

# Chlorine-36 as a Tracer of Perchlorate Origin

NEIL C. STURCHIO,<sup>\*,†</sup> MARC CAFFEE,<sup>‡</sup>  
 ABELARDO D. BELOSO, JR.,<sup>†</sup>  
 LINNEA J. HERATY,<sup>†</sup>  
 JOHN KARL BÖHLKE,<sup>§</sup>  
 PAUL B. HATZINGER,<sup>||</sup>  
 W. ANDREW JACKSON,<sup>⊥</sup> BAOHUA GU,<sup>#</sup>  
 JEFFREY M. HEIKOOP,<sup>∇</sup> AND  
 MICHAEL DALE<sup>○</sup>

University of Illinois at Chicago, Chicago, Illinois 60607,  
 PRIME Lab, Purdue University, West Lafayette, Indiana  
 47907, U.S. Geological Survey, Reston, Virginia 20192, Shaw  
 Environmental Inc., Lawrenceville, New Jersey 08648, Texas  
 Tech University, Lubbock, Texas 79409, Oak Ridge National  
 Laboratory, Oak Ridge, Tennessee 37831, Los Alamos National  
 Laboratory, Los Alamos, New Mexico 87545, and New Mexico  
 Environment Department, Los Alamos, New Mexico 87545

Received April 24, 2009. Revised manuscript received July  
 17, 2009. Accepted August 3, 2009.

Perchlorate ( $\text{ClO}_4^-$ ) is ubiquitous in the environment. It is produced naturally by atmospheric photochemical reactions, and also is synthesized in large quantities for military, aerospace, and industrial applications. Nitrate-enriched salt deposits of the Atacama Desert (Chile) contain high concentrations of natural  $\text{ClO}_4^-$ , and have been exported worldwide since the mid-1800s for use in agriculture. The widespread introduction of synthetic and agricultural  $\text{ClO}_4^-$  into the environment has contaminated numerous municipal water supplies. Stable isotope ratio measurements of Cl and O have been applied for discrimination of different  $\text{ClO}_4^-$  sources in the environment. This study explores the potential of  $^{36}\text{Cl}$  measurements for further improving the discrimination of  $\text{ClO}_4^-$  sources. Groundwater and desert soil samples from the southwestern United States (U.S.) contain  $\text{ClO}_4^-$  having high  $^{36}\text{Cl}$  abundances ( $^{36}\text{Cl}/\text{Cl} = 3100 \times 10^{-15}$  to  $28,800 \times 10^{-15}$ ), compared with those from the Atacama Desert ( $^{36}\text{Cl}/\text{Cl} = 0.9 \times 10^{-15}$  to  $590 \times 10^{-15}$ ) and synthetic  $\text{ClO}_4^-$  reagents and products ( $^{36}\text{Cl}/\text{Cl} = 0.0 \times 10^{-15}$  to  $40 \times 10^{-15}$ ). In conjunction with stable Cl and O isotope ratios,  $^{36}\text{Cl}$  data provide a clear distinction among three principal  $\text{ClO}_4^-$  source types in the environment of the southwestern U.S.

## Introduction

Perchlorate ( $\text{ClO}_4^-$ ) is ubiquitous in trace amounts in precipitation, fresh surface water, groundwater, and soils (1). Synthetic  $\text{ClO}_4^-$  salts are widely used as oxidants in

energetic materials such as propellants and explosives. Natural  $\text{ClO}_4^-$  is present in relatively high concentrations ( $\sim 0.2$  wt %) in natural nitrate-rich salt deposits from the Atacama Desert (Chile) that have been used worldwide in fertilizer production for well over a century (2). As a consequence of the widespread use of  $\text{ClO}_4^-$  in military, aerospace, and other industrial applications, the common application of large amounts of Chilean nitrate fertilizers in agricultural areas, and accumulation of indigenous natural  $\text{ClO}_4^-$  in arid regions (3–5), many groundwater supplies in the southwestern U.S. now have elevated concentrations of  $\text{ClO}_4^-$  in the ppb to ppm range. Perchlorate has been found in a variety of food products (6–9) and is ubiquitous in human urine and milk (10–13). The primary risk to human health from  $\text{ClO}_4^-$  ingestion comes from its inhibitory effect on iodine uptake and interference with thyroidal hormone production. A daily reference dose of 0.0007 mg/kg/day has been established (14, 15), and some states have set regulatory limits or action levels for drinking-water supplies ranging from 1 to 18  $\mu\text{g}/\text{L}$ . Although no federal regulation for  $\text{ClO}_4^-$  in drinking water currently exists, the U.S. Environmental Protection Agency recently issued an interim health advisory level of 15  $\mu\text{g}/\text{L}$  (16). Considerable uncertainty remains, however, about the sources, exposure pathways, and toxicity of  $\text{ClO}_4^-$  in humans (11, 17).

The recent development of methods for analyzing stable isotope ratios of Cl and O in  $\text{ClO}_4^-$  led to their application for distinguishing sources of  $\text{ClO}_4^-$  in the environment and for quantifying isotope effects caused by microbial reduction of  $\text{ClO}_4^-$  to  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  (18–22). Natural  $\text{ClO}_4^-$  from the Atacama Desert has excess  $^{17}\text{O}$ , indicating an atmospheric origin by photochemical reactions involving ozone (19); this finding is consistent with O isotope studies of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  from the Atacama Desert indicating atmospheric sources for those compounds as well (23, 24). Synthetic  $\text{ClO}_4^-$  has a Cl isotope ratio similar to that of its Cl source, and an O isotope ratio related to that of the water used for its production (20, 25). Although synthetic and Atacama  $\text{ClO}_4^-$  are isotopically distinct in terms of both Cl and O stable isotope ratios, some apparently indigenous natural  $\text{ClO}_4^-$ , such as that found in the High Plains region in western Texas and eastern New Mexico (3), has a distinct isotopic composition that cannot be unequivocally distinguished from a biodegraded mixture of synthetic  $\text{ClO}_4^-$  and Atacama  $\text{ClO}_4^-$  (20, 25). The differences in the isotopic composition of these two well-documented types of natural  $\text{ClO}_4^-$  (Atacama and High Plains) are not yet explained; they may represent different production mechanisms and/or different Cl reactants. To better understand the origins of different types of natural  $\text{ClO}_4^-$ , and thus to enable more diagnostic source apportionment in forensic studies, we measured the radioactive isotope  $^{36}\text{Cl}$  in a set of representative samples.

