Aeolian driven oxidant and hydrogen generation in Martian regolith: The role of mineralogy and abrasion temperature

John O. Edgar a, Katie Gilmourb, Maggie L. Whiteb, Geoffrey D. Abbotta, Jon Tellinga*

a School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
b School of Engineering, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
*Corresponding author email address: jon.telling@newcastle.ac.uk

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Abstract

The surface of Mars is a dynamic, cold environment where aeolian abrasion leads to the fracturing of silicate minerals which can produce oxidants upon exposure to water. Here we report results of a series of laboratory experiments where the abrasion of sand sized (125 – 300 µm) quartz, labradorite, forsterite and opal were conducted under a simulated Martian atmosphere at a range of temperatures common to Mars' surface (193 to 273 K). Our results suggest that abrasion rates are controlled by temperature; an observation that may have potential for providing insight into Martian paleo-temperatures. On the addition of water, detectable H$_2$O$_2$ was generated in all abraded experiments with crystalline quartz, labradorite and forsterite, but not amorphous opal – supporting previous inferences that mineral crystal structure plays a role in oxidant production. Dissolved Fe concentrations also indicated a strong additional control on net H$_2$O$_2$ production by Fenton reactions. Detectable H$_2$ was similarly measured in abraded experiments with crystalline minerals and not for amorphous opal. Labradorite and forsterite generated minimal H$_2$ and only in more abraded samples, likely due to the reaction of Si$^+$ with water. In quartz experiments H$_2$ was only present in samples where a black magnetic trace mineral was also present, and where H$_2$O$_2$ concentrations had been reduced to close to detection. In the quartz samples we infer a mechanism of H$_2$ generation via the previously proposed model of spinel-surface-promoted-electron transfer to water. The presence of H$_2$O$_2$ may exert an additional control on net H$_2$ production rates either directly (via reaction of H$_2$ with OH$^-$ and H$_2$O$_2$) or indirectly (by the oxidation of H$_2$ generating sites on mineral surfaces). Overall, our data supports previous inferences that aeolian abrasion can produce additional oxidants within the Martian regolith that can increase the degradation of organic molecules. We further suggest that the apparent control of H$_2$O$_2$ concentrations on net H$_2$ generation in our experiments may help explain some previous apparently contradictory evidence for mineral-water H$_2$ generation at low temperatures.

Keywords

Mars, aeolian abrasion, low-temperature, hydrogen peroxide, hydrogen, Fenton chemistry

1. Introduction

Over geological time large quantities of organic bearing meteoritic material should have been deposited on the Martian surface; however, direct chemical analysis of Martian regolith has detected a maximum of 24.4 ppm organic carbon by mass (Eigenbrode et al., 2018). Better understanding the mechanisms that can alter and destroy organic molecules in Martian regolith can help us to constrain the preservation potential of organic molecules of both abiotic and potentially biotic origin, as well as helping to evaluate the sources of any organic material. Viking lander experiments found the regolith able to oxidise nutrients (Levin & Straat, 1977) and release oxygen upon exposure to water (Oyama & Berdahl, 1977), suggesting the presence of Reactive Oxygen Species (ROS). ROS were also inferred to be responsible for the lack of detection of organic molecules (Bienmann et al., 1977). Hydrogen peroxide (H$_2$O$_2$) can be produced photochemically in Mars' atmosphere (Atreya & Gu, 1994) and has been detected in the atmospheric column (Encrenaz et al., 2004). Photochemical reactions involving mineral surfaces have
been invoked to explain the generation of ROS such as the superoxide radical (O$_2^-$) which can form on labradorite surfaces when they are irradiated under analogue Martian conditions (Yen et al., 2000), and perchlorates (ClO$_4^-$) detected in-situ on Mars by the Wet Chemistry Lab on board the Phoenix Mars lander (Hecht et al., 2009).

Aeolian processes on Mars may further promote ROS production. Electrostatic fields can be generated through triboelectric effects as wind driven dust storms propagate. This can result in the dissociation of atmospheric CO$_2$ and H$_2$O, leading to the formation of new reactive chemical products (Delory et al., 2006) and may produce significant quantities of H$_2$O$_2$ (Atreya et al., 2006). The saltation and subsequent collision of sand particles may also generate additional ROS (Bak et al., 2017). Sand fluxes on Mars have been shown to locally approach levels observed in cold, dry deserts on Earth (Bridges et al., 2012). Analysis of predicted sand fluxes from climate models (Richardson et al., 2007) with measured observations of dune and ripple migration suggest a sand mobility threshold for Mars of 0.82 m s$^{-1}$ (Ayoub et al, 2014; Bridges et al., 2017). Numerical models suggest that sustained saltation is possible where wind speeds remain close to the impact threshold without the requirement to consistently reach or exceed the fluid friction threshold (Sullivan & Kok, 2017).

In prior low energy studies simulating Martian saltation, Bak et al. (2017) demonstrated that the high CO$_2$ content of the Martian atmosphere inhibited the direct production of H$_2$O$_2$ on mineral surfaces, although significant generation of H$_2$O$_2$ still took place. The H$_2$O$_2$ in these experiments was instead most likely produced by triboelectrically induced reactions promoted by the low Martian pressures (Bak et al., 2017). This study was however conducted with limited materials (quartz and basalt) and with abrasion at ambient room temperature; much warmer than average Martian temperatures (Martínez et al., 2017).

