of this perchlorate, although contributions from other sources, such as Chilean fertilizer and chlorate defoliants used in agriculture, or explosives used in seismic exploration for hydrocarbons, also may be present.^{10,32} Two perchlorate samples from this region (sites T1, T2, with $\text{ClO}_4^- \sim 140, 17 \mu\text{g/L}$) have small positive $\Delta^{17}\text{O}$ values ($+0.4, +0.5\%$), indicating that a minor atmospheric component may be present; however, positive values of $\delta^{18}\text{O}$ ($+4.7, +2.5\%$) and $\delta^{37}\text{Cl}$ ($+6.2, +5.1\%$) indicate that the samples either are dominated by a source that has not been isolated elsewhere or have been isotopically fractionated (Figure 1a,b). Given limited information about perchlorate isotopic fractionation during microbial reduction,^{23,33,34} the $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of the Texas samples could be consistent with a mixture dominated by synthetic perchlorate ($>90\%$), possibly with a minor fraction of atmospheric perchlorate ($<10\%$), that was reduced by about one-third of its original amount. Alternatively, the data may indicate another (nonatmospheric?) source of perchlorate¹⁰ with O-isotopic characteristics similar to those of biogenic nitrate (Figure 1c), which contains O atoms derived from H_2O and O_2 .

Potential Complicating Factors. The data summarized above indicate that stable isotope analyses are useful for distinguishing sources of perchlorate in groundwater and surface water, but there are several potential complicating factors that will require more work. For example, limited experimental results³⁵ and field data (e.g., persistence of positive $\Delta^{17}\text{O}$ for 10^5 to 10^7 years in the Atacama Desert) indicate that O isotopic exchange between perchlorate and water is slow and that the isotopic characteristics of the different sources will be preserved in groundwater and surface water for substantial periods of time. Ongoing experiments in the laboratory indicate that the rate of exchange between water and perchloric acid (30%) is less than $0.002/\text{yr}$ (J. K. Böhlke, unpublished data, 2005). Nevertheless, more sensitive tests under a variety of conditions will be needed to determine if there are any situations in which isotopic exchange may alter the source signatures. Furthermore, although perchlorate is relatively per-

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sistent in aerobic aqueous environments, it is subject to biodegradation (reduction) in anaerobic environments.^{3,27} Limited experimental data indicate that microbial reduction of perchlorate may cause $\delta^{18}\text{O}$ to increase about two times as fast as $\delta^{37}\text{Cl}$.^{23,33,34} If these fractionations are consistent and mass-dependent, they should not interfere with the distinction between the sources shown in Figure 1, but more studies are needed on the magnitudes of these effects. With respect to the measurements themselves, it is emphasized that there are no perchlorate isotopic reference materials being distributed for interlaboratory calibration at present. Reference materials with a range of Cl and O isotopic compositions will be useful for testing analytical procedures and normalizing data. Reliable isotope forensics also will require many more analyses of various perchlorate sources, including both natural and synthetic sources that may not be represented by the data in Figure 1.

CONCLUSIONS

This study demonstrates that comprehensive analyses of Cl and O isotopes can be used to distinguish between some of the major natural and synthetic sources of perchlorate. Current techniques for perchlorate extraction, purification, and isotope mass spectrometry permit the application of perchlorate isotope forensics to real environmental samples of groundwater and surface water. Using these techniques, both natural and synthetic isotope signatures have been identified in groundwater samples with perchlorate concentrations that are near the range of some proposed drinking water limits. Some of the groundwater per-

chlorate with natural isotopic characteristics apparently was introduced with imported Chilean natural nitrate fertilizer products, and some may represent local accumulation of atmospheric perchlorate. The veracity of this approach will increase with further analyses of more source materials (especially other natural occurrences) and further evaluation of potential complications from isotopic exchange or fractionation. Finally, although the focus of the current study is on the isotope data, it is emphasized that practical environmental perchlorate forensics will benefit greatly from additional characterization of field sites, for example, by combining the perchlorate isotope data with groundwater dating and other chemical and isotopic analyses.

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