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Production of reactive oxygen species from abraded silicates. Implications for the reactivity of the Martian soil

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ABSTRACT

The results of the Labeled Release and the Gas Exchange experiments conducted on Mars by the Viking Landers show that compounds in the Martian soil can cause oxidation of organics and a release of oxygen in the presence of water. Several sources have been proposed for the oxidizing compounds, but none has been validated *in situ* and the cause of the observed oxidation has not been resolved. In this study, laboratory simulations of saltation were conducted to examine if and under which conditions wind abrasion of silicates, a process that is common on the Martian surface, can give rise to oxidants in the form of hydrogen peroxide (H_2O_2) and hydroxyl radicals (·OH). We found that silicate samples abraded in simulated Martian atmospheres gave rise to a significant production of H_2O_2 and ·OH upon contact with water. Our experiments demonstrated that abraded silicates could lead to a production of H_2O_2 facilitated by atmospheric O_2 and inhibited by carbon dioxide. Furthermore, during simulated saltation the silicate particles became triboelectrically charged and at pressures similar to the Martian surface pressure we observed glow discharges. Electrical discharges can cause dissociation of CO_2 and through subsequent reactions lead to a production of H_2O_2. These results indicate that the reactions linked to electrical discharges are the dominant source of H_2O_2 during saltation of silicates in a simulated Martian atmosphere, given the low pressure and the relatively high concentration of CO_2. Our experiments provide evidence that wind driven abrasion could enhance the reactivity of the Martian soil and thereby could have contributed to the oxidation of organic compounds and the O_2 release observed in the Labeled Release and the Gas Exchange experiments. Furthermore, the release of H_2O_2 and ·OH from abraded silicates could have a negative effect on the persistence of organic compounds in the Martian soil and the habitability of the Martian surface.

1. Introduction

Our understanding of Mars as a habitat for past and present life is closely linked to insight into the chemistry of its surface soil as soil chemistry affects the stability of organic compounds as well as the survival of organisms. Thus, a better qualitative and quantitative understanding of the reactivity of the Martian soil is essential for evaluation of the persistence of organic biomarkers, the risk of forward contamination and for identification of potential habitable sites. The Labeled Release (LR) experiment conducted by the Viking Landers demonstrated that simple ^{14}C-labeled organic compounds in an aqueous medium were oxidized with a concomitant release of $^{14}CO_2$ when exposed to Martian soil (Levin and Straat, 1979). Furthermore, the Gas Exchange (GEx) experiment showed that Martian soil exposed to water vapor released O_2 at higher quantities than what could be accounted for by atmospheric O_2 adsorbed on the sample surfaces (Oyama and Berdahl, 1977). Based on these observations, it has been proposed that one or more reactive oxygen species (ROS) are present in the Martian soil (Ballou et al., 1978; Klein, 1978). Specifically, H_2O_2, at least as an intermediate, has been held responsible for the reactivity observed by the LR and GEx experiments as disproportionation of H_2O_2 can lead to a release of O_2 and because H_2O_2 can oxidize organic compounds to CO_2 if catalyzed

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by e.g. ferrous iron (Fe^{2+}) or maghemite (γ-Fe_2O_3) (Apak, 2008; Oyama and Berdahl, 1979). Likewise, a direct production of ·OH would add to the reactivity of the Martian soil, as ·OH reacts with organic compounds at almost diffusion limited rates (Buxton et al., 1988). A production of ROS would thus influence the habitability of the Martian surface, pose a potential risk for future manned missions and may explain the scarcity of organic compounds (Glavin et al., 2013) despite the steady supply of organic compounds from micrometeorites (Botta and Bada, 2002) and the possible input of reduced carbon due to sequestration of atmospheric methane by abraded silicates (Bak et al., 2016; Jensen et al., 2014).

Various sources of oxidants in the Martian soil have been proposed including reactions between UV radiation and surface minerals (Carrier and Kounaves, 2015; Yen et al., 2000), ionizing radiation and perchlorates (Quinn et al., 2013), triboelectric charging in dust devils (Delory et al., 2006; Mills, 1977; Oyama and Berdahl, 1979; Tennakone, 2016) and fracturing of silicate minerals by meteor impacts (Hurowitz et al., 2007). However, the significance of these processes has not been validated *in situ* and the cause of the oxidation observed in the LR and the GEx experiments is still not resolved. The detection of perchlorate by the Phoenix Lander (Hecht et al., 2009), the indirect evidence for perchlorate from thermal volatilization experiments by the Curiosity Rover (Glavin et al., 2013) and the relatively uniform concentration of chlorine in all analyzed Martian soil samples point to a global presence of perchlorate salts in the Martian soil (Glavin et al., 2013). Perchlorate is a strong oxidant at high temperatures and has proven to complicate the detection of organic compounds when thermal volatilization techniques have been used on Mars (Bak et al., 2016; Glavin et al., 2013). However, at the low temperatures that prevail on Mars and at the temperatures used for the LR and the GEx experiments, perchlorate is largely inert and does not spontaneously oxidize organic compounds (Espenson, 2000).