Here we extend our understanding of ROS production by sand abrasion in Martian regolith by assessing not only a greater range of analogue Martian minerals (quartz, labradorite, forsterite, opal) on H$_2$O$_2$ generation, but also the effect of the temperature of abrasion on oxidant production. We further couple measurements of H$_2$O$_2$ to simultaneous measurements of H$_2$ to gain greater insight into the mechanisms of coupled oxidant-hydrogen generation from abraded mineral-water reactions. Minerals were abraded under an analogue Martian atmosphere at a range of temperatures (193 to 273 K) likely to be encountered on the Martian surface. Generation of H$_2$O$_2$ and H$_2$ was monitored in time series after the addition of water, and the amount of dissolved Fe was also recorded at the end of the experiments.

2. Methods
2.1 Sample preparation & Identification

The quartz, labradorite and forsterite used in this study were commercially sourced from Northern Geological Supplies Ltd, UK and the opal from Fantasia Mining, USA. Mineral phase identification (Figs. S1 & S2) was performed by X-Ray Diffraction (XRD); full details are provided in Appendix A. Equi-granular batches of each mineral were prepared by grinding in a ball mill and sieving to isolate the 125 to 300 µm size fraction. Minerals were then washed and sonicated in 18.2 MΩ cm$^{-1}$ water to remove any adhered fine material before oven drying at 70°C for 48 hours. Submersion of silicate minerals in
Custom made quartz ampoules (100 mm long; Fig. S3) were washed in 0.6 M HCl, rinsed 5 × with 18.2MΩ cm⁻¹ water, then furnaced at 500 °C for four hours. 10 g aliquots of each mineral were added to ampoules in triplicate for each temperature point. Quartz wool (treated the same way as the ampoules) was inserted at the ampoule constriction, followed by Bellco butyl rubber stoppers (part no. 2048-11800A) that had previously been boiled in 1M NaOH for 1 hour then rinsed 5 × with 18.2MΩ cm⁻¹ water. Ampoules were then crimp sealed.

The ampoules were then connected to a vacuum/gassing line and evacuating to < 8 × 10⁻³ mbar, monitored using an Edwards APG100-XM Active Pirani Gauge. 7.0 mbar of a gas mix containing 96.05 % CO₂, 1.9 % Ar, 1.9 % N₂ and 0.15 % O₂ was then introduced, measured by an Edwards ASG2 Active Strain Gauge. This gas mixture replicates the mixing ratios in the Martian near surface atmosphere as measured by the SAM instrument on Curiosity (Mahaffy et al., 2013). Non-abraded controls for each mineral at the four temperatures were prepared in an identical way (n = 48; Appendix B), alongside water-only procedural blanks (n=24).

2.2 Simulated Saltation

A rig to mechanically abrade granular material under conditions simulating saltation was developed following Merrison (2012). Ampoules were fastened tangentially to discs pinned to an axle rotating at 40 rpm. Each full rotation causes two inversions of the ampoule resulting in the contents falling from one end to the other under gravity. The velocity of the mineral particles at impact was ~ 1 m s⁻¹ which represents saltation impact velocities at low mobilisation rates, close to the saltation threshold (Merrison, 2012). For a 142-day experiment this equates to ~ 16 × 10⁶ inversions. The mechanical power input of each inversion can be approximated as the specific gravitational energy (Eₚ) of the grains as they fall the length of the ampoule (h) under gravity (g), corresponding in this instance to ~ 0.8 W Kg⁻¹. The power transferred from the wind to grains at the threshold of saltation has been estimated to be ~ 0.05 W Kg⁻¹ (Iversen and Rasmussen, 1999; Merrison, 2012), hence our experiments simulate ~ 6 years of continuous sand mobilisation at threshold wind speeds.

The rigs were housed and operated within incubators for temperature control. Incubators had side ports allowing the rotator axle through the wall leaving the motor outside at room temperature (Fig. S4). Temperatures within incubators were monitored with temperature probes connected to an Omega OM-CP series data logger. Non-abraded mineral controls were placed in the same incubators for an identical time period, but without rotation, and water-only controls were also run in both rotating and non-rotating configurations.

After simulated saltation, all ampoules were warmed to 293 K and 20 mL of 5.0 grade He gas was added using a gas tight syringe. 10 mL of He sparged water was then added and well mixed with any excess gas equilibrated to atmospheric pressure. Oxygen levels in the water prior to addition were below 1.44 µmol L⁻¹ (~ 0.05 mg L⁻¹), monitored with a PreSens oxygen dipping probe (DP-PSt3).
2.3 Hydrogen peroxide determination

H₂O₂ concentrations were analysed following Baga et al. (1988). The procedure utilises the reduction of copper (II) ions in the presence of 2,9-dimethyl-1,10-phenanthroline (DMP) forming the copper (I) – DMP complex, Cu(DMP)²⁺. At each time point 1.5 mL of helium sparged water was added to the ampoule using a syringe and needle and well mixed. 1.5 mL was then removed and filtered through a 0.2 µm nylon syringe filter, and 1 mL of this used in the assay.

A 1000 µmol L⁻¹ H₂O₂ stock was prepared from a 30 % w/w H₂O₂ solution and from this, a range of fresh standards were diluted in the linear range 1 - 200 µmol L⁻¹ for each day of analysis. Measured standards had a maximum coefficient of variance of 6.4 %. The method detection limit (MDL, based on 3 × SD of water-only controls) was 2.9 µmol L⁻¹. H₂O₂ concentrations are reported as the measured H₂O₂ concentration from each abraded sample minus the average H₂O₂ concentration of three non-abraded mineral controls stored at the same temperature.

