

SECTION 3 SOURCES OF PERCHLORATE IN THE ENVIRONMENT

I. INTRODUCTION

Perchlorate is an inorganic anion, consisting of four atoms of oxygen and one atom of chlorine, and is released in the environment when the highly soluble perchlorate salts, such as ammonium perchlorate are dissolved in water. Perchlorate is not easily degraded, since the chemical reaction by which the perchlorate anion is reduced to chloride anion has a high activation energy. Perchlorate does not bind well to other matter such as mineral surfaces or activated carbon. Due to these factors, perchlorate can persist for decades and move freely within the bodies of water.

Perchlorate is a man made chemical but is also naturally occurring. Widespread perchlorate contamination in the United States was observed after the spring of 1997 when an analytical method was developed by California's Department of Health Services (DHS), able to detect perchlorate levels in water as low as 4 parts per billion (ppb).¹

The presence of perchlorate in U.S. drinking water systems is mostly attributable to anthropological (man made) sources, namely activities associated with rocket fuel manufacturing or testing, and military operations. The U.S. Environmental Protection Agency (EPA) has confirmed that perchlorate releases have taken place in at least 35 states throughout the United States, including California, Nevada and Arizona. An interactive map with known perchlorate releases nationwide can be viewed on (which one) EPA's website.² Sites with more serious contamination levels include Lake Mead, Nevada, and the Colorado River, which supplies drinking water to more than half of Southern California, as well as Arizona and Nevada. Although the testing continues, it is believed that perchlorate may exist wherever rockets or rocket fuel were made or tested.³ So far in California, the perchlorate anion was detected in approximately 58 water systems. Perchlorate is present in more than 399 drinking water sources and primarily wells, and mostly those located in the counties of Los Angeles, San Bernardino and Riverside.⁴

In Europe and other parts of the world, some perchlorate salts are still used for the diagnosis and treatment of some thyroid conditions, such as Grave's disease.

II. NATURAL SOURCES

Chile possesses caliche ores which are rich in sodium nitrate deposits (a.k.a. Chile saltpeter). The sodium nitrate deposits are known to also contain naturally occurring perchlorate. The caliche is mined and leached to obtain the sodium nitrate, which is further refined to produce a commercial fertilizer. The product is marketed in the U.S. under the name Bulldog Soda. Annually, approx. 75,000 short tons of Chilean nitrate products are imported in the United States.⁵ The fertilizer derived from Chilean caliche

is generally marketed to growers of tobacco, citrus fruit, cotton and some vegetable crops.

It is not clear how much perchlorate is contained in caliche ores. Work done by the EPA's Office of Research and Development estimates that sodium nitrate fertilizer derived from Chilean caliche contains perchlorate at a ratio of approximately 0.5 to 2 milligram per gram.^{5 above} The EPA and other agencies have been analyzing fertilizers to determine the perchlorate concern, because the potential for groundwater and surface water contamination via agricultural runoff is a concern. The EPA concluded that at this time, it is premature to take any steps regarding the use of caliche saltpeter as a fertilizer, because further testing and research is needed before specific recommendations can be made.

It is generally accepted that the process of formation of perchlorate in Chilean caliche was natural. Some evidence points to the fact that perchlorate may be generated naturally in the atmosphere, or produce by surface oxidation.⁶ Natural processes for formation of perchlorate are believed to be at play in some areas of the U.S., such as the high planes of Texas. where the occurrence of perchlorate could not be attributed to any anthropological sources. Since the potential for perchlorate impacts began receiving attention in the 1990s, the USGS has undertaken various analytical studies of samples from likely perchlorate containing geological formations in the southwestern U.S.. These include playas, caliche-containing soils, dry lakebeds, and evaporite deposits. Evaporites minerals are those formed by evaporation concentration in arid environments.