Several atmospheric production mechanisms for natural  $\text{ClO}_4^-$  have been proposed and tested with laboratory experiments and balloon-borne measurements (26–29). The presence of  $\text{ClO}_4^-$  associated with stratospheric sulfate aerosols observed by single-particle mass spectrometry (28) supports a stratospheric production mechanism. Other mechanisms proposed for production of natural  $\text{ClO}_4^-$  in the troposphere or at the soil surface include ozone- and UV-catalyzed oxidation of  $\text{Cl}^-$  and  $\text{OCl}^-$ , which have been simulated in laboratory experiments (29, 30), and biogenic production analogous to nitrification. Stratospheric  $\text{ClO}_4^-$ , with its signature  $^{17}\text{O}$ -enrichment inherited from stratospheric ozone, should also have a high initial abundance of cosmogenic  $^{36}\text{Cl}$  because most  $^{36}\text{Cl}$  production occurs in the

\* Corresponding author phone: 312-355-1182; fax: 312-413-2279; e-mail: sturchio@uic.edu.

<sup>†</sup> University of Illinois at Chicago.

<sup>‡</sup> PRIME Lab, Purdue University.

<sup>§</sup> U.S. Geological Survey.

<sup>||</sup> Shaw Environmental Inc.

<sup>⊥</sup> Texas Tech University.

<sup>#</sup> Oak Ridge National Laboratory.

<sup>∇</sup> Los Alamos National Laboratory.

<sup>○</sup> New Mexico Environment Department.

**TABLE 1. Chlorine Isotope Data for Synthetic Perchlorate Reagents and Products<sup>a</sup>**

	$\delta^{37}\text{Cl}$ (‰) <sup>b</sup>	$^{36}\text{Cl}/\text{Cl}$ ( $10^{-15}$ )	<i>n</i> <sup>c</sup>
<b>synthetic perchlorate reagents</b>			
KClO <sub>4</sub> , Aldrich (lot 11921HO)	+1.0	31 ± 4	1
CsClO <sub>4</sub> , Aldrich (lot LI09119JI)	+1.6	34 ± 2	2
HClO <sub>4</sub> , Baker (9656-1, lot 146358)	+0.6	28 ± 4	1
KClO <sub>4</sub> , Baker (lot 45155)	+1.1	0.0 ± 2.5	1
KClO <sub>4</sub> , General Chem. Co. (lot 13)	+0.6	6.2 ± 1.6	2
NaClO <sub>4</sub> , Mallinckrodt (lot 1190 KHJJ)	+1.2	19 ± 4	1
NH <sub>4</sub> ClO <sub>4</sub> , Kerr-McGee (lot 7974F)	+0.7	22 ± 3	1
NH <sub>4</sub> ClO <sub>4</sub> , Kerr-McGee (lot 5094)	+1.5	37 ± 4	1
NH <sub>4</sub> ClO <sub>4</sub> , Kerr-McGee (lot 7914NN)	+0.3	30 ± 3	1
NH <sub>4</sub> ClO <sub>4</sub> , PEPCON (lot 87010)	+0.6	40 ± 3	1
NH <sub>4</sub> ClO <sub>4</sub> , PEPCON (lot 87015)	+0.7	38 ± 4	1
NaClO <sub>4</sub> solution, AMPAC, 2007	+0.4	30 ± 3	1
KClO <sub>4</sub> , Hummel Croton	+0.2	6.4 ± 1.4	1
KClO <sub>4</sub> , Taiwan	+0.3	5.8 ± 1.4	2
NaClO <sub>4</sub> ·H <sub>2</sub> O, EM, Germany (lot SX0693-2)	-3.1	4.5 ± 1.3	1
NaClO <sub>4</sub> ·H <sub>2</sub> O, EM, Germany (1992)	-5.0	7.7 ± 2.8	1
NaClO <sub>4</sub> ·H <sub>2</sub> O, EM, Germany (1995)	n.a.	3.2 ± 1.0	1
<b>synthetic perchlorate products</b>			
ClO <sub>4</sub> <sup>-</sup> in highway safety flare	+0.1	16 ± 5	1
ClO <sub>4</sub> <sup>-</sup> in commercial bleach	+14.0	9.6 ± 1.6	1

<sup>a</sup> n.a. = not analyzed. <sup>b</sup>  $\delta^{37}\text{Cl} = [R_{\text{sample}} - R_{\text{standard}}] - 1$ , where  $R = ^{37}\text{Cl}/^{35}\text{Cl}$ ; std. dev. ± 0.2 ‰. <sup>c</sup> *n* = number of <sup>36</sup>Cl analyses per sample.

stratosphere (31). In contrast, ClO<sub>4</sub><sup>-</sup> produced in the troposphere or at Earth's surface is more likely to have <sup>36</sup>Cl abundances typical of Cl<sup>-</sup> in meteoric deposition, in which cosmogenic <sup>36</sup>Cl-enriched stratospheric Cl is diluted by marine Cl<sup>-</sup> having negligible <sup>36</sup>Cl abundance (32).