2.4 Hydrogen determination

Gas samples were taken at 0, 24 and 168 hours. For each gas analysis, 4 mL of He was added to the ampoule and the syringe pumped three times, then 4 mL of gas injected into a 3 mL Exetainer for analysis. H₂ concentrations in the range 0 - 100 ppm were analysed on a ThermoFisher Gas Chromatograph Pulsed Discharge Detection (GC-PDD) with a 2 m micropacked Shin Carbon ST 100/120 mesh, 1.0 mm ID column, with a constant flow (10 mL⁻¹) of helium carrier gas, column temperature of 60°C and detector temperature of 110°C. Sample concentrations were calculated from multiple dilutions of a 100 ppm certified standard in evacuated Exetainers (linear over 5 – 100 ppm, R² = 0.99, n = 15). Standards were run before and after each day of analysis with a coefficient of variation of 7.3 % (n = 86). The analytical detection limit was 1.4 nmol g⁻¹ and the MDL was 2.2 nmol g⁻¹. Gas concentrations were calculated using the Ideal Gas Law, corrected for dilutions made during sampling and normalised to the starting dry mass of the minerals. H₂ concentrations are reported as the measured value from each abraded sample minus the average H₂ concentration of the specific non-abraded mineral controls.

2.5 Iron determination

Dissolved Fe²⁺ and Fe³⁺ concentrations were sequentially determined in the range 0 – 20 µmol L⁻¹ utilising a revision of the ferrozine (the monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-p,p‘disulphonic acid) spectrophotometric method following Viollier et al. (2000). Standards from 0 – 20 µmol L⁻¹ were prepared from a 1000 µg mL⁻¹ Fe³⁺ stock solution (1.79 x 10⁻² mol L⁻¹ of FeCl₃ in 10⁻² mol L⁻¹ HCl). The MDL was 0.03 µmol L⁻¹ and the maximum coefficient of variance after 5 repetitions of each standard solution in the range 0 – 20 µmol L⁻¹ was 18.7 % (n= 34).

3. Results & Discussion

3.1 The temperature dependence of mineral comminution
These experiments were conducted under a range of temperatures encompassing the diurnal and seasonal variations recorded in situ at a number of geographically distinct locations on Mars (193 K – 273 K; Martínez et al., 2017). Importantly, mechanical properties of minerals exhibit variability with temperature (Weigle, 1949; Evans & Goetz, 1979; Kranjc et al., 2016), suggesting that temperature should affect rates of mineral abrasion. In general, our experimental results support this.

After 142 days of simulated saltation all samples, at all temperatures, had been significantly reduced from their starting grain size (Fig. 1). The amount of comminution was recorded as the mass of grains under the lowest starting grain size of (125 μm) and given as a percentage of the total mass of material. Quartz exhibited the least resistance to abrasion, producing the most fine material at both the warmest and coldest temperatures (15.8 ± 2.2 and 11.0 ± 0.2 % respectively; ±1SD, n = 3); labradorite produced the least material < 125 μm (12.3 ± 2.6 and 9.3 ± 0.5 %; ±1SD, n = 3), whilst the amount of fine material abraded from opal was consistently between those of quartz and labradorite at the warmest and coldest temperatures (13.2 ± 0.8 and 11.2 ± 2.7 % respectively; ±1SD, n = 3). Hurowitz et al. (2007) found that 1.5 minutes of crushing in a swing mill produced surface areas for quartz and feldspar of 0.90, and 0.73 m² g⁻¹ respectively, suggesting mechanical properties of minerals in agreement with the results presented here.

We note that our measurements were taken at the end of the experiment cycle after the minerals had been exposed to water for over one week. Resultantly, minerals may have undergone varying degrees of dissolution, and given that different minerals have different dissolution rates, the data presented in Fig. 1 must be interpreted cautiously. Forsterite appears to have produced less than 10 % fines in 66 % of the experiments and shows no significant correlation (rₛ = -0.24, n = 12, p = 0.46) with temperature. The Goldich dissolution series ranks minerals in stability against weathering (Goldich 1938) in the order: quartz – labradorite – forsterite which is the same order as the level of correlation for each of our major rock forming minerals (rₛ quartz = 0.86, p < 0.001; rₛ labradorite = 0.75, p < 0.01; rₛ forsterite = -0.24, p = 0.46; Fig. 1) perhaps suggesting dissolution processes have been active. In previous tumbling experiments the surface area of abraded minerals has been shown to increase with increased duration of tumbling (Bak et al., 2017). Tumbling experiments conducted by Merrison (2012), showed the generation of sub-micron dust, whilst the distribution of the sand sized fraction remained largely unaltered. The dust fraction will dominate the total surface area; accordingly, the surface area of our samples should also have increased with the amount of comminution, and hence with the temperature of abrasion. An interesting artefact of this method of simulating aeolian abrasion is the formation of dust agglomerates (Merrison, 2012; Nørnberg et al., 2014). We did not observe this phenomenon due to conducting our experiments wholly within the ampoules to ensure environmental control.

### 3.2 Hydrogen peroxide generation

After exposure to water, each mineral type except opal generated detectable quantities of H₂O₂ (MDL = 2.9 μmol L⁻¹; Figs. 2 & 3). The average peak H₂O₂ concentration was recorded in labradorite samples (117 ± 18.0 nmol g⁻¹; Figs. 2 & 3) with a slightly lower average for quartz (113 ± 28.6 nmol g⁻¹; Figs. 2
& 3), the difference between H$_2$O$_2$ production for quartz and labradorite was not statistically significant ($p = 0.87$). Both labradorite and quartz are tectosilicates consisting of silica tetrahedra which share all four corners with a neighbouring tetrahedra in their crystal structure. Forsterite, an orthosilicate, with no shared corners between silica tetrahedra, had a significantly ($p < 0.05$) lower average peak H$_2$O$_2$ concentration (39.1 ± 2.2 nmol g$^{-1}$; Figs. 2 & 3) than both labradorite and quartz. All H$_2$O$_2$ productive minerals exhibited a significant correlation ($p < 0.05$) between the temperature of abrasion and the amount of H$_2$O$_2$ produced (Fig. 2). Strikingly, the sign and strength of these correlations were not the same for each mineral; quartz and forsterite produced maximum concentrations when abraded at 193 K and exhibited a negative trend with temperature ($r_{\text{quartz}} = -0.68$, $n = 12$; $r_{\text{forsterite}} = -0.98$, $n = 12$; Fig. 2) whereas labradorite produced a maximum at 273 K and showed a positive trend with temperature ($r_{\text{labradorite}} = 0.89$, $n = 12$; Fig. 2). This result suggests that within single mineral species, the quantity of fine particulates generated (and by proxy, surface area) was not always the dominant control on net H$_2$O$_2$ generation in experiments.

