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1 **Chlorine-36 Abundance in Natural and Synthetic Perchlorate**

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15 **Abstract**

16 Perchlorate (ClO_4^-) is ubiquitous in the environment. It occurs naturally as a product of
17 atmospheric photochemical reactions, and is synthesized for military, aerospace, and
18 industrial applications. Nitrate-enriched soils of the Atacama Desert (Chile) contain high
19 concentrations of natural ClO_4^- ; nitrate produced from these soils has been exported
20 worldwide since the mid-1800's for use in agriculture. The widespread introduction of
21 synthetic and agricultural ClO_4^- into the environment has complicated attempts to
22 understand the geochemical cycle of ClO_4^- . Natural ClO_4^- samples from the southwestern
23 United States have relatively high ^{36}Cl abundances ($^{36}\text{Cl}/\text{Cl} = 3,100 \times 10^{-15}$ to $28,800 \times 10^{-15}$
24 15), compared with samples of synthetic ($^{36}\text{Cl}/\text{Cl} = 0.0 \times 10^{-15}$ to 40×10^{-15}) and Atacama
25 Desert ($^{36}\text{Cl}/\text{Cl} = 0.9 \times 10^{-15}$ to 590×10^{-15}) ClO_4^- . These data give a lower limit for the initial

26 ^{36}Cl abundance of natural ClO_4^- and provide temporal and other constraints on its
27 geochemical cycle.

28

29 **Introduction**

30 Perchlorate (ClO_4^-) is ubiquitous in trace amounts as the stable anionic form of Cl^{7+} in
31 precipitation, fresh surface water, ground water, soils, plants and food products [*Dasgupta*
32 *et al.*, 2006]. Synthetic perchlorates are widely used as oxidants in energetic materials
33 such as propellants and explosives. Natural ClO_4^- is present in relatively high
34 concentrations in natural nitrate deposits from the Atacama Desert (Chile) that have been
35 used in fertilizer production for over a century [*Ericksen*, 1981]. As a consequence of the
36 widespread use of ClO_4^- in military, aerospace, and other industrial applications, as well as
37 the common agricultural practice of using Chilean nitrate fertilizers, many ground water
38 supplies in the US are now contaminated with elevated concentrations of ClO_4^- . The risk to
39 human health from ClO_4^- ingestion comes from its inhibitory effect on iodine uptake and
40 interference with thyroidal hormone production [*Blount et al.*, 2006].

41

42 The recent development of methods for analyzing stable isotope ratios of Cl and O in ClO_4^-
43 led to their application for distinguishing sources of ClO_4^- in the environment and for
44 quantifying isotope effects caused by microbial reduction of ClO_4^- to Cl^- and H_2O [*Sturchio*
45 *et al.*, 2003; *Bao and Gu*, 2004; *Böhlke et al.*, 2005; *Sturchio et al.*, 2007; *Hatzinger et al.*,
46 2009]. Natural ClO_4^- from the Atacama Desert was found to have excess ^{17}O , indicating
47 atmospheric origin by photochemical reactions involving ozone [*Bao and Gu*, 2004]; this
48 finding is consistent with O isotope studies of NO_3^- and SO_4^{2-} from the Atacama Desert
49 indicating atmospheric sources for those compounds [*Böhlke et al.*, 1997; *Michalski et al.*,
50 2004]. Synthetic ClO_4^- has Cl isotope ratio near that of its Cl source, and O isotope ratio
51 related to that of the water used for its production [*Böhlke et al.*, 2005; *Sturchio et al.*,
52 2006]. Although synthetic and Atacama ClO_4^- are isotopically distinct in terms of both Cl
53 and O stable isotope ratios, some apparently natural ClO_4^- , such as that found in the High
54 Plains region in West Texas [*Rajagopalan et al.*, 2006], cannot be unequivocally
55 distinguished from a biodegraded mixture of synthetic and Atacama ClO_4^- [*Böhlke et al.*,

56 2005; *Sturchio et al.*, 2006]. If the West Texas ClO_4^- is indeed of natural origin, as argued
57 convincingly by *Rajagopalan et al.* [2006], then there exist variations in the stable isotopic
58 composition of both Cl and O in natural ClO_4^- that are yet to be understood.

