

EFFECTS OF MARTIAN SURFACE MATERIALS ON THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE. R. H. Dame¹, P. D. Archer Jr.² and J. V. Hogancamp^{3,1}Department of Physics and Astronomy, Brigham Young University, Provo, UT 84602, ²Jacobs, NASA Johnson Space Center, Houston, TX 77058. ³Geoncontrols Systems Inc., NASA Johnson Space Center, Houston, TX 77058.

Introduction: While hydrogen peroxide (H_2O_2) has been detected in the martian atmosphere, it has not yet been detected in surface materials [1]. Hydrogen peroxide is a powerful oxidant and is destructive to organic molecules; thus, knowledge of its presence would be very useful for future missions with respect to understanding the potential for the survival of organic molecules and for potential life on Mars. Since the Viking lander mission, we have sent instruments to Mars with the capability to detect H_2O_2 . The Sample Analysis at Mars (SAM) instrument on board the Curiosity rover and Thermal and Evolved Gas Analyzer (TEGA) instrument on the Phoenix lander both detected water and oxygen releases from analyzed sediments. Whether or not peroxide could be the source of these gases has not been investigated through laboratory experiments. In this study, Mars-relevant minerals were mixed with hydrogen peroxide and studied using a SAM/TEGA analog laboratory instrument in order to determine the potential for H_2O_2 in martian surface materials.

In studies of perchlorates on Mars, it was found that perchlorates alone have higher oxygen release temperatures than the SAM-analyzed samples from Gale Crater. Therefore, the O_2 releases could not have been due to perchlorates alone. It has also been determined that when mixing Mars analogue iron-phase minerals with perchlorates, the oxygen release temperatures were lowered into the gas release temperature range similar to the gas release temperature of the Gale crater samples[2,3]. Hydrogen peroxide alone decomposes to H_2O and O_2 , with the peak of the decomposition around 100 °C (Fig. 1). This is lower than the O_2 releases detected with SAM or TEGA, but, as described with perchlorates, the presence of other minerals can affect decomposition temperatures. Therefore, we hypothesized that other minerals could alter peroxide decomposition behavior and we could compare lab data to results from Mars to determine whether or not hydrogen peroxide could have been present in the samples analyzed on Mars.

Materials and Methods: ~20 mg of hematite, siderite, San Carlos forsterite, pyrrhotite, magnetite and nontronite (representing a broad range of minerals relevant to Mars) were mixed with 5 μ l 50% H_2O_2 , and were either run immediately or placed in a sealed tube for 2, 4, or 9 days to look for changes over time. Eight samples of each mineral were made so that there would

be two reps for each exposure time. The mineral and hydrogen peroxide were mixed using a dental tool to insure even distribution of the H_2O_2 , after which the samples were then stored in sealed tubes and left in room temperature for their assigned exposure time.

The samples were analyzed in a Setaram Sensys Evo differential scanning calorimeter (DSC) instrument connected to a mass spectrometer to detect the gases released from the sample. The furnace was purged with a helium carrier gas at a pressure of ~30 mbar, and helium gas flow rate of 3 ml/min. Each sample was heated from -60 °C to 500 °C at a rate of 20 °C/min. As a control, ~5 μ l of 50% H_2O_2 was also run following the same procedure.

Each mineral was analyzed with a Panalytical X'pert pro X-ray diffractometer with a Co $K\alpha$ X-ray source to look for changes in mineralogy. A 50 mg sample of each analog mineral was mixed with 12.5 μ l

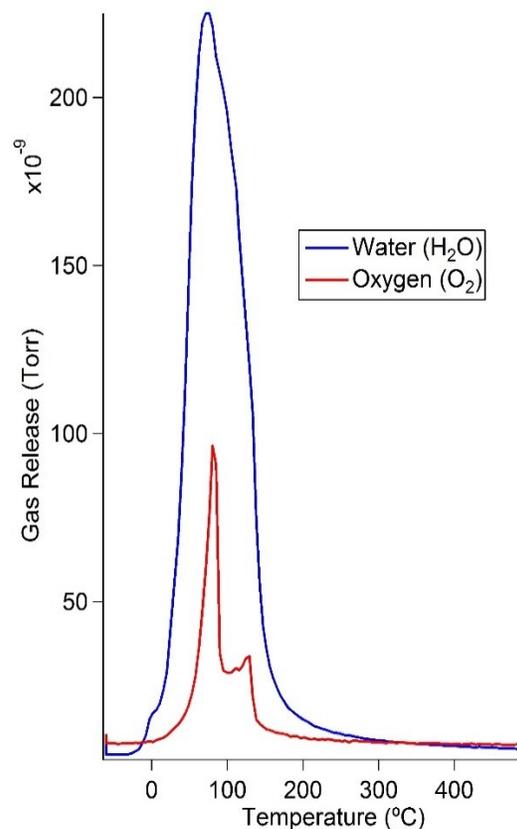


Figure 1. The gas release temperature of (a) water and (b) oxygen for a sample of 5 μ l 50% H_2O_2 . 2 θ step with 1 min per step [4].