Hurowitz et al. (2007) suggested a relationship between the crystal structure of crushed silicates and the production of H$_2$O$_2$, with the number of corners shared by the basic silica tetrahedra determining H$_2$O$_2$ productivity. Opal is a poorly crystalline silicate; the X-ray diffraction pattern for the opal confirmed the weak crystallinity in these samples (Fig. S1). The lack of H$_2$O$_2$ generation in opal therefore supports the hypothesis that crystal structure is important in determining mineral oxidant production. However, Hurowitz et al. (2007) and Hendrix et al. (2019) noted an inverse relationship between shared corners of silica tetrahedra and ROS generation. The crystal structure of the productive minerals in our current study showed the opposite trend (Figs. 2 & 3).

One potential explanation for this disparity could be the maximum temperature reached during the milling process. High energy abrasion experiments (e.g. Hurowitz et al., 2007) have indicated that H$_2$O$_2$ can form after grinding of minerals via the mechanical fracturing of silicate bonds and the subsequent reaction of the fresh, radical hosting silicate surfaces with water (Hendrix et al., 2019):

\[
\text{Si} - \text{O} - \text{Si} \equiv \rightarrow \text{Abrasion} \rightarrow \equiv \text{SiO}^* + \text{Si}^*
\]

\[
2 \equiv \text{SiO}^* + 2 \text{H}_2\text{O} \rightarrow 2 \equiv \text{SiOH} + \text{H}_2\text{O}_2
\]

Kita et al. (1982) show that the SiO$^*$ radical is relatively stable and will not readily react with water until temperatures greater than ~ 493 K are reached, in excess of the controlled temperatures in this study. Strong correlations between atmospheric O$_2$ and H$_2$O$_2$ in low energy tumbling experiments by Bak et al. (2017) suggest that O$_2$ modification of the fresh silicate surfaces enables an alternative H$_2$O$_2$ generation mechanism through the formation of superoxide radicals:

\[
\equiv \text{Si}^* + \text{O}_2 \rightarrow \equiv \text{SiO}^0
\]

\[
\equiv \text{SiO}^0* + \text{H}_2\text{O} \rightarrow \equiv \text{SiOH} + \text{HO}_2
\]
Tumbling experiments where \( O_2 \) levels were varied showed a strong correlation between \( H_2O_2 \) production and atmospheric \( O_2 \) levels, suggesting \( O_2 \) is consumed by reactions 3 - 5 (Bak et al., 2017).

Using the Ideal Gas Law, under the starting conditions reported in our study (\( pO_2= 10.5 \) Pa, \( V = 0.00025 \) m\(^3\), \( R = 8.31 \) J K\(^{-1}\) mol\(^{-1}\), \( T = 293 \) K) there was \( \sim 110 \) nmol of \( O_2 \) in the ampoules available to bond at the silicate surface prior to the addition of water, which contained \( \sim 1.44 \) µmol L\(^{-1}\). From equations 3 – 5, this could have resulted in a maximum production of \( \sim 7.0 \) nmol g\(^{-1}\) \( H_2O_2 \) in our experiments; this equates to 6.0, 6.2 and 17.9% of maximum \( H_2O_2 \) yields for labradorite, quartz and forsterite respectively.

We therefore conclude that only a fraction of the total \( H_2O_2 \) production in some of our experiments could have come from starting \( O_2 \). The average peak \( H_2O_2 \) concentration of the non-abraded controls was 4.9 ± 0.5 nmol g\(^{-1}\) (±SEM, \( n = 48 \); Appendix B), consistent with near quantitative consumption of \( O_2 \) available in the ampoules at the start of experimentation. Any silica radicals not deactivated in the preparatory steps could have reacted with this \( O_2 \) and generated \( H_2O_2 \) via Eq’s. 3 – 5.

One alternative source of \( H_2O_2 \) is from pre-existing peroxy linkages (≡Si-O-O-Si≡) within igneous silicate minerals (Balk et al., 2009). These defects, equivalent to two co-joined SiO\(^{\cdot} \), can be produced during the original cooling of a water-containing magmatic melt to form the silicate minerals (Balk et al., 2009). Under stress, these defects in the minerals can migrate through the crystal matrix to form surface SiO\(^{\cdot} \), and it has been further proposed that these can then form \( H_2O_2 \) via Eq. 2 (Balk et al., 2009).

However, Kita et al (1982) demonstrated that silicate surface SiO\(^{\cdot} \) are stable to temperatures greater than \( \sim 493 \) K - well above the temperatures of our study. We also note that the experiments of Balk et al. (2009) were carried out under air at room temperature and hence the \( H_2O_2 \) generated in these experiments may instead have utilised \( O_2 \) (Eqs. 3 - 5).