The principal atmospheric production mechanism for <sup>36</sup>Cl is from galactic cosmic-ray spallation of <sup>40</sup>Ar (31, 33). The range of measured <sup>36</sup>Cl/Cl ratios of Cl<sup>-</sup> in preanthropogenic groundwater across the continental U.S. is from ~10 × 10<sup>-15</sup> near the coasts to as high as 1670 × 10<sup>-15</sup> in the central Rocky Mountains (34). The lower ratios near the coasts reflect dilution by marine sea-salt aerosols in which <sup>36</sup>Cl/Cl = 0.0 × 10<sup>-15</sup>. Evidence from fossil rat urine in packrat middens dating back to about 40 ka indicates that <sup>36</sup>Cl production rates (and therefore <sup>36</sup>Cl/Cl ratios in meteoric deposition) during the interval 35 to 10 ka may have been up to twice as high as modern values, because of fluctuations in geomagnetic intensity (35). No sample of soil or groundwater Cl<sup>-</sup> having <sup>36</sup>Cl/Cl ratios as high as 2,000 × 10<sup>-15</sup> has ever been reported, except where bomb-produced <sup>36</sup>Cl is present (32, 34). Testing of thermonuclear bombs in the Pacific Ocean during 1952–1958 injected a large amount of <sup>36</sup>Cl, produced by neutron irradiation of seawater chloride, into the stratosphere, and produced worldwide <sup>36</sup>Cl fallout (32). The presence of bomb-pulse Cl<sup>-</sup> may be identified from its anomalously high <sup>36</sup>Cl/Cl ratio relative to natural background values and from its association with high tritium activity. The highest measured <sup>36</sup>Cl/Cl ratio for bomb-affected groundwater Cl<sup>-</sup> is 12,800 × 10<sup>-15</sup> (34). The <sup>36</sup>Cl/Cl ratio of Cl<sup>-</sup> in Long Island (NY) rainwater, sampled in 1957 (during the peak of the nuclear bomb testing era in the Pacific) was as high as 127,000 × 10<sup>-15</sup> (36), and Arctic deposition in 1957 also had high <sup>36</sup>Cl/Cl [28,600 × 10<sup>-15</sup>] as observed in the Dye-3 ice core (37).

### Samples and Methods

A set of 35 samples was chosen to represent the three known principal sources of ClO<sub>4</sub><sup>-</sup> in the environment of the southwestern U.S., i.e., synthetic ClO<sub>4</sub><sup>-</sup>, natural ClO<sub>4</sub><sup>-</sup> from soils and groundwater of the Atacama Desert, and natural ClO<sub>4</sub><sup>-</sup> from the southwestern U.S. They were analyzed for <sup>36</sup>Cl abundance by accelerator mass spectrometry at the

Purdue Rare Isotope MEasurement (PRIME) Lab, and for stable Cl isotope ratio (<sup>37</sup>Cl/<sup>35</sup>Cl) at the Environmental Isotope Geochemistry Laboratory (University of Illinois at Chicago). Methods used for preparation and isotopic analyses of ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> are described elsewhere (21, 22, 38). The synthetic ClO<sub>4</sub><sup>-</sup> samples were mostly laboratory reagents, but also included one sample derived from a highway safety flare and one extracted from a bottle of commercial bleach solution (6.5% NaOCl). The Atacama ClO<sub>4</sub><sup>-</sup> samples were mostly extracted from bulk soils, with the exception of one sample collected from Atacama groundwater, one from industrial grade NaNO<sub>3</sub> produced in Chile from the Atacama nitrate deposits, and one from a New Jersey groundwater believed to have been contaminated with Atacama nitrate fertilizer-derived ClO<sub>4</sub><sup>-</sup>. In addition to the Cl isotopic analyses of ClO<sub>4</sub><sup>-</sup>, five samples of Atacama Cl<sup>-</sup> extracts also were analyzed. The natural ClO<sub>4</sub><sup>-</sup> samples from the southwestern U.S. were mostly extracted from groundwater having ClO<sub>4</sub><sup>-</sup> concentrations ranging from 0.24 to 90 μg L<sup>-1</sup>, with tritium and/or radiocarbon data indicating recharge times from pre-1945 to older than 10 ka (3, 39). However, two ClO<sub>4</sub><sup>-</sup> samples (NM Water Canyon Gallery and TX Martin - shallow) were from groundwater having relatively high tritium activity, and one ClO<sub>4</sub><sup>-</sup> sample was extracted from the leachate of a nitrate-rich caliche-type soil sample from the Mojave Desert at Saratoga Hills, near Death Valley, CA (23, 40).

Stable isotope ratios for Cl are given as  $\delta^{37}\text{Cl}$  values relative to the Standard Mean Ocean Chloride standard, where  $\delta^{37}\text{Cl} = (^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}} / (^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}} - 1$ , reported in parts per thousand (‰). The reproducibility of  $\delta^{37}\text{Cl}$  values for ClO<sub>4</sub><sup>-</sup> is given by the reported standard deviation (±0.2 ‰).

