

THERMAL DECOMPOSITION OF CALCIUM PERCHLORATE/IRON-MINERAL MIXTURES: IMPLICATIONS OF THE EVOLVED OXYGEN FROM THE ROCKNEST EOLIAN DEPOSIT IN GALE CRATER, MARS. A.M. Bruck¹, B. Sutter^{2,3}, D.W. Ming³, and P. Mahaffy^{4,1} Department of Chemistry, Illinois State University, Normal, IL 61761. (ambruc2@ilstu.edu), ²Jacobs Houston, TX 77058, ³NASA-Johnson Space Center, Houston, TX 77058, ⁴NASA Goddard Space Flight Center, Greenbelt, MD 20771

Introduction: A major oxygen release between 300 and 500°C was detected by the Mars Curiosity Rover Sample Analysis at Mars (SAM) instrument at the Rocknest eolian deposit. Thermal decomposition of perchlorate (ClO₄⁻) salts in the Rocknest samples are a possible explanation for this evolved oxygen release [1, 2]. Relative to Na-, K-, Mg-, and Fe-perchlorate, the thermal decomposition of Ca-perchlorate in laboratory experiments released O₂ in the temperature range (400-500°C) closest to the O₂ release temperatures observed for the Rocknest material [1]. Furthermore, calcium perchlorate could have been the source of Cl in the chlorinated-hydrocarbons species that were detected by SAM [2].

Different components in the Martian soil could affect the decomposition temperature of calcium perchlorate or another oxychlorine species. This interaction of the two components in the soil could result in O₂ release temperatures consistent with those detected by SAM in the Rocknest materials. The decomposition temperatures of various alkali metal perchlorates are known to decrease in the presence of a catalyst [4, 5, 6]. The objective of this work is to investigate catalytic interactions on calcium perchlorate from various iron-bearing minerals known to be present in the Rocknest material.

Materials and Methods: Reagent grade Ca(ClO₄)₂•4H₂O from ACROS ORGANICS was dissolved in deionized water, flash frozen with N₂(l), and subsequently, freeze dried in a Labconco Freezone 4.5 Plus evaporator. The dehydrated Ca-perchlorate was ground with an agate mortar/pestle and sieved (≤ 125 μm) in a N₂(g) purged glove box to minimize rehydration. The iron minerals that were mixed with the Ca-perchlorate included a synthetic magnetite (MTS4), synthetic hematite [7], pyrite, and fayalite with a magnetite contaminant (Forsythe Iron Mine in Ontario, Canada, # 49 V 1555). A Mauna Kea Volcano dust sample (HWMK919) was used as a Martian soil analog [8] (≤ 5 microns) and also mixed with Ca-perchlorate. With the exception of the HWMK919 material, all samples were ground with an agate mortar and pestle and sieved to less than 125 microns.

Each iron mineral (except pyrite) used for the mixtures represented a mineral component discovered in Rocknest material [9]. HWMK919 contains Fe-

amorphous material which is analogous to the amorphous material detected in the Rocknest material [9].

Simulated SAM analyses were conducted using a Setaram Sensys-Evo differential scanning calorimeter (DSC) coupled to a Stanford Research Systems Universal Gas Analyzer (MS) which together have been configured to operate similarly to the SAM oven/QMS system. Samples in the JSC-SAM-testbed were heated from 25 to 715°C at a heating rate of 35°C/min while being purged (3 mL/min) under 30-75 mbar He carrier gas. Rehydration of Ca-perchlorate was minimized by quickly mixing 3.2 mmol Ca-perchlorate outside of the glovebox with 1 and 5 molar equivalent (3.2 and 16 mmol, respectively) of each individual Fe phase. The HWMK919 is a palagonitic material with a complex mineralogy which made it difficult to determine molecular weight of the sample. Therefore, the sample was prepared with 0.5 or 2.5 mg of HWMK919 to mimic the relative amounts of material used for the other Fe-bearing minerals

Calcium Perchlorate Thermal Decomposition:

The thermal decomposition of Ca-perchlorate typically occurs as follows [11].

- (a) $[\text{Ca}(\text{H}_2\text{O})_4](\text{ClO}_4)_2 \rightarrow \text{Ca}(\text{ClO}_4)_2 + 4\text{H}_2\text{O}$
- (b) $\text{Ca}(\text{ClO}_4)_2 \rightarrow \text{Ca}(\text{ClO}_4)_2 (\text{melt})$
- (c) $\text{Ca}(\text{ClO}_4)_2 \leftrightarrow \text{CaCl}_2 + 4\text{O}_2$

Reaction (a) is a summary reaction that represents multiple dehydration steps. Ca-perchlorate melts (b) and then finally decomposes by releasing O₂ and forming CaCl₂ (c) [11].