Instead, we suggest that the additional source of oxygen in the abraded experiments is from the more abundant starting concentrations of \( CO_2 \). In prior tumbling experiments simulating Martian saltation, electrostatic discharges between grains, evidenced by triboluminescence from agitated abraded material, has been hypothesised to dissociate atmospheric species, including \( CO_2 \), providing a third \( H_2O_2 \) generation mechanism (Bak et al., 2017; Thøgersen et al. 2019):

\[
CO_2 + e^- \rightarrow CO + O^-
\]  
\[
Si - O^\cdot + O^- \rightarrow SiOO^-
\]  
\[
SiOO^- + H_2O \rightarrow SiO^- + H_2O_2
\]

Given the stability of the SiO\(^{\cdot} \) radical (Kita et al., 1982) at the temperatures recorded here and the insufficient availability of \( O_2 \) in the ampoules, we suggest that equations 6 – 8 were likely to dominate \( H_2O_2 \) generation in our study. The measurement of CO in future experiments (Eq. 6) would further help test this hypothesis. In prior high energy milling experiments, substantial heat will have been generated during high energy impacts, reducing the stability of the \( H_2O_2 \) generating intermediary - SiOO\(^{\cdot} \) (Kita et
al., 1982; Yen et al., 2000). In contrast in our study the grinding temperature was carefully controlled to low temperatures, allowing the build-up of SiOO•− on mineral surfaces over time. This scenario is also consistent with the results of Hendrix et al. (2019) where an inverse relationship was found between grinding time and ROS generation, suggesting that increased temperature resulted in the instability/reaction of oxidant generating mineral surface radical species.

Time series for each of the mineral phases allowed the evolution and stability of H₂O₂ to be monitored (Fig. 3). In forsterite experiments, maximum H₂O₂ concentrations were recorded at 24 hours after the addition of water, decreasing over 168 hours (Fig. 3). Maximum H₂O₂ concentrations in quartz experiments were quantified within 5 minutes of the addition of water, decreasing over the subsequent 168 hours. A varnish-type material was also observed on the inside of the ampoules within which quartz was abraded (Fig. S5), but not with other minerals. We suggest that this fine material/varnish would have provided an enhanced surface area for reactions to proceed and could potentially explain the rapid observed increase in H₂O₂ concentrations in the quartz samples. Uniquely, labradorite samples consistently maintained H₂O₂ levels after an initial 24-hour increase through the end of the analytical period (Fig. 3). Bak et al. (2017) suggested that silica radicals partake in both the generation and the destruction of H₂O₂; the absence of any degradation of H₂O₂ in the labradorite samples could indicate that secondary mineral phases formed on silica surfaces, depleting the available silica sites that could consume H₂O₂. Alternatively, the lack of iron in labradorite (Fig. S6) would also limit Fenton chemistry (Hurowitz et al., 2007) which would consume H₂O₂.

3.3 Iron availability and Fenton chemistry

Whilst forsterite was the only mineral abraded with iron in its chemical structure, dissolved iron was only consistently recorded in samples from quartz experiments (maximum 0.86 ± 0.16 μmol L⁻¹; Figs. 4 & S6). Iron measured in the residual liquids of the other minerals were below quantification except for one forsterite sample abraded at 193 K, one labradorite sample abraded at 223 K and several opal samples abraded above 223 K (LOQ = 0.11 μmol L⁻¹; Fig. S6). Small quantities of a black magnetic mineral below the level of detection with XRD analysis (LOQ ~ 1%; Fig S2) were observed in the initial quartz substrate. There was a significant correlation between the concentration of dissolved iron and the proportion of quartz abraded to fines (r = 0.85, n = 12, p < .001; Fig. 4) suggesting a relatively homogenous distribution of the magnetic mineral within the quartz. In all cases, whilst both Fe²⁺ and Fe³⁺ were measured, only Fe³⁺ was detected. This result is likely due to the nature of the oxidising environment produced by H₂O₂ and other ROS generated in experiments, rapidly oxidizing any dissolved Fe²⁺.

Iron species can partake in Fenton-type reactions (Eq’s. 9 - 11) in both the solid (heterogeneous) and aqueous (homogeneous) phases. It is kinetically favourable for heterogeneous Fenton reactions to proceed when suitable iron minerals are present as solid phases with aqueous H₂O₂ (Araujo et al., 2011). Soluble Fe²⁺ and Fe³⁺ can subsequently enter the aqueous phase leading to simultaneous homogeneous Fenton reactions propagating and enhancing the overall reaction (Araujo et al. 2011):
The measured H₂O₂ concentrations in experiments must thus be considered the net product of multiple simultaneous productive and destructive reactions. The inverse relationships between H₂O₂ generation and temperature of abrasion for forsterite and quartz samples can be explained by consideration of competing H₂O₂ generating and consuming reactions (Fig. 2). At higher temperatures, minerals are more susceptible to abrasion resulting in the generation of a higher number of silica radical sites and in the case of Fe bearing minerals, a greater surface area for Fenton-type reactions to proceed. H₂O₂ is generated by silica radical sites and consumed by Fe phases according to availability of both Fe²⁺ and Fe³⁺. If the rate of consumption of H₂O₂ is greater than its rate of generation then H₂O₂ cannot accumulate. In this study, H₂O₂ generation is suppressed for Fe bearing samples at higher abrasion temperatures suggesting that either Fenton reactions are more efficient than silica radical – water reactions under these conditions or that Fenton active species were generated at a faster rate than silica radicals during the abrasion process.

