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Perchlorate on Mars: a chemical hazard and a resource for humans

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Abstract: Perchlorate (ClO_4^-) is widespread in Martian soils at concentrations between 0.5 and 1%. At such concentrations, perchlorate could be an important source of oxygen, but it could also become a critical chemical hazard to astronauts. In this paper, we review the dual implications of ClO_4^- on Mars, and propose a biochemical approach for removal of perchlorate from Martian soil that would be energetically cheap, environmentally friendly and could be used to obtain oxygen both for human consumption and to fuel surface operations.

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Introduction

Perchlorate (ClO_4^-) has been directly detected at two landing sites on Mars at concentrations between 0.5 and 1%: at the Phoenix landing site at 68°N (Hecht *et al*. 2009) and at Gale Crater at 4.5°S (Glavin *et al*. 2013). In addition, perchlorate has been inferred at the two Viking landing sites, 22.5°N and 48.3°N (Navarro-Gonzalez *et al*. 2013). Measured abundances of ClO_4^- at each of these sites match total abundances of Chlorine measured from orbit using the Gamma Ray Spectrometer on board Mars Odyssey (Fig. 1), suggesting that ClO_4^- could be globally distributed on the planet, in top tens of centimetres of the regolith. This is consistent with models advocating an atmospheric origin of ClO_4^- (Catling *et al*. 2010). The amount of ClO_4^- in the surface regolith of Mars is significant compared with soils on Earth, where typical concentrations are three to four orders of magnitude lower than on Mars.

Since its discovery on Mars, ClO_4^- has become the focus of interest due to its possible role in destroying organics in thermal stage of analytical instruments sent to Mars to detect organics (Navarro-González *et al*. 2010). Quinn *et al*. (2013) have shown that ionizing radiation decomposes ClO_4^- resulting in the formation of hypochlorite, other lower oxidation state oxychlorine species and production of O_2 gas that remains trapped in the salt crystal. They suggest that ionization processing of ClO_4^- alone can explain the Viking LR and GEX results. Perchlorate could also lead to transient, metastable brines by way of deliquescence, even under current climate conditions (Rennó *et al*. 2009; Zorzano *et al*. 2009), and therefore play a role in the meagre hydrological cycle on Mars. In addition, ClO_4^- can be used as a terminal electron acceptor by a variety of prokaryotes (cf. Coates & Achenbach 2004), which has potential implications for habitability of Martian soils.

Aside from its scientific implications, ClO_4^- is also of considerable interest with respect to the exploration of Mars by humans. NASA has identified key strategic knowledge gaps (SKGs) that need to be addressed before humans can be sent to the planet (MEPAG 2010). Two key SKGs are potential hazards to humans and the existence of resources that can support human and robotic operations. Perchlorate could play a central role in both instances: it could be an important source of oxygen both for life support and to fuel surface operations, but it could also become a critical chemical hazard for astronauts. The possible implications of ClO_4^- on Mars as a hazard and as a resource could become a key aspect in design and implementation of future missions, particularly since the highest concentrations might occur in equatorial regions (Fig. 1), where humans are more likely to land. Here, we review the dual implications of ClO_4^- on Mars, and suggest an approach to ClO_4^- utilization that would minimize the hazard and maximize its use as a resource.

Perchlorate on Mars: a chemical hazard to humans

Perchlorate salts are very soluble in water, and the ClO_4^- ion is kinetically inert to reduction, and has little tendency to absorb in minerals or organic surfaces, which make it a very persistent compound in the environment and also in solution. Perchlorate is a health concern because it can impair proper functioning of the thyroid gland, by competitively inhibiting the uptake of iodine ions, thereby hindering hormonal output (Fig. 2) (cf. Smith 2006). Thyroid hormones are responsible for regulating mammalian metabolism; a long-term reduction in iodide uptake in an adult can ultimately result in thyroid hyperplasia, goitre, decreased metabolic rates and slowing of the function of many organ systems. The competitive effect of ClO_4^- on iodine uptake is reversible once ClO_4^- exposure