The initial test areas included samples from California, Utah, Nevada, Arizona, and New Mexico. Although USGS (spellout) studies are ongoing, preliminary analytical results reveal that perchlorate appears to be naturally present in geological terrain where evapotranspiration greatly exceeds precipitation. In the initial round of sampling, more than 90 percent of the samples had detectable perchlorate, some at low concentrations and others involving sylvite potash deposits with perchlorate values up to 489 ppm (USGS Reports, 2003, 2004). Further USGS studies to verify and to expand possible areas are in progress. It appears that arid environments with little rainfall and high saline and mineral concentrations are conducive to perchlorate formation.⁷ Therefore, it is believed that some perchlorate may also be generated by natural processes, under certain conditions, although the exact mechanism is still largely unknown.⁸

III. ANTHROPOGENIC SOURCES

Most of the perchlorate contamination in the U.S. is attributed to the use of ammonium perchlorate as an oxidizer and primary ingredient in solid rocket fuel. The majority of sites where perchlorate was detected as a contaminant in groundwater are associated with the manufacturing or testing of solid rocket fuel by the Department of Defense (DOD), and by the National Aeronautics and Space Administration (NASA), and with the manufacture of ammonium perchlorate.⁹

Ammonium perchlorate is manufactured by the electrolysis of brine (sodium chloride dissolved in water). Sodium chlorate (NaClO_3) is formed as an intermediate chemical product, followed by sodium perchlorate (NaClO_4). Sodium perchlorate is subsequently reacted with ammonium chloride (NH_4Cl) to form ammonium perchlorate (NH_4ClO_4). The ammonium perchlorate crystals are removed from solution, dried and packaged. Ammonium perchlorate is further processed to make rocket fuel.¹⁰

The large scale production of perchlorate began in the US in the 1940s. Since the 1950's, over 870 million pounds of perchlorate have been manufactured in the U.S (EPA memo, May 1, 1998). The defense and aerospace industries purchase of more than 90 percent of all perchlorate manufactured, or roughly 20 million pounds per year.¹¹ The approximate percentages of perchlorate sold for specific uses are believed to be approximately 90 percent for oxidizer use, 7 percent for explosive use, and 1 percent for other uses, mostly pyrotechnics. Perchlorate typically counts for over 65 percent of the fuel in certain missiles, and nearly 70 percent of the solid propellant aboard the space shuttle.³ above

DOD has developed a prioritization for perchlorate impacts to drinking water (DOD, August 2004). Many locations have been contaminated by the production, testing, use, and disposal of conventional military munitions such as missiles and rockets, explosives, pyrotechnics, and flares. Activities identified in this guidance which may have contributed to perchlorate releases include the:

- manufacture and maintenance of solid fuel for missiles and rockets;
- manufacture of munitions;
- use of munitions for training or testing purposes;
- munitions demilitarization;
- flare disposal;
- munitions disposal;
- use of pyrotechnics;
- open burning/open detonation operations for disposal of perchlorate materials;
- Dye marker disposal as an impurity; and
- Electroplating as an impurity.

Perchlorate contamination also been suspected by other common industrial processes, including the:

- manufacture and uses of explosives, including the use of explosives for mining;
- manufacture and uses of fireworks;
- highway, railroad, and marine safety flares;
- use as the initiator component of air bag inflators; and
- use as a laboratory reagent in chemical studies.

IV. PAST PRACTICES THAT HAVE OR MAY HAVE LED TO PERCHLORATE CONTAMINATION

Solid Propellant Disposal

A large portion of the waste materials were either energetic or energetic-contaminated materials recovered from munitions and rockets including perchlorate-containing debris, scraps of rocket fuel and explosives, and rejected rocket motors.

Traditional methods of treatment and disposal include disassembly with some recovery of materials, open burning, open detonation, and incineration. The principal disposal method for the perchlorate material was burning in open burn/open detonation areas.

The growing public concern over open burn/open detonation methods has made these disposal methods difficult to authorize. Rocket fuel or explosives residuals not burned to completion can dissolve and cause contamination in soils and waters. Therefore, the OB/OD practice has been replaced with processes such as hydro-mining or a hog out process to wash solid rocket fuel with high-pressure water jets in order to reuse the rocket motor hardware.

In addition to the manufacture of missiles, rockets, and/or munitions, military operations can also produce large quantities of water contaminated with ammonium perchlorate. This is due to the fact that ammonium perchlorate has a limited shelf life and has to be periodically replaced in the country's missile and rocket inventory with a fresh supply.

The accepted method for ammonium perchlorate removal is manual removal followed by high-pressure water washout (hogout or hydrolysis). This method to wash solid rocket fuel with high-pressure water jets allows the reuse the rocket motor hardware, but generates large amounts of aqueous solution containing low concentrations of ammonium perchlorate. These dilute wastewaters are expensive to treat.