59 Several atmospheric production mechanisms for natural ClO_4^- have been proposed and
60 tested with laboratory experiments and balloon-borne measurements [*Simonaitis and*
61 *Heicklen*, 1975; *Jaegle et al.*, 1996; *Murphy and Thomson*, 2000; *Dasgupta et al.*, 2005].
62 The presence of ClO_4^- associated with stratospheric sulfate aerosols was observed by
63 single-particle mass spectrometry [*Murphy and Thomson*, 2000], in support of a
64 stratospheric production mechanism. Other mechanisms proposed for production of
65 natural ClO_4^- in the troposphere or at the soil surface include both ozone- and UV-catalyzed
66 oxidation of Cl^- and OCl^- , which have been simulated in the laboratory [*Dasgupta et al.*,
67 2005; *Kang et al.*, 2006], as well as biogenic production. Stratospheric production of ClO_4^- ,
68 and its inheritance of excess ^{17}O from stratospheric ozone, indicates that natural ClO_4^- so
69 produced might also exhibit a naturally high initial abundance of cosmogenic ^{36}Cl , perhaps
70 in excess of ^{36}Cl abundances commonly seen in meteoric deposition. In contrast, ClO_4^-
71 produced in the troposphere or at the Earth's surface would be more likely to have ^{36}Cl
72 abundances typical of Cl^- in meteoric deposition.

73 The principal atmospheric production mechanism for ^{36}Cl is from galactic cosmic-ray
74 spallation of ^{40}Ar [*Lehmann et al.*, 1993]. The range in measured $^{36}\text{Cl}/\text{Cl}$ ratios of Cl^- in pre-
75 anthropogenic groundwater across the continental U.S. is from $\sim 10 \times 10^{-15}$ near the coasts
76 to as high as 1670×10^{-15} in the central Rocky Mountains [*Davis et al.*, 2003]. The lower
77 ratios near the coasts reflect dilution by marine sea-salt aerosols in which $^{36}\text{Cl}/\text{Cl} = 0.0 \times$
78 10^{-15} . Evidence from fossil rat urine in packrat middens dating back to about 40 ka
79 indicates that ^{36}Cl production rates (and therefore $^{36}\text{Cl}/\text{Cl}$ ratios in meteoric deposition)
80 during the interval 35 to 10 ka may have been up to twice as high as modern values,
81 because of fluctuations in geomagnetic intensity [*Plummer et al.*, 1997]. No sample of soil
82 or groundwater Cl^- having $^{36}\text{Cl}/\text{Cl}$ ratios as high as $2,000 \times 10^{-15}$ has ever been reported
83 (except where bomb-produced ^{36}Cl is present) [*Phillips*, 2000; *Davis et al.*, 2003]. The
84 presence of Cl^- from bomb fallout may be identified from its anomalously high $^{36}\text{Cl}/\text{Cl}$ ratio
85 relative to natural background values and from its association with high tritium activity; the
86 highest $^{36}\text{Cl}/\text{Cl}$ ratio for groundwater Cl^- reported by *Davis et al.* [2003] is $12,800 \times 10^{-15}$.

87 **Samples and Methods**

88 A set of 35 samples chosen to represent three major sources of ClO_4^- , i.e., (1) synthetic, (2)
89 natural from the Atacama Desert, and (3) natural from southwestern U.S., was analyzed for
90 ^{36}Cl abundance by accelerator mass spectrometry at the PRIME Lab (Purdue University)
91 and for stable Cl isotope ratio ($^{37}\text{Cl}/^{35}\text{Cl}$) at the Environmental Isotope Geochemistry
92 Laboratory (University of Illinois at Chicago). Methods used for preparation of ClO_4^- and
93 Cl^- for isotopic analysis are as described elsewhere [Patterson *et al.*, 2005; Sturchio *et al.*,
94 2007; Hatzinger *et al.*, 2009]. The synthetic ClO_4^- samples were primarily laboratory
95 reagents, but also included one sample derived from a highway safety flare and one
96 extracted from a bottle of bleach (6.5% NaOCl) solution. The Atacama ClO_4^- samples were
97 mostly extracted from bulk soils, with the exception of one sample collected from Atacama
98 groundwater, one from industrial grade NaNO_3 produced in Chile from the Atacama nitrate
99 deposits, and one from a New Jersey groundwater believed to have been contaminated
100 with fertilizer-derived ClO_4^- from Atacama. In addition to the Cl isotopic analyses of ClO_4^- ,
101 five samples of Atacama Cl^- extracts also were analyzed. The natural ClO_4^- samples from
102 the southwestern U.S. were mostly extracted from groundwater having tritium and/or
103 radiocarbon data indicating recharge times from pre-1945 to about 30 ka (Plummer *et al.*,
104 2006; Rajagopalan *et al.*, 2006; Jackson *et al.*, in prep.). Two ClO_4^- samples (NM Water
105 Canyon Gallery and TX Martin shallow) were from groundwater having relatively high
106 tritium activity, and one ClO_4^- sample was extracted from the leachate of a nitrate-rich
107 caliche-type soil sample from the Mojave Desert near Death Valley (Ericksen *et al.*, 1988;
108 Böhlke *et al.*, 1997).

