

Discovery of Natural Perchlorate in the Antarctic Dry Valleys and Its Global Implications

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In the past few years, it has become increasingly apparent that perchlorate (ClO_4^-) is present on all continents, except the polar regions where it had not yet been assessed, and that it may have a significant natural source. Here, we report on the discovery of perchlorate in soil and ice from several Antarctic Dry Valleys (ADVs) where concentrations reach up to $1100 \mu\text{g}/\text{kg}$. In the driest ADV, perchlorate correlates with atmospherically deposited nitrate. Far from anthropogenic activity, ADV perchlorate provides unambiguous evidence that natural perchlorate is ubiquitous on Earth. The discovery has significant implications for the origin of perchlorate, its global biogeochemical interactions, and possible interactions with the polar ice sheets. The results support the hypotheses that perchlorate is produced globally and continuously in the Earth's atmosphere, and that it typically accumulates in hyperarid areas, and that it does not build up in oceans or other wet environments most likely because of microbial reduction on a global scale.

Introduction

Contributions of anthropogenic and natural processes to terrestrial sources of perchlorate (ClO_4^-) and its effects have been the subject of numerous investigations over the past several decades (1–4). In the past few years, it has become increasingly apparent that perchlorate is present on all continents, except the polar regions where it had not yet been assessed, and that it may have a significant natural source (5, 6). Widespread use of perchlorate salts in a variety

of products, including solid rocket propellants, pyrotechnics, explosives, paint production, batteries, lubricants, automotive air bag systems, and as a byproduct of pulp processing (1, 2, 5), has also resulted in its release to aquifers and soils in populated areas and has increased concerns as to its effects on human health (4).

Naturally occurring ClO_4^- has been identified in the stratosphere and locally in mineral deposits in several arid locations (7–12). The largest accumulation, known since the 1800s, is in the nitrate deposits of the Atacama Desert in Chile (7, 8). It has also been reported in Death Valley, California (9), in potash deposits of Saskatchewan (Canada) and Bolivian playas (10), in geological formations in the Mission Valley Eocene deposits in San Diego, California (5), and in prehistoric aquifers of Texas and New Mexico (11, 12).

Several mechanisms have been proposed for the formation of natural perchlorate: photochemically in the atmosphere (11–15), on chloride-coated mineral surfaces as the end-product of photochemical reactions of chlorine precursors such as hypochlorite, chlorite, and chlorate upon exposure to ultraviolet (UV) radiation (16), by ozone oxidation of chloride in aqueous and dry systems (17), and by electrical discharge (6). Although the exact mechanism is not known, isotopic analysis demonstrates a stratospheric origin of the ClO_4^- in the Atacama Desert (15, 18–20). Consequently, it is likely that perchlorate is produced globally in the stratosphere and deposited everywhere but accumulates only in arid locations because of its high aqueous solubility. Widespread atmospheric deposition is also supported by the presence of trace levels of ClO_4^- in rainwater across the entire North American continent (21).

In the summer of 2008, NASA's Phoenix Lander found that the soil on Mars contained 0.6 wt % perchlorate (22, 23). This level of natural ClO_4^- is rarely attained on Earth; however, even though average concentrations in nitrate ore from the Atacama Desert contain 0.03 wt % ClO_4^- , concentrations as high as ~0.6 wt % have been measured (7, 8). With increasing evidence, the implication for Mars and Earth appears to be that given enough time, an appropriate environment, and a source of chlorine, perchlorate will accumulate.

The Antarctic Dry Valleys (ADV) are the largest ice-free expanse on continental Antarctica, encompassing an area of ~4800 km². The arid conditions of the ADV are due to the blocked flow of ice from the Polar Plateau by the Transantarctic Mountains and a lack of any significant precipitation. Figure 1 shows a view of a portion of the upper elevation Beacon Valley. The mean annual temperatures in the valleys are about -20 °C in the lower valleys (<1000 m elevation; Taylor, Wright, Victoria) to about -33 °C in the upper valleys (Beacon, University). The lower valleys can reach temperatures of 10 °C during the summer months and are relatively less arid with intermittent flowing meltwater streams. In the lower reaches of the coastal valleys, the permafrost is wet in the summer with an active zone (i.e., depth of moisture-related shrinkage or expansion over the seasons) of ~50 cm. However, in the higher elevation (~1600 m) Beacon and University Valleys, conditions are so cold (<0 °C) and moisture levels so low that dry permafrost (i.e., subfreezing unconsolidated soil) overlies ice-cemented ground throughout the year (24).