50% H_2O_2 and left in a sealed tube for 10+ days. Samples were analyzed at 45 kV and 40 mA with a 0.02°

Results and Discussion: The results and data from both evolved gas and XRD are as follows:

EGA: Hydrogen peroxide alone has oxygen and water release temperatures that peak around the 100°C (Fig. 1). The nontronite and hematite EGA samples data shows that as the exposure time of the samples increased, the oxygen and water gas releases did not change. For the magnetite samples, the oxygen and water release temperatures slowly decreased as exposure time increased (Fig 2). The magnitude of the gas releases also decreases as the exposure time increases. The San Carlos forsterite samples also have a decrease in oxygen gas releases as time exposure increases and only a slight shift to lower temperature (not shown); its water gas release temperature shifts slightly to lower temperature but maintains roughly the same magnitude. When mixing the siderite sample and H_2O_2 the mixture visibly reacted. The siderite EGA sample data shows that the mixing decreased the gas release temperature but all the exposure time samples had similar release temperatures.

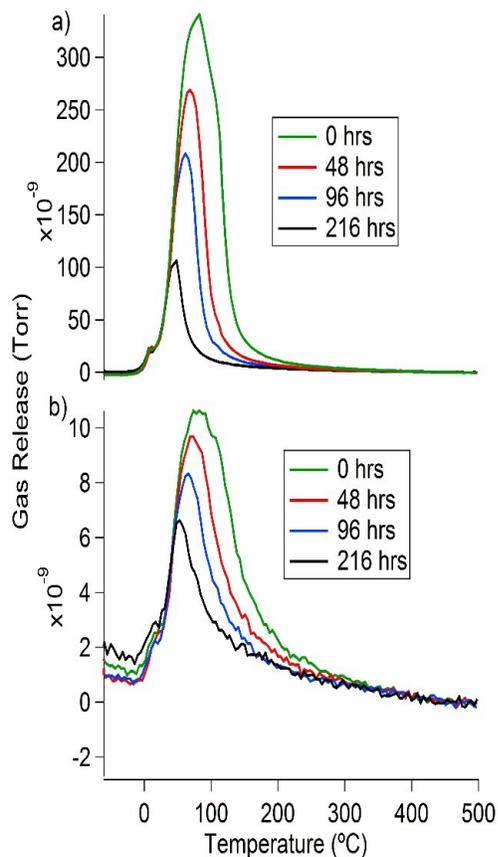


Figure 2. The gas release temperature of (a) water and (b) oxygen for the mineral magnetite with varying time exposure.

The results from the EGA data show that mixing these minerals and hydrogen peroxide can cause a lower gas release temperature over time, a decrease in the gas release magnitude over time or no change.

XRD: Samples of unaltered minerals were compared with the samples with 10-12 days of exposure to $12.5\ \mu\text{l}$ 50% H_2O_2 . Hematite, magnetite, nontronite and siderite samples did not display changes in mineralogy which was particularly surprising for the siderite which visibly reacted with the peroxide when mixed. The XRD analysis showed that the mineralogy of pyrrhotite and San Carlos forsterite changed when mixed with hydrogen peroxide. The change of the pyrrhotite was most dramatic. The results showed that the sample went from being pure pyrrhotite to being about 56% pyrrhotite and 44% iron sulfate hydrate (Fig. 4).

Conclusions: Preliminary results show three potential outcomes of the peroxide/mineral mixtures: 1) no noticeable effect on the peroxide or the sample (e.g., hematite, nontronite), 2) the mineral is unaffected but catalyzes peroxide decomposition (magnetite, siderite), or 3) peroxide alters the mineral (pyrrhotite, San Carlos forsterite). In all of these cases, if peroxide decomposition changed, the $\text{O}_2/\text{H}_2\text{O}$ releases were shifted to slightly lower, not higher temperature, making it less likely that peroxides have been present in martian samples.

References: [1] Clancy et al. (2004) *Icarus*, 168, 116–121. [2] Sutter et al. (2015) *LPSC XLVI, Abst. #2137*. [3] Sutter et al. (2013) *LPSC XLIV, Abst. #2046*. [4] Peretyazhko et al. (2016) *Geochemica et Cosmochimica Acta*, 188, 284–496.