109 **Results and Discussion**

110 The results of Cl isotopic analyses for all samples are given in Table 1. The Cl isotopic
111 compositions of the ClO_4^- samples define three distinct, non-overlapping clusters in a
112 diagram of $^{36}\text{Cl}/\text{Cl} \times 10^{-15}$ vs. $\delta^{37}\text{Cl}$ (Figure 1). The highest values of $^{36}\text{Cl}/\text{Cl}$ are those of
113 the natural perchlorate samples from the southwestern United States ($3,100 \times 10^{-15}$ to
114 $28,800 \times 10^{-15}$); these samples have a range of $\delta^{37}\text{Cl}$ values from 0.4 to 4.5 ‰. Natural
115 perchlorate samples collected from the Atacama Desert nitrate deposits have much lower
116 values of $^{36}\text{Cl}/\text{Cl}$ and $\delta^{37}\text{Cl}$ than those from the southwestern U.S. The difference in ^{36}Cl
117 abundances between these two types of natural perchlorate, assuming they had similar

118 initial ^{36}Cl abundances, can easily be reconciled by considering that the mean age of the
 119 Atacama perchlorate could be as much as 3 to 8 million years [Alpers and Brimhall, 1988;
 120 Hartley and Chong, 2002], which is 10 or more half-lives of ^{36}Cl ($t_{1/2} = 301,000$ a). During
 121 this time, most of the initial ^{36}Cl would have decayed and the ^{36}Cl abundance of the
 122 accumulated salt would have approached secular equilibrium with its environment. For two
 123 Atacama samples in which $^{36}\text{Cl}/\text{Cl}$ was determined for coexisting ClO_4^- and Cl^- , the values
 124 are identical (within analytical uncertainty) and are within the range of typical subsurface
 125 equilibrium nucleogenic $^{36}\text{Cl}/\text{Cl}$ ratios [Lehmann et al., 1993]. The Atacama ClO_4^- having
 126 the highest $^{36}\text{Cl}/\text{Cl}$ ratio (590×10^{-15}), even if it had an initial $^{36}\text{Cl}/\text{Cl}$ ratio equal to the lowest
 127 of any natural ClO_4^- sample from the SW U.S. ($3,100 \times 10^{-15}$), would require a mean age of
 128 $\sim 750,000$ a, which can be estimated from (Bentley et al., 1986):

$$129 \quad t = -1/\lambda_{36} \ln [(R_m - R_{se})/(R_i - R_{se})] \quad \text{eq. \{1\}}$$

130 where t = time, λ_{36} = decay constant of ^{36}Cl ($= 2.303 \times 10^{-6}$), R_m = measured $^{36}\text{Cl}/\text{Cl}$, R_i =
 131 initial $^{36}\text{Cl}/\text{Cl}$, and R_{se} = secular equilibrium value of $^{36}\text{Cl}/\text{Cl}$ (assuming a typical secular
 132 equilibrium $^{36}\text{Cl}/\text{Cl}$ ratio of 50×10^{-15}). The difference in $\delta^{37}\text{Cl}$ values between the natural
 133 ClO_4^- samples from the Atacama Desert ($\delta^{37}\text{Cl} = -14.3$ to -12.8) and the southwestern U.S.
 134 ($\delta^{37}\text{Cl} = +0.4$ to $+4.5$) is more enigmatic. It may imply a significant difference in either the
 135 reaction mechanism or the reactants that produce ClO_4^- at the two localities.