Here, we report on the discovery of perchlorate in soil and ice from several ADVs. Isolated from direct anthropogenic activity, ADV perchlorate provides unambiguous evidence that natural perchlorate is ubiquitous on Earth, produced globally and continuously in the Earth's atmosphere, and typically found in hyperarid areas or other locations where

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FIGURE 1. View of Beacon Valley, an ice-free sampling area in the Antarctic Dry Valleys, located at an altitude of ~1400 m.

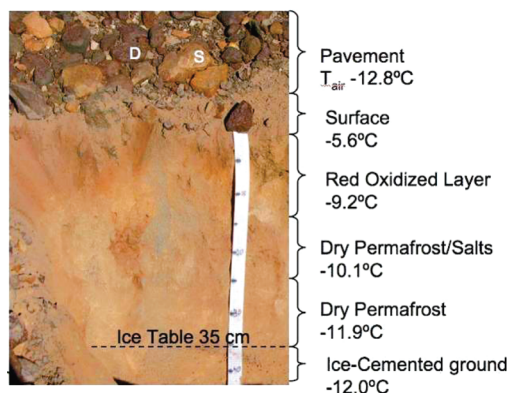


FIGURE 2. Soil pit #7 in University Valley, where samples were obtained, is a typical pit for a high-elevation dry valley. Because of extreme aridity and the predominance of Fe-rich dolerite and sandstone in the valley walls, the soil has a reddish cast and sandy loam consistency.

it has not been removed by leaching or bioreduction. The discovery has significant implications for the origin of perchlorate, its global biogeochemical interactions, and possible interactions with the polar ice sheets.

Experimental Section

Sampling. Soil samples were collected during the 2007–2008 field season from pits dug in all three of the microclimate zones of the Antarctic Dry Valleys, subxerous (wetter coastal), xerous (inland), and ultraxerous (highlands), where these terms describe increasing aridity (25). A typical pit for a high-elevation dry valley is shown in Figure 2. Samples of ~1 kg each (~500 g for Upper Wright Valley) were collected from a total of 10 pits from every distinctly identifiable horizon down to and including the ice-cemented soil. Table 1 summarizes the latitude, longitude, and elevation of all 10 pits. It also includes the depth to the ice-cemented soil and number of soil horizons sampled. All soil samples were maintained at $-20\text{ }^{\circ}\text{C}$ and shipped to our laboratories for analysis.

Analysis. Soil samples were homogenized by pulverizing with a mortar and pestle. A 1:5 weight ratio of soil to water was used for extraction of soluble species. Three grams of each soil was aliquoted and 1 g was placed in three separate 10 mL glass vials with 5 mL of 18.0 M Ω cm deionized water. The vials were capped, shaken for 30 s, and leached at room temperature for 23 h. Each solution was filtered once using a 0.2 μm filter. Ion chromatography was used to measure ClO_4^- in the leached solution. Analysis was performed on a

Dionex ICS-2000 Reagent Free IC using a 100 μL sample loop, an IonPac AG16 guard column (4 \times 50 mm I.D.), an IonPac AS16 analytical column with 35 mM potassium hydroxide at a flow rate of 1.25 mL/min, an anion self-generating suppressor 300 (4 mm) with a suppression current of 200 mA, and a DS6 heated conductivity cell. Samples were run undiluted in triplicate. The method detection limit (MDL) for ClO_4^- was 5 $\mu\text{g/L}$ in the leachate or 25 $\mu\text{g/kg}$ (dry weight) in the soil. Additional analysis of other common anionic species (Cl^- , NO_3^- , and SO_4^{2-}) was performed using the same procedure as for the ClO_4^- but with a 1:25 weight ratio of soil to water for the extraction of soluble species. The same Dionex ICS-2000 Reagent Free IC was used with a 25 μL sample loop, an IonPac AG18 guard column, an IonPac AS18 analytical column with 23 mM potassium hydroxide at a flow rate of 1.0 mL/min, an anion self-generating suppressor 300 (4 mm) set as a suppression current of 59 mA, and a DS6 heated conductivity cell. Samples were diluted 100-fold and run in triplicate.

