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Hot Idea

posted June 19, 2007

# **Oxidants from Pulverized Minerals**

--- Laboratory measurements of hydrogen peroxide produced from crushed basaltic minerals immersed in water have important implications for Martian and lunar dust.



#### Written by Linda M. V. Martel

Hawai'i Institute of Geophysics and Planetology

**J** oel Hurowitz (previously at State University of New York at Stony Brook and now at the Jet Propulsion Laboratory), Nick Tosca, Scott McLennan, and Martin Schoonen (SUNY at Stony Brook) studied the production of hydrogen peroxide ( $H_2O_2$ ) from freshly pulverized minerals in solution. Their experiments focused on olivine, augite, and labradorite; silicate minerals of basaltic planetary surfaces, such as the Moon and Mars, that are exposed to the intense crushing and grinding of impact cratering processes. The  $H_2O_2$  produced in the experiments was enough to adequately explain the oxidizing nature of Martian regolith first determined by the <u>Viking</u> Landers and the results suggest, for the first time, that mechanically activated mineral surfaces may be an important part of the overall explanation for the Viking Lander biology experiment results. Hurowitz and coauthors further showed that when the pulverized minerals are heat-treated to high temperature under vacuum (to cause dehydroxylation) there is almost a 20 times increase in  $H_2O_2$  production, a result which may be highly relevant to lunar dust. These careful studies demonstrate the importance of and concern about reactive dusts on planetary surfaces from two standpoints: the health of astronauts on surface maneuvers who may inadvertently breath it and the viability of possible Martian organic species to survive in such a corrosive, antiseptic surface environment.

Reference:

• Hurowitz, J. A., Tosca, N. J., McLennan, S. M., and Schoonen, M. A. A. (2007) Production of Hydrogen Peroxide in Martian and Lunar Soils, *Earth and Planetary Science Letters*, v. 255, p. 41-52.

**PSRDpresents:**Oxidants from Pulverized Minerals--<u>Short Slide Summary</u> (with accompanying notes).

#### **Oxidizing Dust**

**F** rom the time of the 1976 Viking Lander Gas Exchange (GEX) and Labeled Release (LR) experiments on the surface of Mars, researchers have known that Martian regolith is highly oxidizing. What the oxidant is and how it is formed has been debated ever since. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was an early candidate and scientists using powerful telescopes finally reported in 2004 the detection of H<sub>2</sub>O<sub>2</sub> in the Martian atmosphere. Yet, researchers discovered that the observed abundance of H<sub>2</sub>O<sub>2</sub> in the Martian atmosphere was at least a factor of 1000 to 10,000 lower than the amount of oxidizer in the Martian regolith estimated from the Viking experiments at Chryse and Utopia Planitia.



Viking Lander 1, NASA press release image #77-HC-62

Trenches in the regolith at Chryse Planitia made by the Viking Lander 1 trenching arm can be seen in the lower right of this image, which was taken by the onboard camera. In the distance are low dunes composed of fine-grained material. Part of the Lander can be seen in the lower left, as well as the extended meteorology boom that was used for atmospheric experiments.

There have been many ideas proposed to explain the excess oxidant on the Martian surface, including biogenic processes or chemical changes above the Martian surface when dust devils and storms generate large-scale electrostatic fields. Hurowitz and coauthors addressed the issue by considering the effects that impact cratering has on planetary surfaces and how the resulting mechanically pulverized mineral dust would react with water to produce reactive oxygen species, such as H<sub>2</sub>O<sub>2</sub>. Though the Martian surface is dry today, there is abundant evidence of a warmer and wetter past [see, for example, **PSRD** articles: <u>Magma and Water on Mars</u>, <u>Gullies and Canyons</u>, <u>Rocks and Experiments</u>: <u>The Mystery of Water on Mars</u>, and <u>Liquid Water on Mars</u>: <u>The Story from Meteorites</u>] and a chance for H<sub>2</sub>O<sub>2</sub> production. Whenever water flowed or clouds drizzled, water could come in contact with reactive surface grains. On the Moon it never rains, but water would come in contact with dust grains when astronauts carried dust into their habitats and when they breathed the activated dust.

The idea of experimenting with reactive dusts follows naturally from years of medical research of human exposure to fine-grained carcinogenic quartz dusts and associated lung diseases. So, Hurowitz and coauthors used their cosmochemistry expertise to extend the study of  $H_2O_2$  production from quartz dust to freshly ground silicate minerals that are known to exist in the basaltic crusts on Mars and the Moon.

#### H<sub>2</sub>O<sub>2</sub> from Mineral Powders in Solution

**H**ydrogen peroxide is a powerful oxidizer and disinfectant and has been referred to previously (e.g. Atreya and others) as a possible answer to why no organics have ever been detected by spacecraft on the surface on Mars. So the task laid out by Hurowitz and colleagues was to measure the quantity of  $H_2O_2$  produced from a suite of basaltic silicate minerals common on Mars and the Moon, including olivine, augite, and labradorite. These minerals are pulverized into planetary regolith and dust during impact cratering events. Hurowitz and coauthors simply opted for a rock mill in the laboratory. They used an electron microprobe to determine the chemical compositions of their samples and then crushed the mineral samples into powders with grain sizes ranging from about 0.5 to 350 micrometers. These lab powders were slightly coarser-grained with a lower surface area compared to Martian regolith, but similar in grain size and surface area to lunar regolith. Each separate mineral

powder was mixed with deionized water, then filtered and analyzed for  $H_2O_2$  concentration. This formation mechanism for  $H_2O_2$  works because the process of grinding causes chemical bonds to break and the surfaces of the freshly pulverized minerals become sites of highly reactive radical species. These radical species are stable while dry, but produce  $H_2O_2$  when immersed in water.