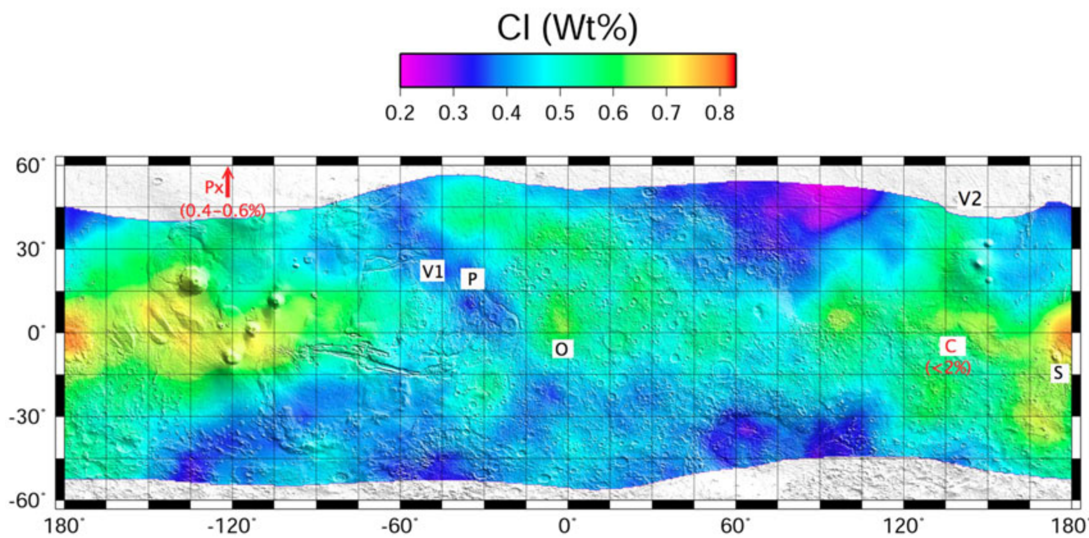

Fig. 1. Equatorial and mid latitude distribution of Cl within the top 1 m of Mars measured by the Gamma Ray Spectrometer onboard Mars Odyssey (from Keller *et al.* 2006). The global concentration of Cl is similar to the measured concentration of ClO_4^- at two landing sites (Px = Phoenix; C = Curiosity), suggesting that ClO_4^- could be globally distributed. V1-Viking 1; V2 = Viking 2; O = Opportunity; S = Spirit; P = Pathfinder.

ceases. Once ingested, ClO_4^- is rapidly absorbed and has a short residence time in the human body (ca. hours). The reference dose (RfD) for ClO_4^- is 0.7 μg kg^{-1} of body weight per day (i.e. Brown & Gu 2006). This is the daily oral exposure that is to remain without an appreciable risk of deleterious effects during a lifetime, and corresponds to drinking water equivalent level of 24.5 μg l^{-1}. The possible deleterious effects of ClO_4^- are still unclear, particularly with regard to long-term exposure (ATSDR 2008), which only emphasizes the need to understand the potential of ClO_4^- as a hazard to humans on Mars before the first manned mission.

The persistence of ClO_4^- in the environment, and its possible widespread distribution on the Martian surface, make it a global hazard to humans on the planet. The main routes of exposure of astronauts to ClO_4^- on Mars would be through direct inhalation of dust into the respiratory system, ingestion of contaminated water and ingestion of foods grown in the presence of ClO_4^-. Incorporation through direct skin contact is less likely. Exposure to ClO_4^- through inhalation is not a serious problem on Earth, where concentrations are typically low, but it could become a major concern on Mars. Like the Moon, an important fraction of the Martian surface is covered in dust. Dust became one of the main hazards to astronauts on the Moon largely due to the abrasive nature of lunar dust particles, which could cause lung damage. Inhalation of dust particles <5 μm in size was of particular concern, because particles of this size cannot be expelled by lung mucus. Aside from abrasiveness, mobile fraction of Martian dust may contain up to 1% ClO_4^- or more, and inhalation of a few milligrams of dust would already surpass the RfD, if perchlorate were quickly absorbed into human blood circulation. Astronauts could breathe airborne dust from their dusty spacesuits after extra-vehicular activity (EVA), as occurred with astronauts on the Moon during the Apollo missions, and exposure to ClO_4^- could also be critical during dust storms. Contrary to the Moon, and due to the presence of perchlorate, *all* dust particle sizes on Mars are a potential human hazard.