To ensure the aliquot of soil analyzed was representative of the whole sample collected, we homogenized the soil prior to leaching. Three aliquots of soil were individually leached and run in triplicate through the IC on separate days. Thus, accuracy and precision standard deviations were calculated along with the average perchlorate values. A new set of calibration standards were run at the start of each day along with quality control blanks (solutions of Nanopure 18 m Ω /cm water containing no perchlorate) at the start of each run, between the calibration and the soil samples, and in between different soil samples to ensure no perchlorate cross over between standards or samples.

There was no internal standard utilized in this analysis. The Dionex column utilized (IonPac AS16) for perchlorate analysis was chosen specifically for its ability to separate perchlorate from other interfering ions. Likewise, a program was created specifically for this analysis, which allowed for a gap of approximately eight minutes between the previously eluted ion and the perchlorate ion.

Results and Discussion

Perchlorate was found to be present in all soil horizons, from the pavement to the ice-cemented soil, in all the samples from University and Beacon Valleys. The concentration of ClO_4^- in these soils ranged from 31 to 630 $\mu\text{g/kg}$ in University Valley and 167 to 575 $\mu\text{g/kg}$ in Beacon Valley. Figure 3 shows the perchlorate versus depth profile for the University and Beacon Valley soils. The depth profiles indicate a decrease in the concentration of ClO_4^- with depth below the surface pavement level, suggesting a surface depositional process.

While ClO_4^- was ubiquitous in the higher elevation ultraxerous zone, this was not the case for the lower elevation, xerous, and subxerous microclimate zones. Perchlorate was $\leq 25\text{ }\mu\text{g/kg}$ (MDL) in the Wright Valley pit and was only detected in one soil horizon from one pit dug in Victoria Valley at a concentration of 62 $\mu\text{g/kg}$. In Taylor Valley, perchlorate was present in 6 of the 23 sampled soil horizons but with no regular or discernible pattern. The concentrations were highly variable in this valley, ranging from the MDL to as high as 1100 $\mu\text{g/kg}$. The horizon containing this high concentration was between 9–12 cm in depth, sandwiched between two visible oxidized horizons, and composed of lithic fragments, perhaps a buried pavement. The observed distribution of ClO_4^- in these lower valleys is in keeping with the expectation that more frequent episodic wetting events will have mobilized portions of a relatively regular or homogeneous distribution, creating a “spotty” pattern in vertical and horizontal directions.

The presence of a continuous profile of perchlorate in all soil horizons of the ultraxerous zone valleys is the result of

TABLE 1. Description of Samples Collected

valley	pit number	latitude	longitude	elevation (m)	depth to ice table (cm)	number of soil horizons
subxerous (coastal)						
Lower Taylor	1	77°36''06.1' S	163°08''19.2' E	21 ± 5.5	28	5
Lower Taylor	2	77°36''06.1' S	163°08''19.6' E	21 ± 5.5	28	8
Lower Taylor	4	77°35''59.9' S	163°08''00.4' E	41 ± 4.9	29	5 ^b
Lower Taylor	3	77°35''43.8' S	163°07''23.4' E	108 ± 5.5	34	6
xerous (inland)						
Upper Wright	13	77°30''45.9' S	161°09''17.6' E	182 ± 5.9	23	4 ^b
Middle Victoria	8	77°22''28.9' S	161°48''29.9' E	357 ± 5.8	19	5 ^b
Middle Victoria	7	77°22''05.3' S	161°48''56.5' E	394 ± 5.2	27	5 ^b
ultraxerous (highlands)						
Lower Beacon	11	77°49''29.1' S	160°38''34.1' E	1209 ± 6.4	>75 ^a	5 ^b
Middle Beacon	20	77°49''49.5' S	160°38''58.8' E	1240 ± 5.6	20	5
University	7	77°51''43.6' S	160°42''23.8' E	1683 ± 5.9	34	5
University	10	77°51''52.9' S	160°43''40.2' E	1703 ± 5.5	19	4

^a The ice table was never reached. ^b The top (pavement) level soil horizon was not included because of insufficient homogeneity.