The Martian soil is mainly composed of silicates (Bish et al., 2013) and the high abundance of primary minerals indicates that it predominantly originates from physical abrasion rather than chemical weathering (Gunnlaugsson et al., 2009). Wind is a significant factor for changes on the Martian surface at present, and movement of surface material by wind leads to erosion and abrasion (Bridges et al., 2014). Wind stress can mobilize surface particles by creeping, saltation and suspension and the repeated low velocity impacts in saltation is the driving force for abrasion. There is evidence for active saltation in the form of e.g. mobile sand dunes (Bridges et al., 2012) and the accumulation of sand-size particles on the deck of the Spirit Rover (Greeley et al., 2006). Furthermore, erosion and abrasion is evident by the presence of deflated areas and wind faceted rocks (Bridges et al., 2014).

Saltation of silicates could be a source of ROS via the production of reactive sites on the surfaces produced during fractioning of silicate minerals (Fubini and Hubbard, 2003; Vallyathan et al., 1988) and/or as an effect of triboelectric charging which in the low-pressure atmosphere of Mars (6–10 mbar, Harri et al., 2014) can lead to electrical discharges and a production of ROS by dissociation of atmospheric gases (Delory et al., 2006). Further support for our hypothesis that saltation of silicates may lead to the production of ROS is provided in the study by Merrison et al. (2010) which showed that magnetite is oxidized into hematite when mixture of quartz and magnetite were subjected to simulated saltation. The effect of fractioning of silicates has previously been studied in relation to meteor impacts on Mars (Hurowitz et al., 2007). However, it is not clear whether the effects of milling of silicates, as done by Hurowitz et al. (2007), is similar to the effects caused by abrasion by the low energy impacts in saltation. Additionally, the effect of the atmospheric composition was not taken into account by Hurowitz et al. (2007). Glow discharges have been reported for sand agitated in low-pressure atmospheres (Eden and Vonnegut, 1973; Mills, 1977) and the effects of triboelectric charging and electrical discharges on Mars have been modeled and discussed (Atreya et al., 2006; Farrell et al., 2015; Kok and Renno, 2009; Melnik and Parrot, 1998). Nevertheless, the production of ROS by these processes has so far not been demonstrated experimentally.

In the present study, we have conducted a series of laboratory simulations of saltation of silicates to investigate whether abraded silicates in the Martian soil can be a source of H_2O_2 and ·OH. Additionally, we have investigated the effects of the atmospheric composition to elucidate which processes dominate the production of H_2O_2.

2. Methods

2.1. Preparation of silicate samples

A large stock of crushed quartz and basalt was prepared based on a single batch of commercially available quartz (Merck, Cat. No. 1.07536) and an olivine basalt rock collected near Gufunes, Reykjavik in Iceland (64°08′22.18″N, 21°47′21.27″W). The quartz and basalt stocks were sieved to obtain the size fraction between 125 and 1000 µm. This fraction was sonicated and washed to remove fine particles. After drying, aliquots of 10 g were produced using a Fritsch Rotary Cone Sample Divider to ensure equal size distributions of all samples.

2.2. Simulation of wind driven saltation

Wind driven saltation was simulated by tumbling silicate samples in quartz glass ampoules (Fig. S1a). One end of the ampoules was pulled out to a narrow orifice through which the 10 g silicate samples were added. To prepare samples with gas compositions other than ambient air the ampoules were connected to a vacuum line. The line was evacuated to $P < 0.12$ mbar, the desired gas was added and the ampoules were sealed by melting. The pressure was monitored using a Pfeiffer TPR 265 gauge for $P < 1$ mbar and a Pfeiffer APR 250 gauge for $P > 1$ mbar. For samples prepared with a mixture of gases the gases were mixed in a 2.3 l container integrated in the vacuum line to ensure sufficient homogenization before the gas was directed to the ampoules. O_2, CO_2 and N_2 gas was obtained from AGA, Denmark (purity > 99.9%). For the preparation of a simulated Martian atmosphere 95% CO_2 and 5% of a gas mixture containing 60% N_2, 35% Ar, 3% O_2 and 2% CO (purity > 99%, Air Liquid, Denmark) were mixed to obtain a final composition of 95% CO_2, 3% N_2, 1.75% Ar, 0.15% O_2 and 0.1% CO, which closely resembles the composition of the Martian atmosphere (Mahaffy et al., 2013). The sealed ampoules were mounted in a turning wheel rotating at 30 rpm (Fig. S1b), which allowed the silicate sand to fall from one end of the ampoule to the other causing repeated low velocity impacts with velocities of maximum 2 m/s, as is characteristic of saltation (Merrison, 2012).

2.3. Opening of the ampoules and suspension of the samples for H_2O_2 measurements

The ampoules with samples abraded in ambient air were opened in ambient air whereas the samples abraded in vacuum or in defined gas mixtures of O_2, CO_2 or a simulated Martian atmosphere were opened and handled inside a glove box in a N_2 atmosphere. The ampoules were opened by scoring and breaking the narrow neck of the ampoule and the abraded material was mixed with water and vortexed. Triple distilled water or Milli-Q water was used for all experiments. The samples were vortexed again before subsamples were taken for determination of the H_2O_2 concentration.