Managing ClO_4^- exposure on Mars would be in many ways no different than managing for example, uranium, lead or general heavy metal contaminated areas in modern mines where dust suppression, dust extraction and regular blood monitoring is employed. The primary dust suppression method in mines is water spray dust suppression systems (Xie *et al.* 2007). These could be employed in airlocks in the form of fine fog sprays to clean dust particles <1 μm. Water sprays using ultrasonic generated droplets that match the target dust particles (Xie *et al.* 2007) ensure dust affects the droplets. Dust particles smaller than water droplets do not affect the droplets but flow around them in the airstream above the boundary layer, and generating water droplets suited for all dust sizes would be a challenge. A wash down spray could also be employed to clean suits and equipment with dust deposits. Perchlorate dust would quickly go into solution in this water environment and be drained away. A separated process could be used to recycle water for the sprays and to decompose ClO_4^- into usable O_2 (see below). Vacuum systems with air-purged filters are also used in the mining industry in particular for habitable spaces. This includes, electrostatic cleaners or High Efficiency Particular Air filters (HEPA) technology and can be applied to habitats on Mars. These practices can be coupled with appropriate spacesuit technology specific to the type of exploration being undertaken. Regular monitoring toxicity levels in astronaut blood, as per many mining practices can be employed to manage individual exposure risks.

Another critical aspect of ClO_4^- as a chemical hazard to astronauts is its possible presence in ground ice. The Phoenix Lander detected ClO_4^- in the regolith at polar latitudes down to the ice table (Hecht *et al.* 2009), but no data exist regarding its

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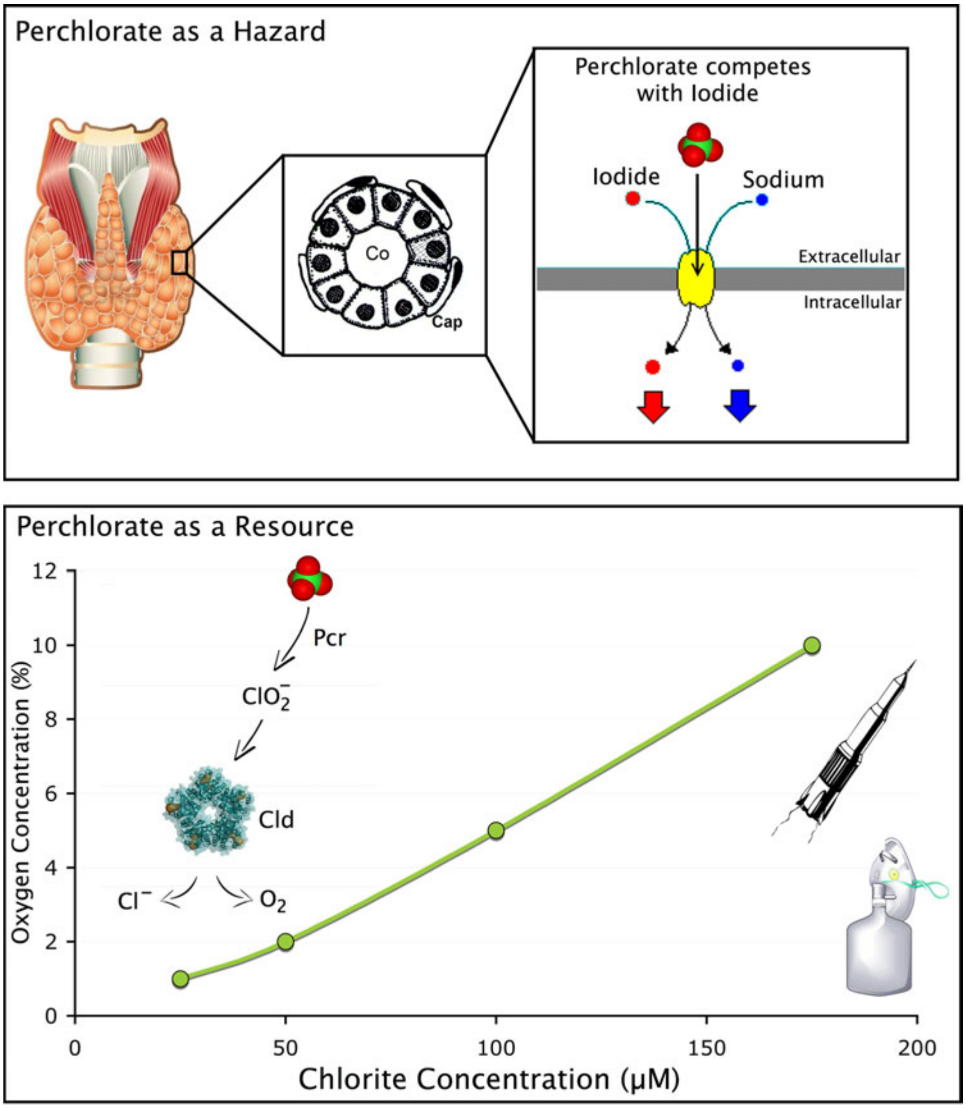