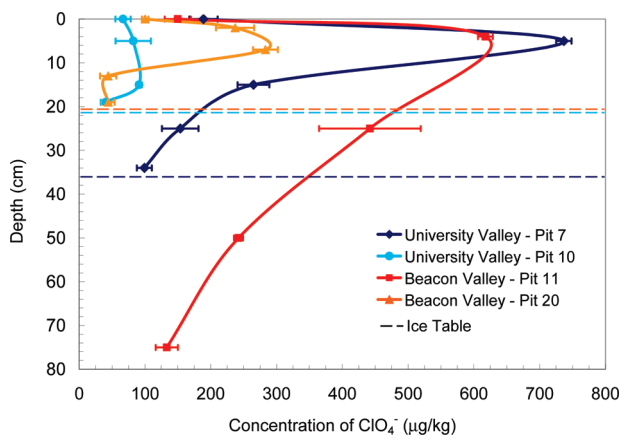


FIGURE 3. Depth profile for perchlorate in the ultraxerous soils from University and Beacon Valleys.

the hyper-arid conditions, which prevent the long-range aqueous migration of this highly soluble salt. In contrast, its lack of detection at concentrations >25 µg/kg (the MDL) in the soils of the xerous and subxerous zones is most likely due to the moderate climate present in these valleys. The higher temperatures and thus the presence of liquid water could facilitate transport of ClO₄⁻ to inaccessible locations or eventually to the ocean. It is also possible that the ClO₄⁻ is being utilized by perchlorate-reducing bacteria and ending up as chloride. However, most of these bacteria will preferentially reduce nitrate rather than perchlorate, unless anaerobic conditions are present, which is not likely in the shallow soil column (26, 27).

If both perchlorate and chloride are atmospherically deposited, we would expect their concentrations to be correlated in proportion to their deposition fluxes. In the ultraxerous zone, chloride was present in all soil horizons ranging from 166 to 994 mg/kg in University Valley and from 774 to 1886 mg/kg in Beacon Valley. As shown in Figure 4, the two ions are highly correlated in University ($R^2 = 0.98$) and Beacon ($R^2 = 0.94$) Valley. This correlation between perchlorate and chloride reinforces the idea of a common depositional and evapoconcentrated source. In the xerous and subxerous zones, the chloride levels were an order of magnitude higher with no apparent correlation to perchlorate ($R^2 = 0.03$). This is most likely due to the inconsistent presence of ClO₄⁻ in the wetter zones and also the variable contribution of chloride to these zones from marine aerosols.

Additional evidence for atmospheric production of ClO₄⁻ in the ultraxerous areas is its corresponding profile with that

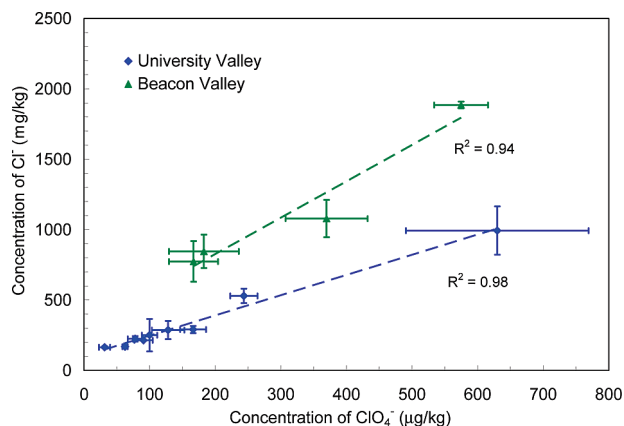


FIGURE 4. Correlation between perchlorate and chloride in soil samples from the ultraxerous zones.

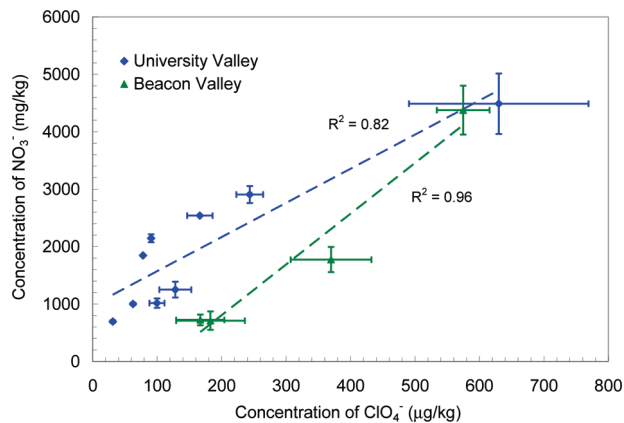


FIGURE 5. Correlation between perchlorate and nitrate in soil samples from the ultraxerous zones.