### Results and Discussion

The results of Cl isotopic analyses for all samples are given in Tables 1–3. The Cl isotopic compositions of the ClO<sub>4</sub><sup>-</sup> samples define three distinct, nonoverlapping clusters in a diagram of <sup>36</sup>Cl/Cl × 10<sup>-15</sup> vs  $\delta^{37}\text{Cl}$  (Figure 1). The highest values of <sup>36</sup>Cl/Cl are those of the natural ClO<sub>4</sub><sup>-</sup> samples from the southwestern U.S. (3100 × 10<sup>-15</sup> to 28,800 × 10<sup>-15</sup>); these samples have a range of  $\delta^{37}\text{Cl}$  values from -1.3 to +4.5 ‰. Natural ClO<sub>4</sub><sup>-</sup> samples collected from the Atacama Desert nitrate deposits have much lower values of <sup>36</sup>Cl/Cl and  $\delta^{37}\text{Cl}$

**TABLE 2. Chlorine Isotope Data for ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> from Atacama Desert Nitrate Deposits and Products<sup>a</sup>**

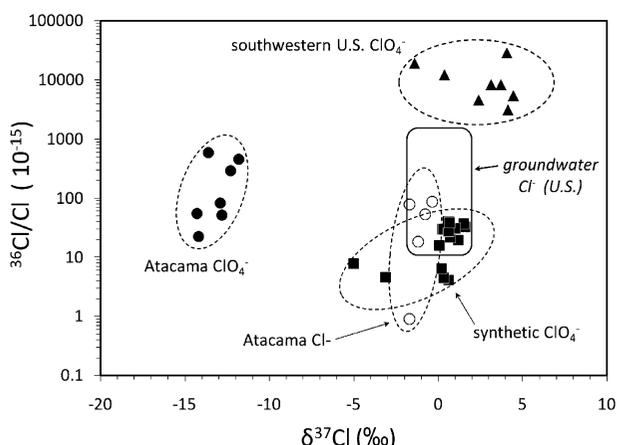
	$\delta^{37}\text{Cl}$ (‰) <sup>b</sup>	<sup>36</sup> Cl/Cl (10 <sup>-15</sup> )	<i>n</i> <sup>c</sup>
<b>Atacama Desert (Chile) nitrate deposits</b>			
ClO <sub>4</sub> <sup>-</sup> , Baquedano District, shallow groundwater	-12.9	83 ± 10	1
Cl <sup>-</sup> , Baquedano District, shallow groundwater	-0.3	87 ± 6	1
ClO <sub>4</sub> <sup>-</sup> , Baquedano District, vertical vein fill	-12.8	52 ± 16	1
Cl <sup>-</sup> , Baquedano District, vertical vein fill	-0.8	53 ± 4	1
Cl <sup>-</sup> , N. Tarapaca District, caliche soil	-1.7	0.9 ± 1.0	1
Cl <sup>-</sup> , S. Tarapaca District, caliche soil	-1.2	18 ± 3	1
Cl <sup>-</sup> , Tocopilla District, caliche soil	-1.7	79 ± 4	1
ClO <sub>4</sub> <sup>-</sup> , Estanque Oasis, fracture fill at -6 m (TTU-P1)	-14.3	55 ± 8	2
ClO <sub>4</sub> <sup>-</sup> , Estanque Oasis, fracture fill at -6 m (TTU-P2)	-13.6	590 ± 20	1
ClO <sub>4</sub> <sup>-</sup> , Estanque Oasis, surface pit mine (TTU-P4)	-11.8	460 ± 23	1
<b>Atacama Desert (Chile) nitrate products</b>			
ClO <sub>4</sub> <sup>-</sup> , SQM industrial grade NaNO <sub>3</sub> (purchased 2003)	-14.2	22 ± 3	1
Cl <sup>-</sup> , SQM industrial grade NaNO <sub>3</sub> (purchased 2003)	n.a.	46 ± 7	1

<sup>a</sup> n.a. = not analyzed. <sup>b</sup>  $\delta^{37}\text{Cl} = [R_{\text{sample}} - R_{\text{standard}}] - 1$ , where  $R = {}^{37}\text{Cl}/{}^{35}\text{Cl}$ ; std. dev. ± 0.2 ‰. <sup>c</sup> *n* = number of <sup>36</sup>Cl analyses per sample.

**TABLE 3. Perchlorate Concentrations, Chlorine Isotope Data, and Tritium Activities of Groundwaters and Soil Leachate from the Southwestern United States<sup>a</sup>**

	[ClO <sub>4</sub> <sup>-</sup> ], μg L <sup>-1</sup>	<sup>3</sup> H, TU	$\delta^{37}\text{Cl}$ (‰) <sup>b</sup>	<sup>36</sup> Cl/Cl (10 <sup>-15</sup> )	<i>n</i> <sup>c</sup>
<b>Southwest United States natural perchlorate</b>					
Texas: Martin County, well water - shallow (36 to 39 m)	24	2.5 ± 0.2	+2.4	4550 ± 120	1
Texas: Martin County, well water - deep (48 to 54 m)	19	0.3 ± 0.2	+4.1	3130 ± 100	1
New Mexico: Roosevelt County, Kountry Jct., well water	15	0.2 ± 0.2	+4.5	5440 ± 170	1
New Mexico: Water Canyon Gallery Spring water	0.32	2.2 to 8.0	+4.1	28800 ± 920	1
New Mexico: Valle Grande Spring water	0.24	0.03 ± 0.09	+0.4	12300 ± 360	1
New Mexico: Albuquerque, RR 8-2 well water	0.67	-0.2 ± 0.3	+3.1	8240 ± 240	2
New Mexico: Albuquerque, RR 16-1 well water	0.85	0.3 ± 0.3	+3.7	8370 ± 270	2
California: Mojave Desert soil leachate <sup>d</sup>	n.a.	n.a.	-1.4	19200 ± 890	1
<b>contaminated groundwater</b>					
New Jersey: Bergen County, Park Ridge, well water	90	n.a.	-12.3	290 ± 12	1

<sup>a</sup> TU = tritium unit = <sup>3</sup>H atoms/10<sup>18</sup> H atoms. n.a. = not analyzed. <sup>b</sup>  $\delta^{37}\text{Cl} = [R_{\text{sample}} - R_{\text{standard}}] - 1$ , where  $R = {}^{37}\text{Cl}/{}^{35}\text{Cl}$ ; std. dev. ± 0.2 ‰. <sup>c</sup> *n* = number of <sup>36</sup>Cl analyses per sample. <sup>d</sup> Mojave Desert soil sample from Saratoga Hills, near Death Valley; bulk [ClO<sub>4</sub><sup>-</sup>] = 0.85 mg/kg.