136 Synthetic ClO_4^- has a well-known production mechanism involving electrochemical
 137 oxidation of NaCl brine [Schumacher, 1960]. The Cl isotopic characteristics are therefore
 138 inherited from the source of NaCl used in the brine. Most of the synthetic ClO_4^- samples
 139 have $\delta^{37}\text{Cl}$ values in the range 0.2 to 1.6 ‰, which is consistent with a predominantly
 140 marine halite source ($\delta^{37}\text{Cl} = 0.0 \pm 0.9$) [Eastoe et al., 2007]. The synthetic ClO_4^- reagent
 141 samples obtained from EM Co. (Germany) have anomalous $\delta^{37}\text{Cl}$ values of -3.1 and -5.0 ‰
 142 that may reflect a Cl source other than marine halite, such as North Sea brine [Eggenkamp,
 143 1994]. The range in $^{36}\text{Cl}/\text{Cl}$ ratios of synthetic ClO_4^- samples (0.0×10^{-15} to 40×10^{-15}) is
 144 consistent with marine halite Cl sources, provided some nucleogenic ^{36}Cl contribution (e.g.
 145 from mudstone layers in bedded halites) to the higher values. The ClO_4^- samples known to
 146 have been produced in the southern Nevada area (Kerr-McGee and PEPCON samples,
 147 Table1) all have similar $^{36}\text{Cl}/\text{Cl}$ ratios around 22×10^{-15} to 40×10^{-15} , whereas those
 148 produced in Germany, Taiwan, and by General Chem. Co. (production location unknown)

149 and Hummel-Croton Co. (NJ) appear to have a distinctly lower range in $^{36}\text{Cl}/\text{Cl}$ (3.2×10^{-15}
150 to 7.7×10^{-15}). Only one sample (from a jar of Baker KClO_4 dated 1963) has a $^{36}\text{Cl}/\text{Cl}$ ratio
151 ($0.0 \pm 2.5 \times 10^{-15}$) consistent with pure marine Cl.

152 The high values of $^{36}\text{Cl}/\text{Cl}$ ratios in ClO_4^- from groundwater and soil samples from the SW
153 U.S. ($3,100 \times 10^{-15}$ to $28,800 \times 10^{-15}$) relative to the range of $^{36}\text{Cl}/\text{Cl}$ ratios in pre-bomb
154 meteoric Cl^- deposition over the same geographic area (300×10^{-15} to $1,110 \times 10^{-15}$) [Davis
155 *et al.*, 2003], seem to preclude a significant amount of ClO_4^- formation from Cl^- at or near
156 the Earth's surface (e.g., by lightning, UV irradiation, tropospheric ozone, or biogenic
157 mechanisms). Such near-surface production mechanisms could not possibly account for
158 the elevated ^{36}Cl abundances observed in our samples of pre-anthropogenic (yet Holocene
159 or latest Pleistocene) ClO_4^- , unless they also involve extreme enrichments of ^{36}Cl . Although
160 we are not aware of any evidence indicating production of ^{36}Cl -enriched ClO_4^- during the
161 nuclear bomb tests in the western Pacific that produced worldwide ^{36}Cl fallout during 1952-
162 1958, we acknowledge that if such ClO_4^- was produced it would probably have had an
163 extremely high $^{36}\text{Cl}/\text{Cl}$ ratio. Several of our samples (NM Water Canyon Gallery spring, W.
164 Texas Martin well (shallow), and Mojave Desert soil leachate), on the basis of their ^3H
165 abundances (waters) or exposure history (Mojave soil), could contain bomb-pulse ClO_4^- .
166 The Water Canyon Gallery spring water and Mojave soil leachate samples have the highest
167 $^{36}\text{Cl}/\text{Cl}$ ratios of all we measured, and that of the Martin well shallow sample ($^3\text{H} = 2.5$ TU) is
168 45% larger than that of the Martin well deep ($^3\text{H} = 0.3 \pm 0.2$ TU) sample, which may indicate
169 presence of bomb-produced ClO_4^- in the younger, shallower Martin well water. The
170 Atacama soil samples are mostly from pits or trenches and their exposure histories are less
171 well documented; the presence of a small amount of bomb-pulse ClO_4^- cannot be ruled out
172 for every sample.

173 In summary, characteristic ^{36}Cl and ^{37}Cl isotopic abundances found in the three major
174 sources of ClO_4^- present in the environment of the continental U.S. allow these sources to
175 be distinguished completely from each other. These results have immediate applications in
176 environmental forensics [Böhlke *et al.*, 2005] as well as profound importance for
177 understanding the natural geochemical cycle of perchlorate. Further studies of the Cl
178 isotopic composition of stratospheric Cl species including ClO_4^- may yield better insights
179 into the role of ClO_4^- in the atmospheric Cl cycle.