Fig. 2. *Top*. Perchlorate as a hazard. ClO_4^- can impair proper functioning of the thyroid gland, by competitively inhibiting the uptake of iodine ions, thereby hindering hormonal output. *Bottom*. Perchlorate as a resource. Perchlorate can be biochemically degraded into innocuous Cl^- and usable O_2 by means of concentrated extracts of naturally occurring enzymes. Data from Coates and Achenbach (2004)

concentration within ground ice. Given the persistence of ClO_4^- in water, extraction of ground ice for human consumption would be compromised if ClO_4^- were present at concentrations similar to those in the dry regolith or higher. Similarly, the use of extracted water for food growth would also be compromised because ClO_4^- can bio-accumulate in the tissue of vegetables (Ha *et al*. 2011). Knowledge of the chemical composition of ground ice on Mars with respect to ClO_4^- would be critical to assess whether ground ice can be used as a resource for humans, or whether ClO_4^- removal prior to use would be a requirement.

At the time of writing ClO_4^- is the only Cl-oxyanion that has been found on Mars. However, studies on Earth show that chlorate (ClO_3^-) co-occurs with ClO_4^- in all environments, often at equimolar concentrations. While the possible effects of ClO_3^- on human health are far less understood, they cannot be disregarded in the event of a human mission, unless further investigations suggest otherwise. In addition, as mentioned above, ionizing radiation can decompose small quantities of ClO_4^- into other Cl-oxyanions, such as ClO_2^- and ClO^- (Quinn *et al*. 2013), which are much more reactive and can be the cause of other health concerns such as respiratory difficulties, headaches, skin burns, loss of consciousness and vomiting. These more reactive species might also be cause for concern with regard to the corrosion of astronaut suits, instruments and other materials. As such, in preparation for human exploration it is important to fully characterize the composition of the Martian regolith, and specially its most mobile fraction, with respect to ClO_4^- and other reactive Cl-oxyanions, such as ClO_3^-, ClO_2^-, ClO_2 gas and ClO^-.

Perchlorate removal from Martian dust and regolith could be done in a number of ways, but in the next section we propose a mechanism for removal that would be energetically cheap, environmentally friendly and could be used as a source of oxygen both for human consumption and for surface operations.

