

MECHANICALLY PRODUCED RADICAL SPECIES AT SILICATE SURFACES AND THE OXIDANT IN MARTIAN SOILS. J.A. Hurowitz¹, N.J. Tosca¹, S.M. McLennan¹ and M.A.A. Schoonen¹. ¹Department of Geosciences, State University of New York at Stony Brook, Stony Brook, NY 11794-2100 (joel.hurowitz@stonybrook.edu).

Introduction: The Labeled Release (LR) and Gas Exchange (GEx) experiments onboard the Viking Landers determined that the Martian soils at Chryse and Utopia Planitia contain unknown inorganic species of a highly oxidizing nature [1, 2, 3]. The LR experiment demonstrated that the addition of a radioactive ¹⁴C labeled nutrient solution to soil samples resulted in the production of ¹⁴C labeled CO₂ due to the breakdown of the organic species introduced [3]. In the GEx experiments, humidification of a 1cm³ Martian soil sample resulted in the production of as much as 790 nanomoles of O₂ gas [1]. The presence of a highly oxidizing species in the fine, wind-blown soils on Mars has obvious implications for both the stability of organic species in the Martian near-surface environment, as well as health implications for future human explorers who may be exposed to reactive dust particles through inhalation. At present, the nature of the oxidant in the Martian soils remains enigmatic. Explanations for their reactivity have called on both exotic chemical compounds and/or unusual formation processes to produce oxidants [see review in 3].

In the medical literature, specifically that related to silicosis and the toxicity of mineral dusts, it has long been known that the surfaces of freshly ground quartz particles are characterized by highly reactive radical species generated by the rupture of bonds during the grinding process [see review in 4]. These surface radical species are stable in dry environments (e.g. the Martian surface) and are capable of producing H₂O₂ and other Reactive Oxygen Species (ROS) in solution [4, 5]. Here, we extend the study of the reactivity of freshly ground mineral surfaces to include the silicate minerals most commonly encountered in basalts and soils at the Martian surface: feldspar, clinopyroxene and olivine [6, 7]. We propose that the oxidizing nature of the Martian soils can be explained by the presence of such mineral surface radical species and propose mechanisms by which they might be formed under ambient conditions at the Martian surface.

Methods: Samples of high-purity labradorite, augite, forsterite, and fayalite were obtained from Ward's Natural Science and analyzed by X-Ray diffraction and electron microprobe to confirm their purity. Each mineral phase was ground separately in an agate disk mill and the surface area of the resulting powder was measured by the BET N₂ technique using a Micromeritics ASAP 2010 surface area analyzer.

The grain size produced by milling in an agate disk mill is approximately 10-63 μm. This is considered a reasonable size range relative to Martian soils which exhibit grain sizes as low as ~1 μm for wind-blown dust [8]. Most of the soils examined by the Microscopic Imager (MI) onboard the Mars Exploration Rover Spirit exhibit grain sizes at the margin of MI resolution (~100 μm) [9].

Mineral powders were placed in individual Teflon[®] beakers and 5 mL of deionized water were pipetted onto them. The beakers were capped, gently shaken, and allowed to stand for 3 minutes. The sample solutions were then filtered using a 0.2 μm syringe filter, and analyzed for H₂O₂ by fluorimetry using a method modified after that of Holm et al. [10] and Zhang and Wong [11]. Two analyses of a 220 nanomolar (nM) H₂O₂ standard (as determined by gravimetry) yielded results of 215 ± 5.8 nM and 218 ± 4.0 nM. The minimum detection limit of the H₂O₂ analysis technique is determined by the ability to produce H₂O₂-free reagents [10]. A full process blank was run before each mineral was analyzed for H₂O₂ release, and the blank subtracted from the determined concentration. Typical blank concentrations range from 15-35 nM.

Results: Results of H₂O₂ analysis indicate that when 108.8 mg of powdered labradorite sample is exposed to 5mL of DI water, the concentration of H₂O₂ formed by reaction between the powder and DI water is 33.5 ± 4.1 nM (after subtraction of blank) [12]. When these results are normalized to the labradorite surface area, the number of nanomoles of H₂O₂ produced per m² = 0.86 ± 0.11 [12].

Results of H₂O₂ analysis for reactivity tests on powdered augite indicate a release of ~75 nanomoles H₂O₂/m². Results of reactivity testing for forsterite yield qualitatively higher amounts of H₂O₂ than augite. Fayalite yielded a non-detect for H₂O₂; we suggest that this may be the result of H₂O₂ consumption by Fe²⁺ (either in solution or at the mineral surface) to produce hydroxyl radical (OH[•]) via the Fenton reaction. Our analysis technique is not sensitive to OH[•]. The results for augite, forsterite and fayalite are considered preliminary and require additional reactivity tests to assess their reproducibility.