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183

184 **References**

185 Alpers C. N. and Brimhall G. H. (1988) Middle Miocene climatic change in the Atacama
186 Desert, northern Chile—evidence from supergene mineralization at La-Escondida, *Geol.*
187 *Soc. Am. Bull.* 100, 1640–1656.

188 Bao, H. and Gu, B. (2004), Natural perchlorate has a unique oxygen isotope signature,
189 *Environ. Sci. Technol.* 2004, 38, 5073–5077.

190 Bentley, H.W., Phillips, F.M. and Davis, S.N. (1986) Chlorine-36 in the terrestrial
191 environment. In: Fritz, P. and Fontes, J.C (Eds.) *Handbook of Environmental Isotope*
192 *Geochemistry*, vol. 2, part B, Elsevier, Amsterdam, pp. 427-480.

193 Blount, B. C., Pirkle, J. L., Osterloh, J. D., Valentin-Blasini, L., and Caldwell, K. L. (2006),
194 Urinary perchlorate and thyroid hormone levels in adolescent and adult men and women
195 living in the United States. *Environ. Health Perspect.* 14, 1865–1871.

196 Böhlke, J.K., Ericksen, G.E., and Revesz, K.M. (1997) Stable isotope evidence for an
197 atmospheric origin of desert nitrate deposits in northern Chile and Southern California,
198 USA, *Chem. Geol.* 136,135–152.

199 Böhlke, J. K., Sturchio, N. C., Gu, B., Horita, J., Brown, G. M., Jackson, W. A., Batista, J.,
200 and Hatzinger, P. B. (2005), Perchlorate isotope forensics, *Anal. Chem.* 77, 7838–7842.

201 Dasgupta, P. K., Martinelango, P. K., Jackson, W. A., Anderson, T. A., Tian, K., Tock, R.
202 W., and Rajagopalan, S. (2005), The origin of naturally occurring perchlorate: The role of
203 atmospheric processes. *Environ. Sci. Technol.* 39, 1569–1575.

204 Dasgupta, P.K., Dyke, J.V., Kirk, A.B., and Jackson, W.A. (2006) Perchlorate in the United
205 States. Analysis of relative source contributions to the food chain. *Environ. Sci. Technol.*
206 40, 6608-6614.

- 207 Davis, S.N., Moysey, S., Cecil, L.D., and Zreda, M. (2003), Chlorine-36 in groundwater of
208 the United States: empirical data, *Hydrogeol. J.* 11, 217-227.
- 209 Eastoe, C.J., Peryt, T.M., Petrychenko, O.Y., and Geisler-Cussy, D. (2007) Stable chlorine
210 isotopes in Phanerozoic evaporites. *Applied Geochem.* 22, 575-588.
- 211 Eggenkamp, H. (1994) *The Geochemistry of Chlorine Isotopes*. Unpublished Ph.D. Thesis,
212 Utrecht University, The Netherlands, 150 p.
- 213 Ericksen, G. E. (1981), *Geology and Origin of the Chilean Nitrate Deposits*, Prof. Paper
214 1188, U.S. Geological Survey, Washington, DC.
- 215 Ericksen, G.E., Hosterman, J.W., and St. Amand, P., 1988, Chemistry, mineralogy, and
216 origin of the clay-hill nitrate deposits, Amargosa River valley, Death Valley region,
217 California, U.S.A.: *Chemical Geology*, v. 67, p. 85-102.
- 218 Hartley A. J. and Chong G. (2002) Late Pliocene age for the Atacama Desert: Implications
219 for the desertification of western South America, *Geology* 30, 43–46.
- 220 Hatzinger, P.B., Böhlke, J.K., Sturchio, N.C., Gu, B., Heraty, L.J. and Borden, R.C. (2009),
221 Fractionation of stable isotopes in perchlorate and nitrate during in situ biodegradation in a
222 sandy aquifer, *Env. Chem.* (in press).
- 223 Jackson et al., 2009 (in prep)
- 224 Jaegle, L., Yung, Y. L., Toon, G. C., Sen, B., and Blavier, J. F. (1996), Balloon observations
225 of organic and inorganic chlorine in the stratosphere: The role of HClO₄ production on
226 sulfate aerosols, *Geophys. Res. Lett.* 23, 1749-1752.
- 227 Kang, N., Anderson, T. A., and Jackson, W. A. (2006), Photochemical formation of
228 perchlorate from aqueous oxychlorine anions, *Anal. Chim. Acta* 567, 48–56.
- 229 Lehmann, B.E., Davis, S.N., and Fabryka-Martin, J. T. (1993), Atmospheric and subsurface
230 sources of stable and radioactive nuclides used for groundwater dating, *Water Resour.*
231 *Res.* 29, 2027-2040.
- 232 Michalski, G., Böhlke, J.K., and Thiemens, M. (2004), Long term atmospheric deposition as
233 the source of nitrate and other salts in the Atacama Desert, Chile: New evidence from