**FIGURE 1. <sup>36</sup>Cl/Cl (atom ratio) vs  $\delta^{37}\text{Cl}$  (‰) in representative samples of synthetic ClO<sub>4</sub><sup>-</sup> reagents and products; natural ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> extracted from soil and groundwater from the Atacama Desert, Chile; and natural ClO<sub>4</sub><sup>-</sup> extracted from groundwater and soil from the southwestern United States. Sizes of symbols exceed analytical errors. Delineated square area shows ranges of <sup>36</sup>Cl/Cl ratios and  $\delta^{37}\text{Cl}$  values for Cl<sup>-</sup> in U.S. groundwater (46, 47).**

than those from the southwestern U.S. If the ClO<sub>4</sub><sup>-</sup> in these two different regions formed by similar mechanisms and had similar initial <sup>36</sup>Cl abundances, then the contrast in measured <sup>36</sup>Cl abundance could be interpreted chrono-

metrically if the southwestern U.S. ClO<sub>4</sub><sup>-</sup> is assumed to have formed in Holocene or Pleistocene time (2, 39) and the mean age of the Atacama ClO<sub>4</sub><sup>-</sup> is assumed to be 3–8 million years (41, 42), which is 10 or more half-lives of <sup>36</sup>Cl (*t*<sub>1/2</sub> = 301,000 a). In a landscape as old as the Atacama Desert, with continuous deposition of atmospheric ClO<sub>4</sub><sup>-</sup> since Miocene time, most of the <sup>36</sup>Cl would approach secular equilibrium with its environment. For the two Atacama samples in which <sup>36</sup>Cl/Cl was determined for coexisting ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup>, the ratios are identical (within analytical uncertainty) and are within the range of typical subsurface equilibrium nucleogenic <sup>36</sup>Cl/Cl ratios in silicate rocks (33). The Atacama ClO<sub>4</sub><sup>-</sup> sample having the highest <sup>36</sup>Cl/Cl ratio (590 × 10<sup>-15</sup>), even if it had an initial <sup>36</sup>Cl/Cl ratio equal to the lowest of any natural ClO<sub>4</sub><sup>-</sup> sample from the southwestern U.S. (3100 × 10<sup>-15</sup>), would imply an apparent age of ~750,000 a, which can be estimated from (43)

$$t = -1/\lambda_{36} \ln[(R_m - R_{se}) / (R_i - R_{se})] \quad (1)$$

where *t* = time (a),  $\lambda_{36}$  = decay constant of <sup>36</sup>Cl (= 2.303 × 10<sup>-6</sup> a<sup>-1</sup>), *R<sub>m</sub>* = measured <sup>36</sup>Cl/Cl, *R<sub>i</sub>* = initial <sup>36</sup>Cl/Cl, and *R<sub>se</sub>* = secular equilibrium <sup>36</sup>Cl/Cl ratio (assuming a typical value of 50 × 10<sup>-15</sup>). This assumes the sample behaved as a closed system following its formation at time = *t*.

The reason for the difference in  $\delta^{37}\text{Cl}$  values between the natural ClO<sub>4</sub><sup>-</sup> samples from the Atacama Desert ( $\delta^{37}\text{Cl} = -14.3$  to  $-12.8$  ‰) and the southwestern U.S. ( $\delta^{37}\text{Cl} = -1.3$  to  $+4.5$  ‰) is not known because of the scarcity of available

data on the isotopic composition of stratospheric Cl species and their global variations. Our data may imply a significant difference in the Cl isotopic compositions of the reactants that produce  $\text{ClO}_4^-$  at the two localities. Resolution of this issue could benefit from isotopic analyses of stratospheric Cl species and terrestrial  $\text{ClO}_4^-$  from other regions of the world, along with experimental studies of kinetic isotope effects accompanying potential stratospheric reactions that produce  $\text{ClO}_4^-$ .

Synthetic  $\text{ClO}_4^-$  typically is produced by electrochemical oxidation of NaCl brine (44). The Cl isotopic characteristics are therefore inherited from the source of NaCl used in the brine. Most of the synthetic  $\text{ClO}_4^-$  samples have  $\delta^{37}\text{Cl}$  values in the range +0.2 to +1.6 ‰, which is consistent with a predominantly marine halite source having  $\delta^{37}\text{Cl} = 0.0 \pm 0.9$  ‰ (45). The synthetic  $\text{ClO}_4^-$  reagent samples obtained from EM Co. (Germany) have anomalous  $\delta^{37}\text{Cl}$  values of -3.1 and -5.0 ‰ that may reflect a Cl source other than typical marine halite (46), or fractionation during synthesis. The range in  $^{36}\text{Cl}/\text{Cl}$  ratios of synthetic  $\text{ClO}_4^-$  samples ( $0.0 \times 10^{-15}$  to  $40 \times 10^{-15}$ ) is consistent with marine halite Cl sources, provided some nucleogenic  $^{36}\text{Cl}$  contribution (e.g., from mudstone layers in bedded halites) to the higher values. The  $\text{ClO}_4^-$  samples known to have been produced in the southern Nevada area (Kerr-McGee and PEPCON samples, Table 1) all have similar  $^{36}\text{Cl}/\text{Cl}$  ratios around  $22 \times 10^{-15}$  to  $40 \times 10^{-15}$ , whereas those produced in Germany, Taiwan, and by General Chem. Co. (production location unknown) and Hummel-Croton Co. (imported from China) appear to have a distinctly lower range in  $^{36}\text{Cl}/\text{Cl}$  ( $3.2 \times 10^{-15}$  to  $7.7 \times 10^{-15}$ ). Only one synthetic  $\text{ClO}_4^-$  sample (from a jar of Baker  $\text{KClO}_4$  dated 1963) has a  $^{36}\text{Cl}/\text{Cl}$  ratio ( $0.0 \pm 2.5 \times 10^{-15}$ ) consistent with pure marine Cl.