for nitrate, another anion known for its atmospheric production in the form of nitric acid aerosols (28), and its stratospheric origin in the ADVs from isotopic studies (29). Nitrate in the ultraxerous zone, like chloride and perchlorate, is present in all soil horizons, ranging from 695 to 4488 mg/kg in University Valley and from 712 to 4377 mg/kg in Beacon Valley. As shown in Figure 5, nitrate correlates highly with perchlorate in University ($R^2 = 0.82$) and Beacon ($R^2 = 0.96$) Valleys. As with chloride, no correlation was found between perchlorate and nitrate in the xerous and subxerous zones. The decreasing concentration of ClO₄⁻ from hyperarid valleys to areas with more moisture in the Antarctic demonstrates the

strong influence of a lack of water for the retention of ClO_4^- , while the correlation of ClO_4^- with atmospherically deposited NO_3^- (29) suggests an atmospheric source for ClO_4^- .

The large mass ratio of $\text{NO}_3^-/\text{ClO}_4^-$ production $\sim 10000/1$ in the ADVs is consistent with modeled atmospheric sources. A recent photochemical model of fluxes of NO_3^- and ClO_4^- over the Atacama Desert suggests a $\text{NO}_3^-/\text{ClO}_4^-$ flux ratio of $\sim 1000/1$, although this ratio is highly dependent upon poorly known rates of reactions that produce higher molecular weight chlorine oxides (ClO_x) (30). Thus, the difference of the Antarctic ratio with this model could be simply due to overestimated perchlorate production in the photochemical model or a smaller source of volatile chlorine in the troposphere over the Antarctic highlands compared to the Atacama Desert. These ratios can also be compared to the mass ratios found in precipitation 60000/1 (21) and in unsaturated zones 24000/1 (31), across and in the southwest of the United States, respectively. All these ratios may have errors of $\pm 50\%$, but even taken at face value, their differences most likely reflect the differences in the environment and its effects on persistence of the perchlorate.

The potential widespread presence of perchlorate, not only in the ADVs, but on the broader extent of the polar ice sheet is suggested by two additional findings: (1) a surface sample from Battleship Promontory at the northern extreme of the ADVs (~ 100 km north of Beacon Valley) containing $\sim 110 \mu\text{g}/\text{kg}$ ClO_4^- , and (2) an analysis of the sawdust from the Mars meteorite EETA79001 (collected during a 1979 Antarctic expedition in Elephant Moraine, ~ 200 km north of Beacon Valley) also showed the presence of $\sim 400 \mu\text{g}/\text{kg}$ ClO_4^- . However, the perchlorate leached from this meteorite may originate from either Mars or from the ice that may have melted around the meteorite while sitting on the ice surface. Future analyses will determine its provenance, but if it is from absorbed melted terrestrial water, it suggests that ClO_4^- is indeed widespread in the south polar ice cap at significant concentrations. If the ClO_4^- is from Mars, it would suggest that ClO_4^- is widespread on Mars, either way a tantalizing conclusion.

Combining the present results for the ADV with recent reports for the Arctic and the continental United States, provides an emerging picture of global perchlorate deposition, extent, and persistence in the ADV. The annual deposition of ClO_4^- across North America has been reported as 5.1×10^4 kg (21), or for a total land area of 9.5×10^6 km², about 5.3×10^{-3} kg/km²/yr. For the arctic (between 65°N and 90°N) an estimated 4.4×10^4 kg was deposited per year (32), or for a total area of 2.4×10^7 km², about 1.8×10^{-3} kg/km²/yr. Taking $\sim 3.6 \times 10^{-3}$ kg/km²/yr as a plausible estimate for the average global flux of perchlorate, gives us an annual deposition of $\sim 5.0 \times 10^4$ kg of perchlorate for the Antarctic continent. If we use this value (= 40 ng/cm²/yr) to calculate the total amount of ClO_4^- in a 1 cm² \times 35 cm deep section of soil in University Valley (Figure 3) representing the accumulation of ClO_4^- in the soil above the ice table, we obtain an integrated accumulation period of ~ 7 million years. This age is similar to that reported for the ice table in a pit in upper Beacon Valley that has been dated at ~ 8 million years using $^3\text{He}/^{21}\text{Ne}$ cosmogenic dating of surface boulders and laser fusion $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric dating of surface ash fall deposits (33).