- 234 mass-independent oxygen isotopic compositions, *Geochim. Cosmochim. Acta* 68, 4023-
 235 4038.
- 236 Murphy, D. M. and Thomson, D. S. (2000), Halogen ions and NO⁺ in the mass spectra of
 237 aerosols in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.* 27, 3217-
 238 3220.
- 239 Patterson L. J., Sturchio N. C., Kennedy B. M., van Soest M.C., Sultan M.I., Lu Z.T.,
 240 Lehmann B. E., Purtschert R., El Kaliouby B., Dawood Y., and Abdallah A.M. (2005),
 241 Cosmogenic, radiogenic, and stable isotopic constraints on groundwater residence time in
 242 the Nubian Aquifer, Western Desert of Egypt. *Geochemistry, Geophysics, Geosystems* 6,
 243 no. 1, Q01005, DOI 10.1029/2004GC000779.
- 244 Phillips, F.M. (2000) Chlorine-36. In: *Environmental Tracers in Subsurface Hydrology*,
 245 Cook, P. and Herczeg, A., Eds., Kluwer Academic Publishers, Boston, pp. 299-348.
- 246 Plummer, L.N., Böhlke, J.K., and Doughten, M.W. (2006), Perchlorate in Pleistocene and
 247 Holocene groundwater in North-Central New Mexico, *Environ. Sci. Technol.* 40, 1757–1763.
- 248 Plummer, M.A., Phillips, F.M., Fabryka-Martin, J.T., Turin, H.J., Wigand, P.E., and Sharma,
 249 P. (1997), Chlorine-36 in fossil rat urine: an archive of cosmogenic nuclide deposition over
 250 the past 40,000 years, *Science* 277, 538-541.
- 251 Rajagopalan, S., Anderson, T. A., Fahlquist, L., Rainwater, K. A., Ridley, M., and Jackson,
 252 A. W. (2006), Widespread presence of naturally occurring perchlorate in high plains of
 253 Texas and New Mexico, *Environ. Sci. Technol.* 40, 3156–3162.
- 254 Rao, B., Anderson, T. A., Orris, G. J., Rainwater, K. A., Rajagopalan, S., Sandvig, R. M.,
 255 Scanlon, B. R., Stonestrom, D. A., Walvoord, M. A., and Jackson, W. A. (2007),
 256 Widespread natural perchlorate in unsaturated zones of the Southwest United States,
 257 *Environ. Sci. Technol.* 41, 4522–4528.
- 258 Schumacher, J. (1960) *Perchlorates: Their Properties, Manufacture, and Uses*, Amer.
 259 Chem. Soc. Monograph Series No. 146, Reinhold Publ. Co., New York.
- 260 Simonaitis, R. and Heicklen, J. (1975), Perchloric acid: Possible sink for stratospheric
 261 chlorine, *Planet Space Sci.* 23, 1567-1569.

- 262 Sturchio, N. C., Hatzinger, P. B., Arkins, M. D., Suh, C., and Heraty, L. J. (2003), Chlorine
263 isotope fractionation during microbial reduction of perchlorate, *Environ. Sci. Technol.* 37,
264 3859-3863.
- 265 Sturchio, N. C., Böhlke, J. K., Gu, B., Horita, J., Brown, G. M., Beloso, A., Patterson, L. J.,
266 Hatzinger, P. B., Jackson, W.A., and Batista, J. (2006), Stable isotopic composition of
267 chlorine and oxygen in synthetic and natural perchlorate, In *Perchlorate: Environmental*
268 *occurrence, interactions, and treatment*, Gu, B. and Coates, J. D., Eds., Springer: New
269 York, pp 93-110.
- 270 Sturchio, N.C., Böhlke, J.K., Beloso, A.D., Jr., Streger, S.H., Heraty, L.J., and Hatzinger,
271 P.B. (2007) Oxygen and chlorine isotopic fractionation during perchlorate biodegradation:
272 Laboratory results and implications for forensics and natural attenuation studies, *Environ.*
273 *Sci. Technol.* 41, 2796-2802.

