



Mechanochemical generation of perchlorate

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ABSTRACT

Perchlorate (ClO_4^-) is widespread in the solar system having been detected on Earth, on Mars, in chondrite meteorites and in lunar samples. On Mars, perchlorates expand the potential for habitable conditions by lowering the freezing point of liquid water in the formation of brines. In future manned space exploration their presence poses a hazard to human health, however, it also represents opportunities as a source of oxygen and fuel. Despite their prevalence, the mechanism(s) of perchlorate formation in different solar system environments are poorly understood. Here we demonstrate that perchlorate can be generated through the mechanical activation of silicates in the presence of chloride.

1. Introduction

Natural terrestrial perchlorates are found in arid, desert environments. The Atacama Desert hosts the most extensive deposits with perchlorate abundancies of 0.03 wt% (300 ppm) typical of recovered nitrate ore (Erickson, 1983). Perchlorates have also been detected in both chondrite meteorites (including the Murchison meteorite) and lunar samples ($\text{ClO}_4^- < 1$ ppb; Jackson et al., 2010). On Mars, the Phoenix Scout Lander determined the presence of 0.4 to 0.6 wt% perchlorate in three soils sampled from the ejecta blanket of Heimdal crater in the Martian northern Arctic region (Hecht et al., 2009; Kounaves et al., 2010). A more global distribution of perchlorates has also been indirectly inferred by the detection of chlorohydrocarbons by the Viking landers and the NASA rover Curiosity; consistent with the decomposition of perchlorate salts during pyrolysis (Navarro-González et al., 2010; Glavin et al., 2013). However, the origin(s) of perchlorates remains uncertain.

On Mars, gas-phase reaction pathways alone are insufficient by orders of magnitude to explain the abundancy of measured perchlorate due to the low levels of atmospheric ozone and chlorine (Smith et al., 2014). A number of heterogeneous mechanisms have therefore been posited for the formation of perchlorates on Mars. Photo-oxidation of the naturally occurring semiconducting minerals rutile and anatase (TiO_2) produces highly oxidising valence band holes (h^+) capable of inducing perchlorate formation in the presence of H_2O (Schuttlefield et al., 2011). Quartz (SiO_2), with its larger band gap than TiO_2 , has also been shown to

enhance the production of photo-chemically produced perchlorate, where an increased UVC dose correlates with increased perchlorate production (Carrier and Kounaves, 2015). Electrostatic discharges generated in dust storms, with an oxidative power (per electron) orders of magnitude higher than the corresponding UVC energy (per photon), have also been shown to produce perchlorate under laboratory conditions (Wu et al., 2018).

Importantly, however, the mechanical fracturing of silicate minerals may provide an alternative mechanism for perchlorate generation. The mechanical fracturing of silicate minerals produces chemically active sites via the homolytic (Eq. 1) or heterolytic (Eq. 2) breaking of covalent silica-oxygen bonds (Schrader et al., 1969; Hochstrasser and Antonini, 1972; Kita et al., 1982):



In the presence of O_2 these sites react to form surface-bound reactive oxygen species (ROS) (e.g. SiO_2^\bullet , SiO_3^\bullet and $\text{Si}^+\text{O}_2^\bullet$) (Kita et al., 1982; Schrader et al., 1969; Fubini et al., 1987). Surface-bound ROS can participate in a series of reactions with H_2O that generate further ROS, such as hydrogen peroxide (H_2O_2), hydroxide ions (OH^-), hydroxyl radicals (OH^\bullet), superoxide radicals (O_2^\bullet), and singlet oxygen ($^1\text{O}_2$) (Fubini and Hubbard, 2003; Shi et al., 1995; Hurowitz et al., 2007; Bak et al., 2017; Hendrix et al., 2019). Further to this, the presence of Fe (II/III) can generate $\text{OH}^{\bullet/-}$ in reactions with H_2O_2 via Fenton processes, and

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O₂ as an intermediary in the Haber-Weiss cycle (Fubini et al., 1987).

The breaking of the silica-oxygen bond occurs naturally via a number of mechanisms including, but not limited to, seismic faulting (Kita et al., 1982), meteorite impact events (Hurowitz et al., 2007), glacial crushing (Telling et al., 2015) and wind driven particle saltation (Merrison et al., 2010) as well as by human activities such as sand blasting and rock drilling (Castranova, 1994). To address the question of whether ROS generated from mechanically activated silicate surfaces can facilitate the oxidation of chloride to perchlorate, we conducted laboratory experiments on a suite of single phase minerals.