In conclusion, the results presented here support an emerging paradigm for the global presence of natural perchlorate on the Earth. These and previous results support the hypothesis that ClO_4^- is globally formed in the atmosphere, but that the surviving deposits are restricted to hyperarid environments and that elsewhere ClO_4^- must have a long-term sink. For example, by using the above estimated global flux of perchlorate $\sim 3.6 \times 10^{-3}$ kg/km²/yr, the oceans would accumulate ClO_4^- at a rate of 1.8 pg/L/yr. Given the

measured seawater concentration of between the MDL ~ 0.09 to $\leq 0.1 \mu\text{g}/\text{L}$ (34), all oceanic ClO_4^- must be lost on a time scale of $\sim 5 \times 10^4$ years or less. Because aqueous ClO_4^- is very inert inorganically (3), we hypothesize that its lack of accumulation in the ocean or global ground waters may be attributable to microbial conversion to chloride in areas of low nitrate or anaerobic zones (35–37). Perchlorate provides an ideal electron acceptor for microbial utilization under anoxic conditions where it is reduced to chloride (4). Close to 100 strains of dissimilatory (per)chlorate reducing bacteria (DPRB) have been isolated from a variety of environments (4, 36). Interestingly, two genera of bacteria have been isolated and identified in pristine sediment and water from Lake Fryxell and Lake Hoare in the lower ADV (38).

Another possible implication for the presence of ClO_4^- in various ice caps is the ability of perchlorate salts to significantly suppress the freezing point of water. The alkaline earth salts of ClO_4^- have eutectic points that can form brines and depress the freezing point of water to as low as -70°C (39). It is a plausible hypothesis that continuous deposition of ClO_4^- on polar ice sheets over tens of millions of years (e.g., Antarctica and Greenland) could result in the concentration of its salts in the basal ice layers. The question then arises as to whether such accumulations would be sufficient to lower the melting point at certain locations under the ice cap, form lubricating brines, and possibly contribute to an increased rate of movement of the ice sheet that is currently not taken into account by ice flow models? Even though the answer to this question will have to await measurement of basal ice ClO_4^- , recent calculations for the north polar cap of Mars suggest that in that case there is enough ClO_4^- in the ice cap to generate a lubricating brine and facilitate its flow (40). On the Martian polar caps, however, the soil dust loads are higher and the ClO_4^- is also present at a higher concentration. Thus, the effect may be more significant on Mars than on Earth.

The discovery of perchlorate in Antarctica has significant implications for its origin, global biogeochemistry, and possible interactions with the polar ice sheets. The ADVs provide an ideal set of environments to better understand the deposition and distribution of perchlorate. Free of any local anthropogenic source of perchlorate, they range from the high-elevation valleys with no precipitation with subfreezing average temperatures to the coastal valleys with precipitation and flowing streams during the summer months. Further sampling and analysis of perchlorate is needed to determine its extent on the ice caps, global distribution, interactions with terrestrial ecosystems, and isotope systematics for tracing its atmospheric formation pathways.

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Note Added after ASAP Publication

There was an incorrect reference citation, (31) should be (39), in the version of this paper published ASAP February 15, 2010; the corrected version published ASAP February 18, 2010.

Literature Cited

- (1) Motzer, W. E. Perchlorate: problems, detection, and solutions. *Environ. Forensics* **2001**, *2*, 301–311.
- (2) Trumppolt, C. W.; Crain, M.; Cullison, G. D.; Flanagan, S. J. P.; Siegal, L.; Lathrop, S. Perchlorate: sources, uses and occurrences in the Environment. *Remediation* **2005**, *16*, 65–89.
- (3) Gu, B.; Coates, J. D. *Perchlorate: Environmental Occurrence, Interactions and Treatment*; Springer: New York, 2006.
- (4) National Research Council. *Health Implications of Perchlorate Ingestion*; National Academic Press: Washington, DC, 2005.