The researchers found that the production of  $H_2O_2$  was not so dependent on grain size or surface area or amount of sample used in the experiments as on the actual structure of the mineral phase itself. Silica tetrahedra exist as separate, isolated structures or chains or three-dimensional structures. The isolated silica tetrahedra (e.g. olivine) share no corners, are known to be easily weathered (chemically altered), and produced the highest amounts of  $H_2O_2$  during the experiments (see plot below).

They computed how much  $H_2O_2$  was produced by normalizing the total number of nanomoles of  $H_2O_2$  in solution by the total surface area (m<sup>2</sup>) of the mineral powders. For example, olivine powder produced 21 to 25 nanomoles  $H_2O_2/m^2$ , augite produced 6.6 to 9.1 nanomoles  $H_2O_2/m^2$ , and labradorite produced about 1 nanomole  $H_2O_2/m^2$ . Interesting too, Hurowitz and colleagues measured <1 namomole  $H_2O_2/m^2$  produced from immersed quartz powders, which shows clearly that the basaltic silicate minerals are capable of forming higher concentrations of  $H_2O_2$  in solution than is quartz under the same conditions of mechanical pulverization.



Hurowitz and coauthors were also interested in how much  $H_2O_2$  would form in solution from dehydroxylated mineral samples. Dehydroxylated minerals have surface-bound water ( $H_2O$ ) and hydroxyl (OH) stripped away by heat treatment under vacuum (see diagram below). Two labradorite samples were dehydroxylated before being immersed in water and they yielded  $24 \pm 4$  and  $33 \pm 3$  nanomoles  $H_2O_2/m^2$ , quantities significantly greater than those produced by non-heated samples mentioned above. When the experiments were repeated on the dehydroxylated samples 30 minutes later the  $H_2O_2$  values were slightly lower, which suggests to the research team that there might be another, shorter-lived oxidant produced when heat-treated mineral samples are immersed in water. They don't know what that other oxidant would be. The results, nonetheless, are significant for the Moon where plagioclase-rich regolith may exist in a partially dehydroxylated state that researchers attribute to impact heating in vacuum and high daytime surface temperatures.





## Looking Back to Viking Lander

Assuming that 1 mole of  $H_2O_2$  results in 1 mole of  $O_2$ , Hurowitz and colleagues' experiments show that their mineral powders released enough oxidant to adequately explain the Viking Lander Gas Exchange (GEX) results without having to invoke any other explanation for Martian regolith reactivity. They offer the simple explanation that oxidant was formed as a result of reactions between water and silicate mineral surfaces that had been crushed and activated by impact pulverization. Yet they concede that this mechanically-induced reactivity may really be only one contribution to the overall reactivity of planetary regolith.

Cosmochemical analyses show that the physical, optical, chemical, and mineralogical properties of Martian and lunar regoliths have clearly been modified since formation. For instance, on Mars, water, wind, and chemical weathering have changed material properties and have created new secondary alteration minerals (see **PSRD** article: <u>Pretty Green Mineral--Pretty Dry Mars?</u>) On the Moon, impact gardening and space weathering have caused changes in surface materials (see **PSRD** article: <u>New Mineral Proves an Old Idea about Space</u> <u>Weathering</u>.) How any of these subsequent modification processes and products have influenced the reactivity of the regolith materials and how deep the contamination goes are still to be determined.

## **Looking Forward**

**H**igh concentrations of reactive oxygen species, such as  $H_2O_2$ , in planetary regoliths and dusts are of great concern and there is strong interest in characterizing them so that mitigation procedures can be worked out if fine-grained dust poses a health hazard to the respiratory systems of future astronauts working on the Martian or lunar surface. Furthermore for Mars, the radiation and oxidative environment have important ramifications on "life on Mars" surface and subsurface habitability issues.

Hurowitz and his coworkers' work was funded in part by NASA's Cosmochemistry program, which funds basic research in planetary materials. The applicability to life on Mars and to future missions to the Moon, Mars, and beyond shows how strongly basic research is connected to fundamental scientific questions and to mission planning.

### Additional Resources

LINKS OPEN IN A NEW WINDOW.

- **PSRDpresents:** Oxidants from Pulverized Minerals--<u>Short Slide Summary</u> (with accompanying notes).
- Atreya, S. K., Mahaffy, P. R., and Wong, A-S. (2007) Methane and Related Trace Species on Mars: Origin, Loss, Implications for Life, and Habitability, Planetary and Space Science, v. 55, p. 358-369.
- Atreya, S. K., Wong, A-S., Renno, N. O., Farrell, W. M., Delory, G. T., Sentman, D. D., Cummer, S. A., Marshall, J. R., Rafkin, S. C. R., and Catling, D. C. (2006) Oxidant Enhancement in Martian Dust Devils and Storms: Implications for Life and Habitability, Astrobiology, v. 6, p. 439-450.
- Hurowitz, J. A., Tosca, N. J., McLennan, S. M., and Schoonen, M. A. A. (2007) Production of Hydrogen Peroxide in Martian and Lunar Soils, *Earth and Planetary Science Letters*, v. 255, p. 41-52.
- Zent, A. P., and McKay, C. P. (1994) The Chemical Reactivity of the Martian Soil and Implications for Future Missions, Icarus, v. 108, p. 146-157.
- "Key to Martian Atmosphere Found" <u>Press Release</u> from the Joint Astronomy Centre regarding the 2004 detection of hydrogen peroxide in the atmosphere of Mars.
- Viking: A Laboratory on Mars <u>Website</u>, nice overview from the Smithsonian National Air and Space Museum.



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