Unfortunately, in the original system configuration, the liquid waste from the hog out process was discharged untreated to the ground surface or into leaky lagoons or surface impoundments leading to contaminated surface and groundwater. The high hydraulic gradients generated by the industrial wastewater disposal, might have accelerated the downward migration of the perchlorate-contaminated water. These disposal practices led to groundwater contamination, especially in areas near former rocket manufacturing or testing facilities.

Large amounts of perchlorate contaminated water have been disposed since the 1940s at various sites throughout the country, but especially in Nevada, California, and Utah. This practice of untreated discharge is no longer employed due to the discovery of associated groundwater plumes. Current practice is to capture and treat the waste stream prior to discharge.

Demilitarization

Inventories of solid rocket fuel motors are growing at a significant rate as systems reach the end of their service life and treaties mandate their destruction. Currently, the large solid rocket motor disposal inventory shows 55 million pounds of propellant awaiting

disposal, and this number is expected to grow to 164 million by this year. A significant portion of this inventory contains ammonium perchlorate. The US Army will be required to demilitarize approximately 600,000 missiles over the next 10 to 15 years. There is about 80 million pounds of ammonium perchlorate oxidizer that can be recovered from obsolete missile propellants.

These will eventually require treatment or perhaps recycling of the perchlorate. DOD is currently developing a missile recycling capability. Ammonium perchlorate can now be reclaimed and recycled into new propellant. Alternative destruction technologies which rely on thermal treatment or disassembly/ recovery/ reuse (R3) are now either available or under development. In another process, the energetic-materials processing module uses super-critical anhydrous ammonia in a closed-loop system to recover the propellant for recycling. In 2003 and 2004, 14,600 tactical optical wire-guided missiles were processed in this way. Up to 15,000 missiles are projected for recycling in 2005.

DOD has development programs underway to replace ammonium perchlorate in solid rocket propellants. These efforts have included using alternative oxidizers such as ammonium nitrate, CL-20, and RDX, or using minimum signature or double-phase propellants in lieu of composites, such as perchlorates. While alternative energetic oxidizers exist, significant cost, availability, and performance issues remain that have so far prevented their use in fielded weapon systems and launch vehicles.

NASA recently announced a new paraffin-based rocket fuel being developed and tested to replace perchlorate-based fuels for spacecraft use (NASA, 2003). In testing since 2001, advertised advantages include non-toxicity, carbon dioxide and water combustion products, increased safety due to high stability, and the ability to be shut down and restarted quickly. However, the applicability of this paraffin-based fuel to meet DOD requirements for solid rocket fuels is unknown.

Rocket Launch Operations

During normal launches with solid rocket motors, the solid fuel and oxidizer is burned to completion, and spent solid rocket motor cases are dropped in the ocean. It is generally assumed that only a small amount of residual unburned propellant is left in the spent cases. The National Aeronautics and Space Administration (NASA) Shuttle operation at Kennedy Space Center (KSC) is the only U.S. launch program that systematically retrieves their spent solid rocket boosters (SRBs) from the ocean.

In the event of failure of a solid rocket motor, the debris generated by the destruction of the system will include some unburned solid rocket propellant. When solid propellant is released by an accidental or intentional destruction of an ignited SRM, the propellant will continue to burn although at a slower rate than when contained in the motor. The amount of propellant surviving a launch failure depends on several factors including time after launch. Historically, failure follow-up investigations have focused on safety or operational issues rather than the quantification or retrieval of scattered solid rocket propellant. Launch test programs that use non-ignited SRMs in drop tests can also release perchlorate when the unburned SRMs impact the ground or ocean.

From 1983 to 2000, there have been a total of 16 unmanned space launch failures, comprising approximately 5% of total launches. Fourteen of the failures were launch vehicles that had either a strap-on solid rocket motor or core solid motors. Of those 14, only 6 failures occurred early in flight such that debris would impact within 100 nautical miles (nmi) of the launch pad.(Aerospace 2001,2002) Observations and recovered debris from the actual failures indicate that the propellant fragments burn on descent, and, in fact, much of the solid propellant will burn up entirely during freefall. A method for quantifying the amount of propellant dispersed for a given launch failure is presented in the Aerospace Corporation Report titled "Assessment of Perchlorate Releases in Launch Operations" dated October 2001.¹²¹³

Use of Munitions

Expended munitions found in the impact areas can contribute to perchlorate contamination in two ways: (1) munitions containing perchlorate or rocket motors do not function as intended, either through low order detonation, or function as intended but do not completely consume the propellant or main charge and subsequent precipitation leaches perchlorate into the environment; or (2) complete detonation of these devices still leaves perchlorate residue on the soil, which then leaches into the environment. While the former may contribute a greater proportion of the total perchlorate mass loading, most weapons systems contain perchlorate and will still contribute a relatively low but continuous mass loading of perchlorate over time. As more ranges are tested for perchlorate contamination, it seems likely that more contamination will be discovered over time.