- (5) Duncan, P. B.; Morrison, R. D.; Vavricka, E. Forensic Identification of Anthropogenic and Naturally Occurring Sources of Perchlorate. *Environ. Forensics* **2005**, *6*, 205–215.
- (6) 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.
- (7) Ericksen, G. E. Geology and origin of the Chilean nitrate deposits. U. S. Geol. Surv., 1981, Professional Paper 1188.
- (8) 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.
- (9) Ericksen, G. E.; Hosterman, J. W.; St.Amand, P. Chemistry, mineralogy and origin of the Clay-Hill nitrate deposits, Amargosa River Valley region, California, USA. *Chem. Geol.* **1988**, *67*, 85–102.
- (10) Orris, G. J.; Harvey, G. J.; Tsui, D. T.; Eldrige, J. E. Preliminary analyses for perchlorate in selected natural materials and their derivative products. U. S. Geol. Surv. 2003, Open Field Report 03–314.
- (11) Rajagopalan, S.; Anderson, T. A.; Fahlquist, L.; Rainwater, K. A.; Ridley, M.; Jackson, W. A. Widespread presence of naturally occurring perchlorate in the high plains of Texas and New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 3156–3162.
- (12) Plummer, L. N.; Böhlke, J. K.; Doughten, M. W. Perchlorate in Pleistocene and Holocene groundwater in North-Central New Mexico. *Environ. Sci. Technol.* **2005**, *39*, 4586–4593.
- (13) Simonaitis, R.; Hecklen, J. Perchloric acid: a possible sink for atmospheric chlorine. *Planet. Space Sci.* **1975**, *23*, 1567–1569.
- (14) Rossi, M. J. Heterogeneous reactions on salts. *Chem. Rev.* **2003**, *103*, 4823–4882.
- (15) Bao, H. M.; Gu, B. H. Natural perchlorate has a unique oxygen isotope signature. *Environ. Sci. Technol.* **2004**, *38*, 5073–5077.
- (16) Kang, N.; Jackson, W. A.; Dasgupta, P. K.; Anderson, T. A. Perchlorate production by ozone oxidation of chloride in aqueous and dry systems. *Sci. Total Environ.* **2008**, *405*, 301–309.
- (17) Kang, N.; Anderson, T. A.; Jackson, W. A. Photochemical formation of perchlorate from aqueous oxychlorine anions. *Anal. Chim. Acta* **2006**, *567*, 48–56.
- (18) Sturchio, N. C.; Caffee, M.; Beloso, A. D.; Heraty, L. J.; Böhlke, J. K.; Hatzingerr, P. B.; Jackson, W. A.; Gu, B.; Heikoop, J. M.; Dale, M. Chlorine-36 as a tracer of perchlorate origin. *Environ. Sci. Technol.* **2009**, *43*, 6934–6938.
- (19) Motzer, W. E.; Mohr, T. K. G.; McCraven, S.; Stanin, P. Stable and other isotope techniques for perchlorate source identification. *Environ. Forensics* **2006**, *7*, 89–100.
- (20) Böhlke, J. K.; Sturchio, N. C.; Gu, B.; Horita, J.; Brown, G. M.; Jackson, W. A.; Batista, J.; Hatzingerr, P. B. Perchlorate isotope forensics. *Anal. Chem.* **2005**, *77*, 7838–7842.
- (21) Rajagopalan, S.; Anderson, T.; Cox, S.; Harvey, G.; Cheng, Q.; Jackson, W. A. Perchlorate in wet deposition across North America. *Environ. Sci. Technol.* **2009**, *43*, 616–622.
- (22) Hecht, M. H.; Kounaves, S. P.; Quinn, R. C.; West, S. J.; Young, S. M. M.; Ming, D. W.; Catling, D. C.; Clark, B. C.; Boynton, W. V.; Hoffman, J.; DeFlores, L. P.; Gospodinova, K.; Kapit, J.; Smith, P. H. Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. *Science* **2009**, *325*, 64–67.
- (23) Kounaves, S. P.; Hecht, M. H.; Kapit, J.; Gospodinova, K.; DeFlores, L.; Quinn, R.; Boynton, W. V.; Clark, B. C.; Catling, D. C.; Hredzak, P.; Ming, D. W.; Moore, Q.; Shusterman, J.; Stroble, S.; West, S. J.; Young, S. M. M. Wet chemistry experiments on the 2007 Phoenix Mars Scout lander mission: data analysis and results. *J. Geophys. Res.* **2010**, *115*, E00E10, doi:10.1029/2009JE003424.