The high  $^{36}\text{Cl}/\text{Cl}$  ratios in  $\text{ClO}_4^-$  from groundwater and soil samples from the southwestern U.S. ( $3100 \times 10^{-15}$  to  $28,800 \times 10^{-15}$ ), relative to the range of  $^{36}\text{Cl}/\text{Cl}$  ratios in prebomb meteoric chloride deposition over the same geographic area ( $300 \times 10^{-15}$  to  $1110 \times 10^{-15}$ ) (34), appear to preclude a significant amount of  $\text{ClO}_4^-$  formation from  $\text{Cl}^-$  at or near the Earth's surface (e.g., by tropospheric ozone/UV irradiation, lightning strikes, or biogenic mechanisms). Such near-surface production mechanisms could not account for the elevated  $^{36}\text{Cl}$  abundances observed in our samples of preanthropogenic  $\text{ClO}_4^-$  because the only apparent location of sufficiently  $^{36}\text{Cl}$ -enriched Cl is the stratosphere, where cosmogenic  $^{36}\text{Cl}$  production is highest (31). Although we are not aware of any evidence indicating in situ production of  $^{36}\text{ClO}_4^-$  during the Pacific nuclear bomb tests,  $^{36}\text{Cl}$ -enriched  $\text{ClO}_4^-$  would have been generated by normal production mechanisms from bomb-pulse  $^{36}\text{Cl}$  injected into the stratosphere (i.e., bomb-pulse  $^{36}\text{ClO}_4^-$ ). This phenomenon would have been transient, as the stratospheric residence time of bomb-pulse  $^{36}\text{Cl}$  was around 2 yr (37), and any  $\text{ClO}_4^-$  produced in the stratosphere at this time would have had an anomalously high  $^{36}\text{Cl}/\text{Cl}$  ratio and would have been deposited ultimately at the ocean or land surface within weeks of entering the troposphere.

Several of our samples (Water Canyon Gallery spring water, Martin shallow well water, and Mojave Desert soil leachate), on the basis of their appreciable  $^3\text{H}$  abundances (in water samples) or exposure at the land surface (Mojave soil), could contain bomb-pulse  $^{36}\text{ClO}_4^-$ . The Water Canyon Gallery spring water and Mojave soil leachate  $\text{ClO}_4^-$  samples have the highest  $^{36}\text{Cl}/\text{Cl}$  ratios of all we measured, and that of the Martin well shallow water sample ( $^3\text{H} = 2.5$  TU) is 45% larger than that of the Martin well deep water sample ( $^3\text{H} = 0.3 \pm 0.2$  TU), which also could indicate bomb-pulse  $^{36}\text{ClO}_4^-$  in the younger, shallower Martin well water. For most of the southwest U.S. groundwater samples, however, low  $^3\text{H}$  concentrations provide evidence that the high  $^{36}\text{Cl}/\text{Cl}$  ratios

predate thermonuclear bomb tests and are natural features of the  $\text{ClO}_4^-$ . New Mexico samples RR8 and RR16, with  $^{36}\text{Cl}/\text{Cl}$  ratios exceeding  $8000 \times 10^{-15}$ , were obtained from groundwater with  $^{14}\text{C}$  ages >10 ka ((39), Jackson and others, in preparation). The Atacama soil samples are mostly from pits or trenches and their exposure histories to atmospheric deposition during the past 50 years are less well documented; the presence of a small amount of bomb-pulse  $^{36}\text{ClO}_4^-$  in some of these samples cannot be ruled out, but it would presumably have relatively minor impact because of the large reservoir of much older  $\text{ClO}_4^-$  in these deposits.

In summary, characteristic  $^{36}\text{Cl}$  and  $^{37}\text{Cl}$  isotopic abundances found in the three principal sources of  $\text{ClO}_4^-$  present in the environment of the southwestern U.S. allow these sources to be distinguished from each other. These results may have immediate forensic applications in delineating the sources of  $\text{ClO}_4^-$  in water supplies and foodstuffs, and they may provide important constraints for determining the natural production mechanism of  $\text{ClO}_4^-$ .

## Acknowledgments

This work was supported by the Environment Security Technology Certification Program of the U.S. Department of Defense (Project ER-0509), the Environmental Management Program of the U.S. Department of Energy, and the National Research Program in the Water Resources Discipline of the U.S. Geological Survey. The PRIME Lab is supported by the National Science Foundation. We thank Dale Counce, Michael Rearick, George Perkins, Toti Larson, and Armand Groffman for assistance with collection of Water Canyon Gallery and Valle Grande Spring samples, and Michael Hiskey for the reagent sample from Taiwan. Oak Ridge National Laboratory is managed by UT-Battelle LLC for the U.S. Department of Energy under contract DE-AC05-00OR22725. Use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