Perchlorate on Mars: a useful resource for humans

The ClO_4^- ion consists of a central chlorine atom surrounded by a tetrahedral array of four oxygen atoms. Owing to its strong oxidizing power at higher temperatures, ammonium perchlorate (NH_4ClO_4) is predominantly used as an energetic booster or oxidant in solid rocket fuel. The most beneficial use of ClO_4^- on Mars would be as a source of O_2 for human consumption and to fuel surface operations. For example, humans breathe or consume 550 litres of oxygen per day. Based on the amounts of ClO_4^- measured in Martian regolith, a daily supply of oxygen for one astronaut could be obtained by complete dissociation of ClO_4^- contained in 60 kg of regolith (40 litres).

More importantly, mining out oxygen from ClO_4^- in Martian regolith could be done cleanly and with minor alterations to the regolith, taking advantage of existing microbial biochemical pathways for perchlorate metabolism. It has been known for several decades that some micro-organisms can reduce ClO_4^- under anaerobic conditions, and more than 50 dissimilatory perchlorate-reducing bacteria have been isolated in pure culture (Coates and Achenbach, 2004). The biogeochemical redox cycle of chlorine is well understood (i.e. Coates & Achenbach 2006), and consists of three key steps: (1) ClO_4^- reduction; (2) chlorite dismutation and (3) oxygen reduction. The first enzymatic step of the pathway, perchlorate reduction to chlorite, is performed by perchlorate reductase (*Pcr*). The chlorite is subsequently converted to chloride and oxygen by chlorite dismutase (*Cld*). Finally, oxygen is reduced to water by an oxygen reductase. The entire metabolic pathway converting perchlorate to Cl^- and molecular oxygen occurs in the periplasmic space of the cell, owing to the toxicity of both chlorite and oxygen (Coates and Achenbach, 2004). For our purposes, the key biochemical step in this pathway is reduction of ClO_4^- to chlorite and dismutation of chlorite with resultant formation of oxygen. Studies with washed whole-cell suspensions and purified enzyme preparations demonstrated that *Cld* is highly specific for chlorite, and alternative anions tested are not substitute substrates for dismutation. Purified *Cld* has a specific activity of 1928 μmol chlorite dismutated per mg of protein per minute (Coates and Achenbach, 2004). Purified enzymes involved in microbial ClO_4^- metabolism could be the basis of an automated system of oxygen generation from perchlorate in Martian regolith. Based on the specific activity of *Cld*, 100 g of purified enzyme could generate a daily supply of oxygen for one astronaut in >1 h (Fig. 2). As a proof of concept, we have developed a portable emergency O_2 system that can provide an astronaut with 1 h of breathable O_2 based on soil perchlorate decomposition catalysed by enzymes extracted from perchlorate reducing bacteria. The astronaut would collect ca. 6 kg of Martian regolith into a bag and add water, which would dissolve and carry the highly soluble ClO_4^- into a container holding the *Pcr* and *Cld* enzymes. The O_2 produced could be directly fed into the astronaut's suit.

The biochemical extraction of oxygen from ClO_4^- in Martian regolith would be compliant with Planetary Protection requirements, because it would be based solely on purified enzymes, and not on introduced terrestrial species. Once the oxygen was extracted, the regolith could be returned to the surface free of ClO_4^-, and in the case of ground ice, the water would be suitable for human consumption or food growth.

Conclusions

Perchlorate on Mars has two opposing aspects, it poses a serious risk to astronauts but can also be a life-saving resource. As such, ClO_4^- on Mars ought to be considered an SKG that needs to be addressed prior to exploration of the planet by humans. Inhalation of ClO_4^--bearing dust particles could be a major concern, but mitigation technologies exist in the mining industry that could be applied on Mars. Perhaps the most efficient and cost-effective mechanism to mitigate the risk of ClO_4^- toxicity on Mars is by developing biochemical systems that decompose ClO_4^- into innocuous Cl^- and usable O_2, based on concentrated extracts of natural enzymes. This way, mitigation of ClO_4^- toxicity could be coupled to *in situ* resource utilization.

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