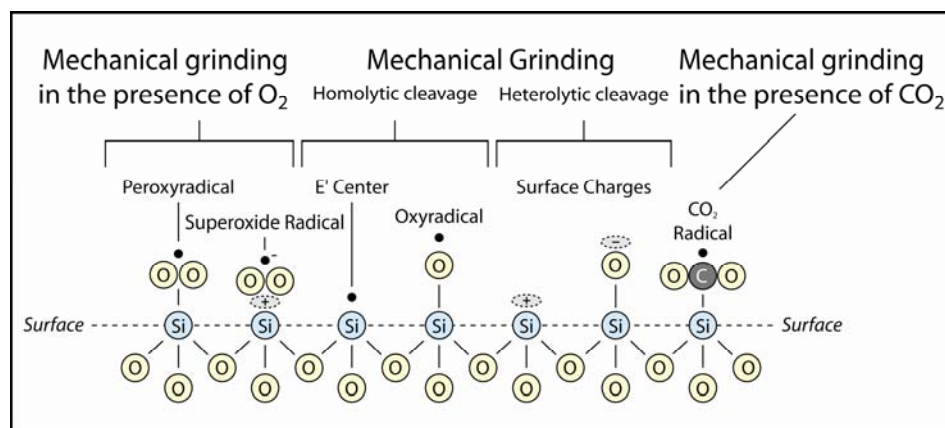


Figure 1: Reactive functionalities at the quartz surface and their formation mechanisms. After Fubini et al. [5]. Aqueous suspensions of freshly ground quartz generate H_2O_2 , OH^\cdot , O_2^\cdot , and other reactive oxygen species [4].

Discussion: Mechanical grinding and its effect on the surface properties of quartz has been studied in great detail in order to better understand the causes of lung damage related to the inhalation of quartz dusts [4, 5, 13, 14]. The cleavage of mineral surfaces during grinding results in the formation of radical species at the mineral surface, a variety of which are shown schematically in **Figure 1**. These species are identified using electron paramagnetic resonance spectroscopy, which is sensitive to compounds having unpaired electron spins. Aqueous suspensions of freshly ground quartz powders have been shown to generate reactive oxygen species in solution, including H_2O_2 , OH^\cdot , and superoxide (O_2^\cdot) [4, 13]. In addition, quartz dusts have been shown to retain much of their initial reactivity after storage for a period of months in a humid atmosphere [5].

Because Mars is a basaltic planet, quartz is unlikely to be an important primary mineral phase. The reactivity of basaltic silicate minerals (plagioclase, pyroxenes, olivine) has not been assessed in the current literature. Our initial results for H_2O_2 release from augite and forsterite indicate highly reactive surfaces capable of producing high concentrations of H_2O_2 in contact with DI water. Fayalite may produce OH^\cdot .

The Viking Labeled Release tests indicated a release of ~ 30 nanomoles of $^{14}\text{CO}_2/\text{m}^2$ of soil sample, and the Viking Gas Exchange tests indicated 4-42 nanomoles O_2/m^2 of soil [1, 3]. If one assumes a 1:1 reaction stoichiometry (1 mole of oxidant = 1 mole of $^{14}\text{CO}_2$ or O_2), then the amount of H_2O_2 detected in our experiments is of the same order of magnitude of oxidant required to explain the LR and GEx tests. These preliminary findings are intriguing in that they provide a potentially simple explanation for the Viking LR and GEx tests: water in contact with crushed silicate minerals results in the production of oxidants in solution. *Possible Mechanisms for Generating Reactive Silicate Surfaces in the Natural Environment:* A valid question to be proposed with regards to our model is how

such reactive particles are produced in the natural environment. We suggest two mechanisms: (1) production of fine-grained reactive particles during eruption of volcanic ashes, and (2) production of such particles as a result of pulverization of the basaltic Martian crust by impact. The former has been studied on Earth in order to understand the toxicity of fresh volcanic ashes deposited as a result of volcanic activity in areas such as Montserrat and Mount St. Helens [15, 16]. The reactivity of the soils might be further maintained by breakdown of soil particulates through aeolian abrasion. Given that silicate mineral surfaces can retain some fraction of their reactivity under humid terrestrial conditions, it is not unreasonable to expect that once formed, such reactive species could persist for long periods of time in the dry Martian environment. These results indicate that the toxicity of basaltic mineral dusts will need to be assessed prior to human exploration of both Mars and the Moon. On the Moon, there is no atmosphere present to provide humidity which might dissipate the reactivity of silicate dusts, and the risk to humans may be even greater than on Mars.

References: [1] Oyama, V. & Berdahl, B., (1977) *JGR*, 82, 4669-4676. [2] Klein, H. (1978) *Icarus*, 34, 666-674. [3] Zent A., & McKay, C. (1994) *Icarus*, 108, 146-157. [4] Fubini, B. & Hubbard, A. (2003) *Free Radical Bio. Med.*, 34, 1507-1516. [5] Fubini, B. et al. (1990) *Toxicol. Ind. Health*, 6, 571-598. [6] Morris, R., et al. (2004) *Science*, 305, 833-836. [7] Bandfield, J. (2002) *JGR*, 107, E6. [8] Moore, H. & Jakosky, B. (1989) *Icarus*, 91, 164-184. [9] Herkenhoff, K. (2004) *Science*, 305, 824-826. [10] Holm, T. et al. (1987) *Anal. Chem.*, 59, 582-586. [11] Zhang, L. & Wong, G. (1999) *Talanta*, 48, 1031-1038. [12] Hurowitz, J. et al. (submitted) *EPSL*. [13] Fenoglio, I. et al. (2000) *Mater. Synth. Process.*, 8, 145-153. [14] Konecny, R. et al. (2001) *J. Environ. Pathol. Toxicol. Oncol.*, 20, 119-132. [15] Horwell, J. et al. (2003) *Environ. Res.*, 93, 202-215. [16] Martin, T. et al. (1986) *Amer. J. Public Health*, 76, 59-65.