Defense Related Research, Development and Manufacturing Practices

At some locations, the past practice of using unlined ponds to collect production-derived wastewater may have resulted in releases of perchlorate to groundwater. Explosive solids containing perchlorate also may have accumulated in ponds as sludge. In other instances, wastewaters may have been discharged to surface waters.

Milling or Transfer of Perchlorate

Perchlorate is sometimes milled into finer grain or simply transferred from storage containers to process equipment. If done outdoors, dust blown onto soils can accumulate over time. Low but continuous concentrations of perchlorate deposited onto soil can contribute to soil and groundwater contamination.

Landfills

Perchlorate contamination may also be associated with landfill operations where perchlorate-containing materials have been disposed over time. Landfills may have been impacted through the disposal into surface impoundments. Leachate from such landfills could have groundwater impacts. Two of the confirmed perchlorate contaminated sites, Stringfellow and Casmalia, are former commercial Hazardous Waste Landfills (Class I).

From 1956 until 1972, the 17-acre Stringfellow site was operated as a hazardous waste disposal facility. In 1969, excessive rainfall caused the disposal ponds at Stringfellow to overflow and resulted in the contamination of Pyrite Creek and Channel. In 1978, heavy rains caused the California Regional Water Quality Control Board to authorize a controlled release of 800,000 gallons of wastewater from the site to prevent further waste pond overflow and massive releases. Heavy rains in 1979 and 1980 again threatened releases from the waste ponds.

The Casmalia Resources Hazardous Waste Management Facility accepted large volumes of waste material from April 1973 to November 1989. The facility included surface impoundments and a number of landfill units. There were releases of hazardous waste from Casmalia that occurred during the facility's operation. After the facility's interim status authorization was revoked in 1991, the facility was ordered to close the ponds pursuant to the Toxic Pits Cleanup Act. Casmalia is located adjacent to Vandenberg Air Force Base which also has handled perchlorate materials.

The Los Angeles Regional Water Quality Control Board has been conducting perchlorate sampling of municipal landfills (Class III). To date, 8 of 11 landfills have completed their groundwater sampling. Out of a total of 48 wells, only two wells at one location had perchlorate detected.

Firework Use and Manufacturing

Massachusetts Department of Environmental Protection (DEP) is investigating perchlorate contamination that appears to be from the residue of fireworks displays conducted over time. Fireworks-based perchlorate residue is suspected to have contributed to perchlorate groundwater contamination. The groundwater contamination appears to be the result of annual fireworks displays that occurred from 1996 to 2003 as well as military pyrotechnics such as smoke pots, smoke grenades, and various perchlorate-containing simulators.

The Santa Ana Regional Water Quality Control Board is investigating various fireworks manufacturers and distributors that located their businesses over a Formerly Used Defense Site with multiple storage magazines. Soil sampling is underway to determine if any of their operations contributed to the drinking groundwater beneath the cities of Colton and Rialto in San Bernardino County.

The California Fire Marshall reported 100,000 to 200,000 pounds of illegal fireworks a year coming out of Pahrump, Nevada every year. And he estimated that this amount only represents about 10% of what is coming into California from Nevada. Illegal fireworks are also brought in from Mexico. DTSC, the US EPA and the Office of State Fire Marshall has managed the destruction of approximately 143 tons of these fireworks which had been seized by local law enforcement and fire agencies throughout the state over the last several years at a cost of close to \$900,000. California will develop a comprehensive long-term solution to the seized illegal fireworks problem.