274 Table 1. Chlorine isotopic data for synthetic and natural perchlorate

<u>Synthetic perchlorate reagents</u>	$\delta^{37}\text{Cl}$ (‰)*	$^{36}\text{Cl}/\text{Cl}$ (10^{-15})	n**
KClO ₄ , Aldrich (lot 11921HO)	1.0	31±4	1
CsClO ₄ , Aldrich (lot LI09119JI)	1.6	34±2	2
HClO ₄ , Baker (9656-1, lot 146358)	0.6	28±4	1
KClO ₄ , Baker (lot 45155)	1.1	0.0±2.5	1
KClO ₄ , General Chem. Co. (lot 13)	0.6	6.2±1.6	2
NaClO ₄ , Mallinckrodt (lot 1190 KHJJ)	1.2	19±4	1
NH ₄ ClO ₄ , Kerr-McGee (lot 7974F)	0.7	22±3	1
NH ₄ ClO ₄ , Kerr-McGee (lot 5094)	1.5	37±4	1
NH ₄ ClO ₄ , Kerr-McGee (lot 7914NN)	0.3	30±3	1
NH ₄ ClO ₄ , PEPCON (lot 87010)	0.6	40±3	1
NH ₄ ClO ₄ , PEPCON (lot 87015)	0.7	38±4	1
NaClO ₄ solution, AMPAC, 2007	0.4	30±3	1
KClO ₄ , Hummel Croton	0.2	6.4±1.4	1
KClO ₄ , Taiwan	0.3	5.8±1.4	2
NaClO ₄ ·H ₂ O, EM, Germany (lot SX0693-2)	-3.1	4.5±1.3	1
NaClO ₄ ·H ₂ O, EM, Germany (1992)	-5.0	7.7±2.8	1
NaClO ₄ ·H ₂ O, EM, Germany (1995)	n.a.	3.2±1.0	1
<u>Synthetic perchlorate products</u>			
ClO ₄ ⁻ in highway safety flare	0.1	16±5	1
ClO ₄ ⁻ in bleach, Chlorox	14.0	9.6±1.6	1
<u>Atacama Desert (Chile) nitrate deposits</u>			
ClO ₄ ⁻ , Baquedano district groundwater	-12.9	83±10	1
Cl ⁻ , Baquedano district groundwater	-0.3	87±6	1
ClO ₄ ⁻ , Baquedano district, vertical vein fill	-12.8	52±16	1
Cl ⁻ , Baquedano district, vertical vein fill	-0.8	53±4	1
Cl ⁻ , N. Tarapaca district	-1.7	0.9±1.0	1

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Cl ⁻ , S. Tarapaca district	-1.2	18±3	1
Cl ⁻ , Tocopilla district	-1.7	79±4	1
ClO ₄ ⁻ , from fracture fill at -6 m, Estanque Oasis area	-14.3	55±8	2
ClO ₄ ⁻ , from fracture fill at -6 m, Estanque Oasis area	-13.6	590±20	1
ClO ₄ ⁻ , from surface pit mine, Estanque Oasis area	-11.8	460±23	1

Atacama Desert (Chile) nitrate products

ClO ₄ ⁻ , SQM industrial grade NaNO ₃ (purchased 2003)	-14.2	22±3	1
Cl ⁻ , SQM industrial grade NaNO ₃ , (purchased 2003)	n.a.	46±7	1