## Literature Cited

- (1) Rajagopalan, S.; Anderson, T.; Cox, S.; Harvey, G.; Cheng, Jackson, W. A. Perchlorate in wet deposition across North America. *Environ. Sci. Technol.* **2009**, *43*, 616–622.
- (2) Ericksen, G. E. *Geology and Origin of the Chilean Nitrate Deposits*; Prof. Paper 1188; U.S. Geological Survey: Washington, DC, 1981.
- (3) Rajagopalan, S.; Anderson, T. A.; Fahlquist, L.; Rainwater, K. A.; Ridley, M.; Jackson, A. W. Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 3156–3162.
- (4) Rao, B.; Anderson, T. A.; Orris, G. J.; Rainwater, K. A.; Rajagopalan, S.; Sandvig, R. M.; Scanlon, B. R.; Stonestrom, D. A.; Walvoord, M. A.; Jackson, W. A. Widespread natural perchlorate in unsaturated zones of the Southwest United States. *Environ. Sci. Technol.* **2007**, *41*, 4522–4528.
- (5) Böhlke, J. K.; Hatzinger, P. B.; Sturchio, N. C.; Abbene, I. J.; Mroczkowski, S. J. Atacama perchlorate as an agricultural contaminant in groundwater: Isotopic and chronologic evidence from Long Island, New York. *Environ. Sci. Technol.* **2009**, *43* (15), 5619–5625.
- (6) Krynetsky, A. J.; Niemann, R. A.; Nortrup, D. A. Determination of perchlorate anion in foods by ion chromatography-tandem mass spectrometry. *Anal. Chem.* **2004**, *76*, 5518–5522.
- (7) Sanchez, C. A.; Crump, K. S.; Krieger, R. I.; Khandaker, N. R.; Gibbs, J. P. Perchlorate and nitrate in leafy vegetables of North America. *Environ. Sci. Technol.* **2005**, *39*, 9391–9397.
- (8) Kirk, A. B.; Martinelango, P. K.; Tain, K.; Dutta, A.; Smith, E. E.; Dasgupta, P. K. Perchlorate and iodide in dairy and breast milk. *Environ. Sci. Technol.* **2005**, *39*, 2011–2017.
- (9) Schier, J. G.; Wolk, A. F.; Valentin-Blasini, L.; Belson, M. G.; Kieszak, S. M.; Rubin, C. S.; Blount, B. C. Perchlorate exposure from infant formula and comparisons with the perchlorate reference dose. *J. Exposure Sci. Environ. Epidemiol.* **2009**, 1–7.
- (10) Blount, B. C.; Pirkle, J. L.; Osterloh, J. D.; Valentin-Blasini, L.; Caldwell, K. L. Urinary perchlorate and thyroid hormone levels in adolescent and adult men and women living in the United States. *Environ. Health Perspect.* **2006**, *14*, 1865–1871.