3.4 Hydrogen generation

After exposure to water, each mineral type except opal generated detectable quantities of H₂ gas (MDL = 2.2 nmol g⁻¹; Fig. S7). Labradorite and forsterite only produced H₂ slightly above detection (maximum = 4.3 ± 0.4 and 3.4 ± 0.3 nmol g⁻¹ for labradorite and forsterite respectively; Fig. S7) and only at higher temperatures of abrasion. In total, 7 out of 12 abraded quartz samples generated detectable H₂ after the addition of water, with a maximum of 37.8 ± 3.7 nmol g⁻¹ at 223 K (Fig. 5a - 5c). In quartz samples H₂ generation generally decreased as abrasion temperature increased to 273 K with no H₂ recorded at 193 K (Fig. 5a). There was unlikely any limitation through the accumulation of H₂ given the ample headspace (~15 cm³) and H₂ concentrations were still increasing at 168 hours, suggesting equilibrium conditions were not reached (Fig. 5c). The considerable variation within replicates in this study suggests that abrasion temperature and fresh silica surface area were not the only variables affecting H₂ production. Crucially, H₂ was only present at the end of the experiment in quartz samples when the liquid phase contained detectable dissolved Fe (MDL = 0.03 µmol L⁻¹; Fig. 5); above this concentration dissolved Fe did not correlate with the amount of H₂ produced suggesting hydrolysis during dissolution of the iron phase was not the source of H₂ (Fig. 5b).

Previous experiments utilising natural rocks and minerals to investigate H₂ production have investigated a number of different mechanisms of H₂ generation. Kita et al. (1982) examined how the presence of O₂ during the milling of quartz altered H₂ yields; their study determined that milling in a pure water vapour atmosphere generated significantly more H₂ than milling in moist air. This was attributed to the formation of SiOO⁻⁻ through the reaction of Si⁺ and SiO⁺ with atmospheric oxygen species (O₂, O⁻).
precluding H₂ generation from the reaction of Si• with H₂O. We suggest that our results are consistent with the oxidation of Si• by starting oxygen and reactive oxygen species produced during abrasion (Eq. 6 - 8). Studies where crushing was performed in the absence of O₂ have produced H₂ with variable yields (Stevens & McKinley, 2000; Neubeck et al., 2011, Mayhew et al., 2013). These studies have all utilised iron bearing minerals although none of these studies controlled the minor mineral phases and importantly, all of these studies prepared their mineral samples by crushing in air but did not measure the production of potential oxidants alongside H₂ in their experiments.

Stevens & McKinley (2000) reported no detectable H₂ generation from the reaction of a magnetite (a spinel) substrate with water whilst Mayhew et al. (2013) observed significant H₂ generation when 40 % (modal abundance by volume) forsterite was present in a magnetite substrate. In the Mayhew et al. (2013) model, H₂ is produced when electrons are transferred to water molecules and protons adsorbed to spinel surfaces. Sustained H₂ production occurs when dissolved Fe species adsorb and donate electrons to the spinel surface resulting in the continuous reduction of water and the generation of H₂. This model is consistent with H₂ generation in our abraded quartz experiments where H₂ production was initially rapid, then decreased but had not appeared to have plateaued after 168 hrs (Fig. 5c). We suggest that spinel-promoted-electron transfer was a source of H₂ in the quartz samples and that competition with oxidants generated from the reactions of SiOO•/- and water exerted a control on this production. Dissolved Fe was not present above detection (MDL = 0.03 µmol L⁻¹) in the labradorite or forsterite samples that generated H₂ and we suggest this limited H₂ generation (Fig. S7) was due to the reaction of Si• with water. It is possible a fraction of the H₂ measured in the quartz samples was also generated by this mechanism. The lack of detectable H₂ generated from amorphous opal potentially indicates that mineral crystal structure exerts a control on H₂ as well as H₂O₂ generation.

3.5 Oxidant regulation of hydrogen generation

Concentrations of H₂ against H₂O₂ for quartz samples are plotted in Figure 6a (n = 36) for the three comparable time points (0, 24, 168 hrs) investigated at all temperatures of abrasion (193, 223, 253, and 273 K). The determining component is the presence of dissolved Fe and thus the presence of an Fe phase abraded from the quartz (Fig. 6b). Net H₂O₂ concentrations increased rapidly before returning to close to detection at 168 hours. Conversely, H₂ accumulated in the headspace of quartz experiments over 168 hours. Prior abrasion studies performed on pure quartz under Martian analogue conditions have reported ~ 40 % yields of HO• radicals compared to H₂O₂ (Bak et al., 2017). This suggests a significant portion of the oxidants produced within our study were not measured. In the presence of available Fe²⁺, Reactions 9 – 11 will have further increased the concentration of ROS in the liquid. H₂ should readily react with HO• radicals and H₂O₂ via the series of reactions comprising the Allen chain reaction (Allen et al., 1952), reducing H₂ yields:

\[ H_2 + HO^* \rightarrow H^* + H_2O \]  \hspace{1cm} (12)

\[ H^* + H_2O_2 \rightarrow OH^* + H_2O \]  \hspace{1cm} (13)
\[ H_2 + H_2O_2 \rightarrow 2H_2O \]  

(14)

Telling et al. (2015) reported a lag between the addition of water to some of their crushed rock samples and net \( H_2 \) production; perhaps indicating these \( H_2 \) consuming redox reactions constrain low level net \( H_2 \) production in low temperature environments. Figures 5 and 6b show that significant concentrations of \( H_2 \) are only measured in quartz samples with dissolved Fe concentrations in excess of 0.03 \( \mu \text{mol L}^{-1} \). In quartz experiments where \( H_2O_2 \) was below detection (samples with a dissolved Fe content above detection \( \sim 0.03 \mu \text{mol L}^{-1} \)), we infer that Fenton processes have inhibited the accumulation of \( H_2O_2 \).