Blasting Operations

Groundwater contamination associated with explosives use is suspected at a construction site in Westford, Massachusetts. In a water sample from a pond near the site, DEP officials obtained a perchlorate concentration of 819 ppb and in an on site retention pond 12 ppb. One town water supply well that tested at 3.3 ppb has been shut down while a privately owned water well several hundred feet from the site also has a perchlorate concentration of 425 ppb. DEP officials believe the perchlorate contamination is related to explosives used to blast rock.

Research Laboratories

Some laboratories in industry, academia, DOD, DOE, or in other settings are using or may have used perchlorate compounds or perchloric acid in their research or analytical work. Los Alamos National Laboratory (LANL), perchlorate found in groundwater has been associated with past actinide research and high explosives synthesis and testing (LANL Perchlorate Update)

Fertilizer Manufacturing

Apache Nitrogen located south of Benson, Arizona on the west side of the San Pedro River, is being remediated for significant contamination of groundwater by nitrates. More recently, perchlorate was discovered in a shallow perched aquifer beneath one of the old unlined evaporation ponds. Perchlorate levels of 700-800 ppb have been found in this aquifer. The source of the perchlorate was Chilean sodium nitrate fertilizer with impurities of sodium perchlorate. This fertilizer was used by Apache Nitrogen as a feedstock for fertilizer production until 1995.¹⁴

V. APPROACHES FOR UNDERSTANDING THE SOURCES

General Methods

There is no single technique that will definitively link a specific perchlorate source to a specific detection at all locations. However, as more information on the various formulations and uses of perchlorate becomes known, a number of tools and techniques are emerging that, used in conjunction with one another, may allow the identification of different and distinct sources responsible for the presence of perchlorate in a water supply. These tools include:

- Applying the chemistry and environmental behavior of the perchlorate ion and its various associated cations to site-specific conditions,
- Differentiating the origins of various perchlorate salts,
- Differentiating perchlorate sources based on different manufacturing processes:
- Identifying specific uses and applications of perchlorate, in addition to its well-known use as an oxidizer for propellants and explosives,
- Establishing milestones in the development and use of perchlorate in its various applications, and
- Developing site-specific timelines for the introduction and use of perchlorate.

Relating historical site-specific uses to established perchlorate development and application milestones, and to local geologic and hydrogeologic conditions, in many cases, may help in linking specific sources to specific receptors.

Stable Isotope Analysis

Several analytic methods have been developed to differentiate between perchlorate that is anthropogenic in origin and perchlorate that is believed to be created by natural geochemical processes. One such method is the stable isotope analysis of chlorine and oxygen in the perchlorate anion. Perchlorate that is of natural origin is generally found in low levels, and is believed to have a unique isotope “signature”, which helps researchers distinguish it from perchlorate that is man made.¹⁵

The widespread occurrence of perchlorate reported in recent years in surface water bodies, ground water aquifers, and agricultural products across the U.S may have both anthropogenic and natural sources. This has led to an increasing interest in the development of forensic techniques for identifying the source of perchlorate in the environment¹⁶. Recent work has shown that there are significant differences in the stable chlorine and oxygen isotope ratios of perchlorate from different sources¹⁷. Isotopic analysis of these stable-isotope ratios of chlorine and oxygen can potentially be used to distinguish the source(s) of perchlorate in a given location.

It had been difficult to extract and recover isotopically measurable amounts of trace perchlorate from natural waters, in which perchlorate concentrations may be of the order of ppb. The recent development of a new class of bifunctional anion exchange resins for efficient sorption and removal of perchlorate, along with a new resin regeneration technique for recovering sorbed perchlorate, both developed at Oak Ridge National Laboratory, provide a means for nearly quantitative recovery of perchlorate from water samples collected in the field for isotopic analysis. Using these innovative separation-recovery technologies, a systematic characterization of the stable isotope ratios of chlorine and oxygen in perchlorate from different sources is possible. The preliminary results indicate that there are unique isotopic differences between various anthropogenic and natural perchlorate sources. When the data set of isotopically characterized perchlorate sources becomes sufficiently representative, stable isotope forensics of perchlorate may become useful for issues of source apportionment, natural attenuation, or monitoring of remediation efforts.

Additional approaches to determine the identification of perchlorate sources include the composition and age of water. The stable isotopic compositions of hydrogen and oxygen in groundwater could be used to distinguish water from precipitation, Colorado River, or a deep aquifer. Tritium-helium measurements can be used to determine the age of groundwater which is considered to be the time since isolation from the atmosphere. These secondary analytical methods do not provide direct evidence but corroborate the fate and transport model of perchlorate through the environment from a source.