- (11) Blount, B. C.; Valentin-Blasini, L.; Mauldin, J. P.; Pirkle, J. L.; Osterloh, J. D. Perchlorate exposure of the U.S. population, 2001–2002. *J. Exposure Sci. Environ. Epidemiol.* **2007**, *17*, 400–407.
- (12) Kirk, A. B.; Dyke, J. V.; Martin, C. F.; Dasgupta, P. K. Temporal patterns in perchlorate, thiocyanate, and iodide excretion in human milk. *Environ. Health Perspect.* **2007**, *115*, 182–186.
- (13) Pearce, E. N.; Leung, A. M.; Blount, B. C.; Bazrafshan, H. R.; He, X.; Pino, S.; Valentin-Blasini, L.; Braverman, L. E. Breast milk iodine and perchlorate concentrations in lactating Boston-area women. *J. Clin. Endocrinol. Metab.* **2007**, *92*, 1673–1677.
- (14) National Research Council (NRC). *Health Implications of Perchlorate Ingestion*; National Academies Press, Board on Environmental Studies and Toxicology: Washington, DC, January 2005; 276 pp.
- (15) U. S. Environmental Protection Agency (EPA). *Perchlorate*; available at <http://www.epa.gov/fedfac/documents/perchlorate.htm>; accessed April 22, 2009.
- (16) U. S. Environmental Protection Agency (EPA). *Drinking Water: Preliminary Regulatory Determination on Perchlorate*; 2008; <http://www.epa.gov/fedrgstr/EPA-WATER/2008/October/Day-10/w24042.htm>; accessed April 23, 2009.
- (17) Dasgupta, P. K.; Dyke, J. V.; Kirk, A. B.; Jackson, W. A. Perchlorate in the United States: Analysis of relative source contributions to the food chain. *Environ. Sci. Technol.* **2006**, *40*, 6608–6614.
- (18) 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.
- (19) Bao, H.; Gu, B. Natural perchlorate has a unique oxygen isotope signature. *Environ. Sci. Technol.* **2004**, *38*, 5073–5077.
- (20) Böhlke, J. K.; Sturchio, N. C.; Gu, B.; Horita, J.; Brown, G. M.; Jackson, W. A.; Batista, J.; Hatzinger, P. B. Perchlorate isotope forensics. *Anal. Chem.* **2005**, *77*, 7838–7842.
- (21) Sturchio, N. C.; Böhlke, J. K.; Beloso, A. D., Jr.; Streger, S. H.; Heraty, L. J.; Hatzinger, P. B. Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: Laboratory results and implications for forensics and natural attenuation studies. *Environ. Sci. Technol.* **2007**, *41*, 2796–2802.
- (22) Hatzinger, P. B.; Böhlke, J. K.; Sturchio, N. C.; Gu, B.; Heraty, L. J.; Borden, R. C. Fractionation of stable isotopes in perchlorate and nitrate during in situ biodegradation in a sandy aquifer. *Environ. Chem.* **2009**, *6*, 44–52.
- (23) Böhlke, J. K.; Erickson, G. E.; Revesz, K. M. Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern Chile and Southern California, USA. *Chem. Geol.* **1997**, *136*, 135–152.
- (24) Michalski, G.; Böhlke, J. K.; Thiemens, M. Long term atmospheric deposition as the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from mass-independent oxygen isotopic compositions. *Geochim. Cosmochim. Acta* **2004**, *68*, 4023–4038.
- (25) Sturchio, N. C.; Böhlke, J. K.; Gu, B.; Horita, J.; Brown, G. M.; Beloso, A.; Patterson, L. J.; Hatzinger, P. B.; Jackson, W. A.; Batista, J. Stable isotopic composition of chlorine and oxygen in synthetic and natural perchlorate. In *Perchlorate: Environmental Occurrence, Interactions, and Treatment*; Gu, B., Coates, J. D., Eds.; Springer: New York; 2006; pp 93–110.
- (26) Simonaitis, R.; Hecklen, J. Perchloric acid: Possible sink for stratospheric chlorine. *Planet Space Sci.* **1975**, *23*, 1567–1569.
- (27) 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 HClO<sub>4</sub> production on sulfate aerosols. *Geophys. Res. Lett.* **1996**, *23*, 1749–1752.
- (28) Murphy, D. M.; Thomson, D. S. Halogen ions and NO<sup>+</sup> in the mass spectra of aerosols in the upper troposphere and lower stratosphere. *Geophys. Res. Lett.* **2000**, *27*, 3217–3220.
- (29) Dasgupta, P. K.; Martinelango, P. K.; Jackson, W. A.; Anderson, T. A.; Tian, K.; Tock, R. W.; Rajagopalan, S. The origin of naturally occurring perchlorate: The role of atmospheric processes. *Environ. Sci. Technol.* **2005**, *39*, 1569–1575.
- (30) Kang, N.; Anderson, T. A.; Jackson, W. A. Photochemical formation of perchlorate from aqueous oxychlorine anions. *Anal. Chim. Acta* **2006**, *567*, 48–56.
- (31) Lal, D.; Peters, K. Cosmic-ray produced radioactivity within the earth. In *Handbuch der Physik*; Band XLVI/2; Fluegge, S., Sitte, K., Eds.; Springer-Verlag: Berlin, 1967; pp 551–612.
- (32) Phillips, F. M. Chlorine-36. In *Environmental Tracers in Subsurface Hydrology*; Cook, P., Herczeg, A., Eds.; Kluwer Academic Publishers: Boston, 2000; pp 299–348.
- (33) Lehmann, B. E.; Davis, S. N.; Fabryka-Martin, J. T. Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Resour. Res.* **1993**, *29*, 2027–2040.
- (34) Davis, S. N.; Moysey, S.; Cecil, L. D.; Zreda, M. Chlorine-36 in groundwater of the United States: empirical data. *Hydrogeol. J.* **2003**, *11*, 217–227.
- (35) Plummer, M. A.; Phillips, F. M.; Fabryka-Martin, J. T.; Turin, H. J.; Wigand, P. E.; Sharma, P. Chlorine-36 in fossil rat urine: an archive of cosmogenic nuclide deposition over the past 40,000 years. *Science* **1997**, *277*, 538–541.
- (36) Schaeffer, O. A.; Thompson, S. O.; Lark, N. L. Chlorine-36 radioactivity in rain. *J. Geophys. Res.* **1960**, *65*, 4013–4016.
- (37) Synal, H.-A.; Beer, J.; Bonani, G.; Suter, M.; Wölfli, W. Atmospheric transport of bomb-produced <sup>36</sup>Cl. *Nucl. Meth. Instr. Phys. Res.* **1990**, *B52*, 483–488.
- (38) Patterson, L. J.; Sturchio, N. C.; Kennedy, B. M.; van Soest, M. C.; Sultan, M. I.; Lu, Z. T.; Lehmann, B. E.; Purtschert, R.; El Kaliouby, B.; Dawood, Y.; Abdallah, A. M. Cosmogenic, radiogenic, and stable isotopic constraints on groundwater residence time in the Nubian Aquifer, Western Desert of Egypt. *Geochem. Geophys. Geosystems* **2005**, (6), no. 1, Q01005, DOI: 10.1029/2004GC000779.
- (39) Plummer, L. N.; Böhlke, J. K.; Doughten, M. W. Perchlorate in Pleistocene and Holocene groundwater in North-Central New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 1757–1763.
- (40) Erickson, 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.
- (41) Alpers, C. N.; Brimhall, G. H. Middle Miocene climatic change in the Atacama Desert, northern Chile—evidence from supergene mineralization at La-Escondida. *Geol. Soc. Am. Bull.* **1988**, *100*, 1640–1656.
- (42) Hartley, A. J.; Chong, G. Late Pliocene age for the Atacama Desert: Implications for the desertification of western South America. *Geology* **2002**, *30*, 43–46.
- (43) Bentley, H. W.; Phillips, F. M.; Davis, S. N. Chlorine-36 in the terrestrial environment. In *Handbook of Environmental Isotope Geochemistry*, Vol. 2, part B; Fritz, P., Fontes, J. C., Eds.; Elsevier: Amsterdam, 1986; pp 427–480.
- (44) Schumacher, J. *Perchlorates: Their Properties, Manufacture, and Uses*; Am. Chem. Soc. Monograph Series 146; Reinhold Publ. Co.: New York, 1960.
- (45) Eastoe, C. J.; Peryt, T. M.; Petrychenko, O. Y.; Geisler-Cussy, D. Stable chlorine isotopes in Phanerozoic evaporites. *Appl. Geochem.* **2007**, *22*, 575–588.
- (46) Eggenkamp, H. The Geochemistry of Chlorine Isotopes. Unpublished Ph.D. Thesis; Utrecht University; The Netherlands, 1994; 150 pp.
- (47) Stewart, M. A.; Spivack, A. J. The stable-chlorine isotope compositions of natural and anthropogenic materials. *Rev. Mineral. Geochem.* **2004**, *55*, 231–254.

ES9012195