Southwest United States natural perchlorate

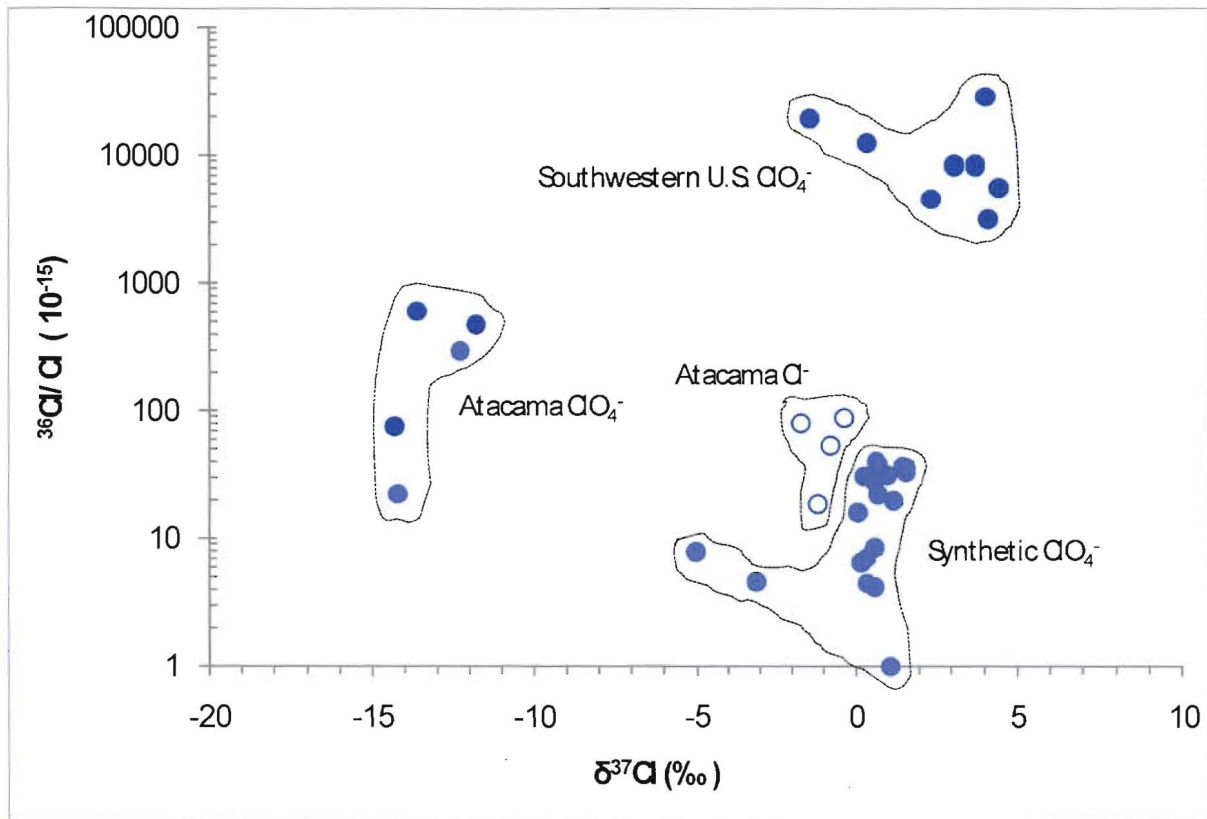
W. Texas, Martin shallow well (³ H = 2.5±0.2 TU)	2.4	4550±120	1
W. Texas, Martin deep well (³ H = 0.3±0.2 TU)	4.1	3130±100	1
NM, Roosevelt County, well (³ H = 0.2±0.2 TU)	4.5	5440±170	1
NM Water Canyon Gallery Spring (³ H = 2.2 to 8.0 TU)	4.1	28800±920	1
NM Valle Grande Spring (³ H = 0.03±0.09 TU)	0.4	12300±360	1
Albuquerque, NM, RR 8-2 (³ H = -0.2±0.3 TU)	3.1	8240±240	2
Albuquerque, NM, RR 16-1 (³ H = 0.3±0.3 TU)	3.7	8370±270	2
Mojave Desert soil leachate	-1.4	19200±890	1

Contaminated groundwater

ClO ₄ ⁻ from NJ Park Ridge well #10	-12.3	290±12	1
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* $\delta^{37}\text{Cl} = [R_{\text{sample}} - R_{\text{standard}}] - 1$, where $R = {}^{37}\text{Cl}/{}^{35}\text{Cl}$; uncertainty ± 0.2 (‰).

**n = number of ³⁶Cl analyses per sample



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277 Figure 1. $^{36}\text{Cl}/\text{Cl}$ (atom ratio) vs. $\delta^{37}\text{Cl}$ (‰) in representative samples of synthetic ClO_4^-
 278 reagents and products; natural ClO_4^- and associated Cl^- extracted from soil and
 279 groundwater from the Atacama Desert, Chile; and natural ClO_4^- extracted from groundwater
 280 and soil from the southwestern United States.

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