2. Experimental procedure

In this study we assessed the perchlorate generation potential of the major rock forming minerals olivine (Fo 93), pyroxene (Wo 46), feldspar (An 53) and quartz, which together constitute >80% of the Martian regolith (Bish et al., 2013; Yen et al., 2005), as well as the clay mineral nontronite, a common Fe(III) rich phyllosilicate typical of altered basalt and common on Mars (Poulet et al., 2005). Apatite and calcium carbonate, both of which are found in inventories of Martian crustal material (Bandfield et al., 2003; Kah and Team, 2015), were also tested as non-silicate controls. Chloride is measured in both bedrock and soils at Gale crater associated with up to ~25 wt% halite (Thomas et al., 2019). Minerals were identified by X-ray diffraction (Fig. S1). Elemental abundancies (wt%), acquired by X-ray fluorescence for olivine, pyroxene, feldspar (this study) and nontronite (Gates et al., 2002) are provided in Supplementary Table 1.

Prior to usage all samples were crushed to between 125 and 300 µm (fine – medium sand) and were repeatedly washed with deionised and then nanopure 18.2 MΩ-cm water to remove any adhered fine particles as well as any ionic/soluble impurities. The sands were then dried at 70 °C for 48 h. This process would also quench any reactive silicate/silica-oxide radicals generated in this initial crushing process (Bak et al., 2017). 10 g of each sample was weighed and added to 0.65 g of NaCl (Sigma Aldrich: S7653) (Carrier and Kounaves, 2015) in a gastight stainless steel encased 80 mL agate ball mill, using a Fritsch P6 Planetary Ball Mill. The ball mill was rotated at 250 rpm for 5 min for each mineral. All experiments were run in triplicate and results are reported as the mean ± 1 standard deviation.

To test the role of atmospheric oxygen in perchlorate generation experiments were carried out where olivine was crushed under N₂ and the powders leached with oxygen free water. An N₂ atmosphere was added to the gastight stainless steel encased agate ball mill by connecting it to a vacuum line, evacuating to <1 × 10⁻² mbar, and flushing with N₂, in five consecutive cycles. The lid of the agate ball mill contained a viton o-ring to ensure a tight seal and this entire apparatus was enclosed within a custom built triaxial clamping system. After the last N₂ flush was performed, the ball mill was equilibrated to atmospheric pressure by opening a valve connecting the gas line to a closed gastight syringe.

Following grinding each sample was leached in 25 mL of 18.2 MΩ-cm water for one hour, without stirring, to dissolve any perchlorate. In oxygen free experiments the samples were transferred to volumetric flasks within an N₂ flushed glove bag, 25 mL of 18.2 MΩ-cm oxygen free water was added and thick butyl rubber bungs were used to seal the flasks before the ball mill was removed from the glove bag. Oxygen levels in the water prior to addition were below detection (< 0.1%) with a PreSens oxygen dipping probe (DP-PSt3). In all cases, 10 mL of the leachate was taken up in a syringe and 8 mL passed through a 0.2 µm nylon filter and Dionex™ Ongaard™ II Ag 2.5 cc pre-treatment cartridge at a flow rate of ca. 2 mL min⁻¹.

The stored sample was then injected onto the Ion Chromatograph (partial cut volume of 20 µL) using a 25 µL sample loop and a Dionex Ionpac AS16 analytical column, and an AG16 guard column. The eluent consisted of 50 mM potassium hydroxide at a flow rate of 0.25 mL min⁻¹ with a suppression current of 31 mA. The method detection limit for

perchlorate was 0.56 nmol corresponding to ~2.3 ppb in leachate which was equivalent to 5.7 ppb in the original solid sample. Example calibration chromatograms are provided in supplementary Fig. S2.

3. Results & discussion

Mechanical activation of olivine, pyroxene, feldspar, quartz and nontronite, in the presence of halite, resulted in significant perchlorate production above instrument blanks ($p < 0.05$; Fig. 1; Table S2). Olivine generated the most perchlorate (7.0 ± 1.5 ppb; $n = 3$); significantly ($p < 0.05$) more than feldspar (4.4 ± 1.5 nmol; $n = 3$), nontronite (3.8 ± 2.2 nmol), pyroxene (3.1 ± 1.9 nmol; $n = 3$) and quartz (1.4 ± 0.1 nmol; $n = 3$). There was no detectable perchlorate generated in experiments conducted with apatite and calcite (< 0.57 nmol ClO₄⁻; Fig. 1), an observation consistent with the hypothesis that the breaking of silicate bonds was required to generate perchlorate. The oxygen free experiments resulted in no significant perchlorate generation above instrument blanks ($p > 0.05$; Fig. 1), indicating that the presence of O₂ and the formation of surface bound ROS is necessary to generate perchlorate. Whilst pressure and oxygen levels on Mars are lower than on Earth, this may not limit the amount of perchlorate that can be generated as the Martian atmosphere represents a large reservoir of O₂ that is continuously replenished by photochemical reactions (e.g. Bak et al., 2017; Catling et al., 2010). Further to this, other atmospheric reactive oxygen species (e.g. O[•]) that are generated during aeolian abrasion (Bak et al., 2017) may contribute to reaction rates. Future experiments designed to clarify these concepts are required.