We propose here an extended version of the Mayhew et al. (2013) model, where abraded samples follow one of two reaction pathways that result in the generation of net \( H_2O_2 \) or net \( H_2 \) dependant on the ratio of spinel surface area (\( H_2 \) production sites) to silica radical sites (\( H_2O_2 \) and \( H_2 \) production sites) and the background concentration of Fe species (Fig. 7). This ratio is expressed by the generation and destruction of \( H_2O_2 \) and \( H_2 \) through a balance of silica radical – water and silica oxide radical - water reactions, Fenton reactions, spinel-surface-promoted-electron transfer as well as tertiary oxidation/reduction reactions such as those described by Allen’s chain reaction. In environments with high spinel surface area to silica radical ratios, the production rate of \( H_2 \) (via electron transfer to water) on spinel surfaces can exceed the production of ROS species at silica oxide radical sites, generating net \( H_2 \). Conversely, when the spinel surface area to silica radical ratio is low, \( H_2O_2 \) generation rates exceed \( H_2 \) production rates, resulting in the net accumulation of \( H_2O_2 \) (Fig 7). \( H_2O_2 \) and other ROS may also oxidize the reactive spinel surfaces and inhibit \( H_2 \) generation. A summary of these reactions is shown in Fig. 7.

### 3.6 Implications for Mars

#### 3.6.1 Water and oxygen availability as a control on ROS production

The mechanisms for ROS production in our experiments are all dependent on the presence of liquid water. Up to 29% of Mars’ surface area has been modelled to experience pressures and temperatures suitable to support liquid water (Harberle et al., 2001). This area increases if brines are considered, which are capable of forming metastable liquids at a much larger range of temperatures and pressures (Rivera-Valentin et al., 2020). Liquid water is predicted to form on Mars as thin films on the order nanometres thick on mineral surfaces, becoming substantially thicker when films containing impurities form (Boxe et al., 2012). In a model proposed by Yen et al. (2005), frosts are deposited at night before rapidly sublimating in the morning. Any condensation in excess of a single monolayer however can behave as a liquid, capable of mobilising ions from the regolith (Yen et al., 2005) and would potentially be available for other water – rock interactions, including mineral surface radicals produced during aeolian abrasion.

In our experiments, the amount of molecular oxygen available to react with mineral surface radicals (Eq. 3) and other reduced species was limited, although a further source of oxygen might be available
from the triboelectric disassociation of CO\textsubscript{2} (Eq. 6; Bak et al., 2017). However, on the surface of Mars, the substantial volume of the Martin atmosphere will potentially provide a non-limiting source of oxygen over time to fuel continued oxidation. We therefore view our rates of oxidant production (after water addition) as a lower limit.

### 3.6.2 Abrasion rate as a function of temperature

While the dissolution of minerals during the experiment precludes an accurate analysis of the different abrasion rates with temperature, the varying mass of fine productions are consistent with a temperature dependence of mineral resistance to abrasion. Further work directly investigating the mechanical properties of minerals at Martian temperatures is ongoing to more robustly test this hypothesis. The composition of aeolian deposits covering volcanic regions is often taken as the average composition of the underlying bedrock (e.g. Stockstill-Cahill et al., 2008). Known aeolian processes can apply sorting effects, systematically altering the composition of this sediment with respect to source rocks (Mangold et al., 2011). We suggest investigation of Martian sedimentary sequences should consider the temperature at which aeolian processes occurred as a further control on sorting and composition.

### 3.6.3 Mineral structure and Fe content as controls on oxidant production

The H\textsubscript{2}O\textsubscript{2} production capacity of the silicates abraded in this study show a dependence on the crystal structure of the abraded mineral as suggested by Hurowitz et al. (2007). In our study tectosilicates had higher H\textsubscript{2}O\textsubscript{2} production capacities than orthosilicates. Quartz commonly makes up < 2 % of the Martian regolith, however labradorite and forsterite have been shown to comprise ~ 40 and ~ 20 % of the crystalline component of the regolith respectively (Bish et al., 2013). Importantly, however, the inactivity of the opal suggests the amorphous content of the Martian regolith does not contribute to its oxidising nature through the mechanisms described here. Equally importantly, our results suggest that net H\textsubscript{2}O\textsubscript{2} production can be regulated not only by mineral structure, but by the presence of Fe bearing mineral species. Haematite, magnetite and nano-phase iron oxides are common on Mars (e.g. Bish et al., 2013). Accordingly, net H\textsubscript{2}O\textsubscript{2} production rates in the Martian regolith are liable to be limited by Fenton reactions (with the consequent production of more reactive OH\textsuperscript{-} and OOH\textsuperscript{-} radicals; Eq. 9 - 11) in the presence of suitable Fe bearing species.

### 3.6.4 The impact of aeolian driven oxidant production on organic matter preservation

The reactions involving the crystalline silicate phases described here are able to produce oxidising environments that would impact on the preservation potential of any meteoritic or native organic material in the Martian regolith. Liquid water may persist as brines for up to 6 hours at a time in some regolith settings (Rivera-Valentin et al., 2020). Within this time frame, our data suggests the potential for mineral driven H\textsubscript{2}O\textsubscript{2} production, with the further potential for Fe species to partake in Fenton reactions, further increasing the oxidative stresses and subsequent degradation of any organic species. Additional
experiments are required to quantify how fast these reactions can proceed at the low temperatures representative of eutectic salt brines (Rivera-Valentin et al., 2020).

3.6.5 Insight into low temperature hydrogen generation

In support of previous studies (e.g. Kita et al., 1982) our results indicate that H$_2$ generated from the reaction of Si$^+$ with water will be limited where oxygen is available to form SiOO$^-$$. Our results further show that spinel surface promoted electron transfer could be initiated on the Martian surface in the presence of liquid water to produce H$_2$ gas (Mayhew et al., 2013). The lifetime of molecular H$_2$ in the Martian atmosphere is measured in centuries, and unlike water vapour, H$_2$ can migrate through the upper atmosphere where a proportion is dissociated and lost to space as H (Chaffin et al., 2017). Oxidants such as H$_2$O$_2$ generated from abraded mineral-water reactions would inhibit net H$_2$ production; limiting the loss of this H$_2$ into and from the Martian atmosphere.