REFERENCES:

- ¹ California Department of Health Services website. *Perchlorate: Early Findings in Drinking Water*. <http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/earlyfindings.htm>
- ² U.S. Environmental Protection Agency website. 2005. *National Perchlorate Detections as of September 23, 2004*. http://www.epa.gov/fedfac/documents/perchlorate_map/nationalmap.htm
- ³ Sharp, R., Walker, B. 2001. *Rocket Science: Perchlorate and the Toxic Legacy of the Cold War*. Environmental Working Group report. Available at: <http://www.ewg.org>.
- ⁴ California Department of Health Services website, 2005. *Perchlorate in California Drinking Water: Overview and Links*. <http://www.dhs.ca.gov/ps/ddwem/chemicals/perchl/monitoringupdate.htm>
- ⁵ Urbansky, E.T., Brown, S.K., Magnuson, M.L., Kelty, C.A. 2001. *Perchlorate Levels In Samples of Sodium Nitrate Fertilizer Derived from Chilean Caliche*. Environmental Pollution, 112, 299-302. Available at: <http://www.clu-in.org/download/contaminantfocus/perchlorate/EPCIO4.pdf>
- ⁶ Erickson, B.E. *Tracing the Origin of Perchlorate*. 2004. Analytical Chemistry, November 1, 2004, 388A – 389A. Available at: <http://www.geol.lsu.edu/News/FacNewsItems/2004BaoPerchlorate.pdf>
- ⁷ U.S. Department of the Interior, U.S. Geological Survey. 2003. *Preliminary Analyses for Perchlorate in Selected Natural Materials and their Derivative Products*. Open-File Report 03-314. Available at: <http://geopubs.wr.usgs.gov/open-file/of03-314/OF03-314.pdf>
- ⁸ Dasgupta P., Martinelango K, Jackson A, Anderson T, Tian K, Tock R, and Rajagopalan S, The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes, Environmental Science and Technology Article 10.(Web Release Date: January 29, 2005)
- ⁹ California Environmental Protection Agency, State Water Resources Control Board. 2002. *Draft Groundwater Information Sheet*. Available at: http://www.waterboards.ca.gov/gama/docs/tcp_jun2003.pdf
- ¹⁰ California Environmental Protection Agency, Office of Environmental Health Hazard Assessment. 2004. *Public Health Goal for Perchlorate in Drinking Water*. Available at: <http://www.oehha.org/water/phg/pdf/finalperchlorate31204.pdf>
- ¹¹ Senate Office of Research report. 2004. *Addressing Perchlorate Contamination of Drinking-Water Sources in California*. Available at: http://www.swrcb.ca.gov/rwqcb4/html/perchlorate/articles/04_0130_SenateOfficeofResearch.pdf

¹² Lang, V. I., Bohman, K. R., Tooley, J. T., Fournier, E. W., Brady, B. B., Nealy, D. C., "Assesment of Perchlorate Releases in Launch Operations," Aerospace Report No. TR-2001(1306)-3, SMC-TR-02-01, 25 October 2001.

¹³ Lang, V. I., Bohman, K. R., Tooley, J. T., Fournier, E. W., Brady, B. B., Nealy, D. C., "Assessment of Perchlorate Releases in Launch Operations II," Aerospace Report No. TR-2003(1306)-1, SMC-TR-03-13, 1 December 2002.

¹⁴ Arizona Department of Environmental Quality, Department of Health Services, Department of Water Resources, and Department of Agriculture, Perchlorate in Arizona: Occurrence Study of 2004

¹⁵ Bao, H., Gu, B., 2004. *Natural perchlorate has a unique oxygen isotope signature*. Environmental Science and Technology, 38(19):5073-7. Available at: http://www.swrcb.ca.gov/rwqcb4/html/perchlorate/articles/Perchlorate_Isotope_Identif.pdf

¹⁶ Stewart M.A., and Spivack A.J., 2004. The Stable-Chlorine Isotope Compositions of Natural and Anthropogenic Materials, Reviews in Mineralogy and Geochemistry; January 2004: v.55: p.231-254

¹⁷ Bao H. and Gu B., 2004. Natural Perchlorate Has a Unique Isotope Signature, Environmental Science and Technology 38, 5073-5077