- (24) Bockheim, J. G.; Campbell, I. B.; McLeod, M. Permafrost distribution and active-layer depths in the McMurdo Dry Valleys, Antarctica. *Permafrost Perigl. Proc.* **2007**, *18*, 217–227.
- (25) Campbell, I. B.; Claridge, G. G. C. A classification of frigid soils - the zonal soils of the Antarctic continent. *Soil Sci.* **1969**, *107*, 75–85.
- (26) Nozawa-Inoue, M.; Scow, K. M.; Rolston, D. E. Reduction of perchlorate and nitrate by microbial communities in vadose soil. *Appl. Environ. Microbiol.* **2005**, *71*, 3928–3934.
- (27) Tipton, D. K.; Rolston, D. E.; Scow, K. M. Transport and biodegradation of perchlorate in soils. *J. Environ. Qual.* **2003**, *32*, 40–46.
- (28) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics*; Wiley and Sons.; New York, 2006.
- (29) Michalski, G.; Bockheim, J. G.; Kendall, C.; Thiemens, M. Isotopic composition of Antarctic Dry Valley nitrate: implications for NO_x sources and cycling in Antarctica. *Geophys. Res. Lett.* **2005**, *32*, L13817.
- (30) Catling, D. C.; Clair, M. W.; Zahnle, K. J.; Quinn, R. C., Clarck, B. C., Hecht, M. H., Kounaves, S. P. Atmospheric origins of perchlorate on Mars and in the Atacama. *J. Geophys. Res.* **2010**, *115*, E00E11, doi:10.1029/2009JE003425.
- (31) 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.
- (32) Furdul, V. I.; Tomassini, F. Trends and sources of perchlorate in arctic snow. *Environ. Sci. Technol.* **2010**, *44*, 588–592.
- (33) Bidle, K. D.; SangHoon Lee, S.-H.; Marchant, D. R.; Falkowski, P. G. Fossil genes and microbes in the oldest ice on Earth. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13455–13460.
- (34) Martinelango, P. K.; Tian, K.; Dasgupta, P. K. Perchlorate in seawater: bioconcentration of iodide and perchlorate by various seaweed species. *Anal. Chim. Acta* **2006**, *567*, 100–107.
- (35) Coates, J. D.; Achenbach, L. A. Microbial perchlorate reduction: Rocket-fuelled metabolism. *Nature Reviews* **2004**, *2*, 569–573.
- (36) Coates, J. D.; Michaelidou, U.; Bruce, R. A.; O'Connor, S. M.; Crespi, J. N.; Achenbach, L. A. Ubiquity and diversity of dissimilatory (per)chlorate-reducing bacteria. *Appl. Environ. Microbiol.* **1999**, *65*, 5234–5241.
- (37) Xu, J.; Song, Y.; Min, M.; Steinberg, L.; Logan, B. E. Microbial degradation of perchlorate: principles and applications. *Environ. Eng. Sci.* **2003**, *20*, 405–422.
- (38) Bender, K. S.; Rice, M. R.; Fugate, W. H.; Coates, J. D.; Achenbach, L. A. Metabolic primers for detection of (per)chlorate-reducing bacteria in the environment and phylogenetic analysis of cld Gene sequences. *Appl. Environ. Microbiol.* **2004**, *70*, 5651–5658.
- (39) Pestova, O. N.; Myund, L. A.; Khripun, M. K.; Prigaro, A. V. Polythermal study of the systems M(ClO₄)₂-H₂O (M²⁺ = Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺). *Russ. J. Appl. Chem.* **2005**, *78*, 409–413.
- (40) Fisher, D. A.; Hecht, M. H.; Kounaves, S. P.; Catling, D. C. A perchlorate brine lubricated deformable bed could facilitate flow of the north polar cap of Mars: possible mechanisms for water table recharging. *J. Geophys. Res.* **2010**, *115*, doi:10.1029/2009JE003405, in press.

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