We suggest that conflicts in the current literature regarding the potential for H$_2$ generation from water-mineral reactions at low temperatures (Kita et al., 1982; Anderson et al., 1998; Telling et al., 2015; Stevens & McKinley, 2000; Nuebeck et al., 2011; Mayhew et al., 2013), may at least in part be reconciled by the contemporaneous production of H$_2$O$_2$ and ROS by the crushing of the studied materials that inhibit net H$_2$ production; particularly those (the majority) of studies that have crushed their experimental minerals under air.

4. Conclusions

Our study suggests that the level of resistance of different minerals to abrasion by simulated saltation is temperature dependent with increased abrasion observed at warmer temperatures. After low energy abrasion for 142 days, the crystalline silicate minerals quartz, labradorite and forsterite all generated significant (p < 0.05) quantities of H$_2$O$_2$ on contact with water. The amorphous mineral opal however did not generate any H$_2$O$_2$ supporting the hypothesis of Hurowitz et al. (2007) that there is a link between mineral crystal structure and oxidant producing capacity. Our results further demonstrate that Fe-driven Fenton chemistry will limit the net accumulation of H$_2$O$_2$ in silica radical - water reactions if appropriate Fe species are available; presumably resulting in the production of more reactive ROS such as OH$^\cdot$. Further research is required to better quantify the rates of potential oxidant production on organic matter preservation in sediments driven by the formation of transient brines on and in active aeolian sediment, and potential interactions with UV irradiation.

Our paired analyses of H$_2$ alongside H$_2$O$_2$ production supports previous studies (e.g. Kita et al., 1982) where H$_2$ generation is limited by the formation of SiOO$^-$. Our results also suggest there may also be a link between mineral structure and H$_2$ generation. Finally, we extend the model of Mayhew et al. (2013), in that spinel surface promoted electron transfer can result in the net production of H$_2$ - but only if H$_2$O$_2$ (and presumably other ROS) have been reduced to close to detection (here ~ 2.9 µmol L$^{-1}$). The production of ROS on crushed mineral surfaces may help provide
at least part of the explanation for prior conflicting experimental results and conclusions on the potential
for low temperature H₂ production from silicate-water reactions.

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Figures:

**Figure 1:** Percentage weight (wt. %) of a) quartz, b) opal, c) labradorite and d) forsterite abraded to less than 125 μm after 142 days of simulated saltation plotted against the temperature of abrasion in Kelvin (K). The strength of correlation for each plot is reported as the Spearman’s rank correlation coefficient (rs).

**Figure 2:** Net H$_2$O$_2$ generated (nmol g$^{-1}$) by abraded quartz, labradorite, opal, and forsterite after simulated saltation in a Martian atmosphere at 193 K, 223 K, 253 K and 273 K. The dashed line signifies the MDL (2.9 nmol g$^{-1}$). Minerals were abraded for 142 days and subsequently exposed to anoxic water. Error bars are shown as the SEM (n=3).
Figure 3: Time series of net H$_2$O$_2$ generation (nmol g$^{-1}$) by abraded: a) quartz b) opal c) forsterite and d) forsterite, at the four temperatures tested (see key). Minerals were abraded for 142 days in a simulated Martian atmosphere. The dashed line signifies the MDL (2.9 nmol g$^{-1}$). Error bars are shown as the SEM (n=3).
**Figure 4:** Concentration of total Fe in the residual liquids from quartz samples abraded in a Martian atmosphere for 142 days and exposed to anoxic water. Fe concentrations are plotted against the percentage weight of quartz abraded below 125 µm. The dashed line signifies the MDL (0.03 µmol L⁻¹). Error bars are shown as the maximum coefficient of variance of standards over the total calibration range (18.7 %).

**Figure 5:** Net H₂ generated over 168 hours from quartz abraded for 142 days in a simulated Martian atmosphere and exposed to anoxic water. H₂ (nmol g⁻¹) is plotted a) against the temperature of abrasion (K) with lines of best fit between Fe bearing samples (black) and all samples (grey), b) against the concentration of total Fe with lines of best fit between Fe bearing samples (black) and all samples (grey), and c) as time series. The dashed lines signify the MDL (0.03 µmol L⁻¹ and 2.2 nmol g⁻¹ for Fe and H₂ respectively). Each data point is a single experiment. Errors are given as the maximum coefficient of variance of standards over the total calibration ranges. Fe concentration of the liquid (above or below detection) from each sample is given in the key.
Figure 6: H₂ generation plotted against H₂O₂ generation from quartz abraded for 142 days in a simulated Martian atmosphere and exposed to anoxic waters: a) measurements for H₂ (nmol g⁻¹) and H₂O₂ (nmol g⁻¹) at time points 0, 24 and 168 hours. Each data point is a single pair of measurements at the stated time, b) H₂ (nmol g⁻¹) at the end of the experiment plotted against maximum measured H₂O₂ (nmol g⁻¹) (this plot is temporally inconsistent). Error bars are given as the maximum coefficient of variance of standards for each species calibration range.

Figure 7: Reaction schematic showing the different processes described in text. a) electrical dissociation of CO₂ and reaction of O with abraded, b) generation of H₂ through the reaction of silica radicals with water, c) generation of H₂O₂ through the reaction of oxygen modified silica radicals with water, d) Fenton reactions, e) oxidants inhibit net H₂ generation, f) spinel-surface-promoted H₂ generation, and g) Allen’s chain reactions.
5. References