In the highly irradiating conditions at the Martian surface, O₂[•] can form on the surface of silicate minerals and metal oxides (Yen et al., 2000; Zent et al., 2008). It has been proposed that this would lead to the generation of perchlorate on Mars (Carrier and Kounaves, 2015). Whilst studies have clearly shown an increase in perchlorate generation with increased UVC dosage, the preparation of substrates using a pestle and mortar in air permits the possibility that some of the perchlorate production was due to the mechanical breaking of silica-oxygen bonds and the generation of surface bound ROS prior to exposure to Martian conditions.

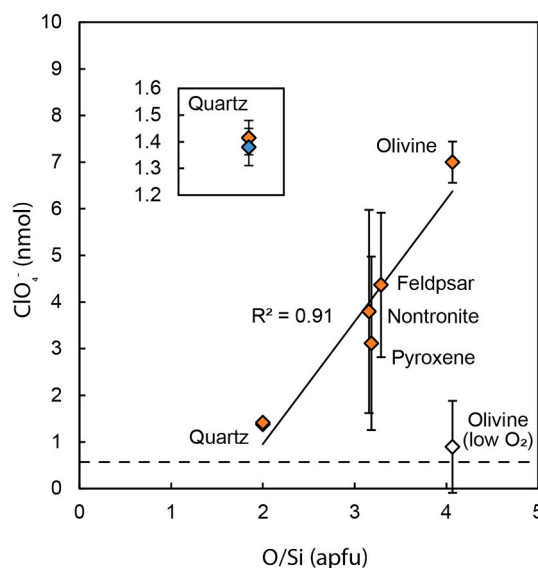
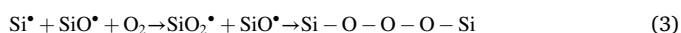


Fig. 1. Perchlorate (nmol) generated from minerals mechanically activated in the presence of chloride(s). Orange diamonds: olivine, feldspar, nontronite, pyroxene and quartz. Blue diamond: quartz data from Carrier and Kounaves (2015). White diamond: Olivine experiments conducted under oxygen free atmosphere. Insert: comparison of our quartz data to the data of Carrier and Kounaves (2015). Dashed line shows the analytical detection limit. Errors are given as ± 1SD of three separate experiments.

In prior studies investigating the reactivity of single-phase minerals, a link between silicate mineral structure and H₂O₂ production has been suggested (Hurowitz et al., 2007), with reactivity related to silicate group by the number of vertices shared by the silicon-oxygen tetrahedron and the order of reactivity: orthosilicates > sorosilicate > inosilicate > tectosilicate. Hurowitz et al., 2007 tested for H₂O₂ immediately after exposure to water, whereas H₂O₂ concentrations generated from crushed lunar and Martian regolith analogues have been shown to increase over time (Bak et al., 2017; Edgar et al., 2022; Kaur et al., 2016). Other published work investigating the production of ROS from crushed minerals supports the reactivity series highlighted above (Hendrix et al., 2019; Edgar et al., 2022). Increased reactivity has been observed in Al bearing tectosilicate phases with respect to quartz in each of these prior studies. We suggest a relationship between perchlorate production and the oxygen to silica ratio of atoms per formula unit (apfu) of the tested minerals ($r^2 = 0.91$; $n = 5$; Fig. 1). The electron spin resonance (ESR) activity of surface defect sites has been reported to degrade with time after crushing in O₂, likely due to the formation of ESR inactive bridges (Fubini et al., 1987):



The aluminosilicates (e.g. feldspars), which incorporate Al into their structure by substitution with Si atoms, may reduce the potential for the formation of ESR inactive bridges and result in the continued availability of peroxide radicals and radical anions for the reaction with water. Overall, we suggest that the restructuring of surface bound ROS may provide a framework for the hierarchy of the mineral reactivity series described above. Greater incorporation of Al decreases the amount of Si*/SiO* available to react to form surface-bound ROS; on the other hand, limiting oxygen bridging by incorporation of Al may result in an increase in net surface reactivity. The precise controls on mineral reactivity and mechanism of oxidant generation, transformation and consumption should provide fruitful avenues of further research.

4. Conclusions

Mechanisms that fracture silicates are widespread on rocky solar system bodies, our new data suggests that perchlorate can be generated in mechanochemical reactions which may have significance for a variety of bodies including Earth and Mars. The reactions appear to be heterogeneous involving fresh silicate surfaces and atmospheric oxygen species and it is possible they have been active in prior research investigating perchlorate generation under Martian conditions. Further laboratory experiments more realistically simulating different solar system environments and processes is necessary to fully understand the in-situ potential for mechanochemical perchlorate generation.

Data availability

Full data for this study is given in the accompanying Supplementary Information.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data for this study is given in Supplementary Information associated with the main manuscript

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.icarus.2022.115202>.

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