Results and Discussion: The above reaction mechanism is reflected by the thermal data (Fig. 1) where the first endotherm corresponds to reaction (a) (≤ 150°C), the second endotherm corresponds to reaction (b) (≤ 400°C), and the large exotherm reaction (c) (≥ 400°C). The Fe-bearing minerals only affect reaction (c) exotherms as indicated by the observed temperatures shifts relative to Ca-perchlorate alone (Fig. 1). The relative order of Fe-minerals that decreased the Ca-perchlorate decomposition peak temperature the most were magnetite (-35°C) > hematite (-30°C) > pyrite (-10°C) > HWMK919 (-0°C) > fayalite (+10°C) (Fig. 1).

Evaluation of the O₂ peak temperature release data of the mixtures relative to the Ca-perchlorate only sample (Fig. 2) followed the same order as the thermal data. The order was magnetite (-25°C) > hematite

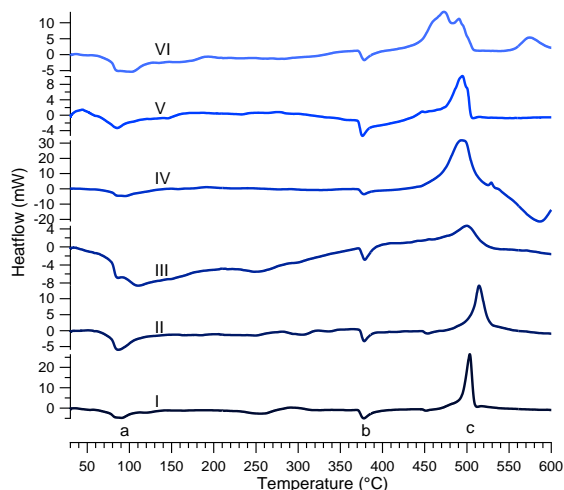


Figure 1: Differential scanning calorimetry results of $\text{Ca}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ with 1 molar equivalent of the corresponding Fe-bearing analog versus temperature. a, b, c correspond to reactions a, b, and c in text, respectively. I. $\text{Ca}(\text{ClO}_4)_2$, II. $\text{Ca}(\text{ClO}_4)_2$ + fayalite, III. $\text{Ca}(\text{ClO}_4)_2$ + HWMK919, IV. $\text{Ca}(\text{ClO}_4)_2$ + pyrite, V. $\text{Ca}(\text{ClO}_4)_2$ + hematite, VI. $\text{Ca}(\text{ClO}_4)_2$ + magnetite.

(-20°C) >pyrite (-10°C) >HWMK919 (-0°C) >fayalite (+10°C).

Between the two methods (DSC and QMS) there is a small difference in the two Fe oxide sample mixtures decomposition temperature (~10°C). However, the largest differentials (~20-25°C) caused by magnetite and hematite does not drop the perchlorate O_2 release to match that of Rocknest. The pyrite, HWMK919, and fayalite-calcium perchlorate mixtures resulted in little to no change in the peak decomposition temperature. However, the HWMK919 mixtures does provide on onset temperature that better correlates to the Rocknest O_2 release (Fig. 2) and needs to be further investigated.

Although fayalite had little effect on the perchlorate O_2 release temperature, HCl (m/z 36) and Cl (m/z 35) releases temperatures (>580°C) were consistent with HCl release temperatures detected in Rocknest (data not shown). Evolved chlorine species were also observed with the pyrite and the HWMK919 mixtures >450°C (data not shown). Evidence of evolved chlorine from pure calcium perchlorate was previously reported [2], but was inconsistent with the results found in this study. These results suggest that Fe-phases may have a role in releasing Cl species at temperatures greater than perchlorate decomposition temperatures.

Conclusions: Iron oxides (magnetite and hematite) have the most effect on reducing the decomposition temperature of calcium perchlorate species. Both iron oxides are reported to exist in Rocknest, about 2 wt. %

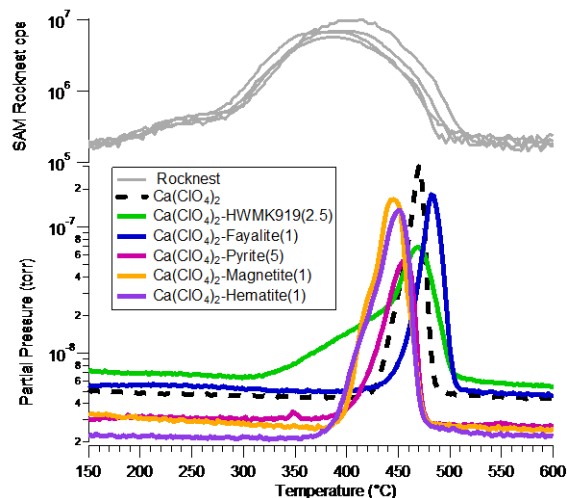


Figure 2: Evolved oxygen release from Rocknest, and MS results for $\text{Ca}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$ +Fe analog materials versus temperature. The numbers represent the Fe-mineral molar equivalent, or weight amount in mg for HWMK919.

magnetite and 1 wt. % hematite [9]. This suggests that these Fe-oxides may be in part responsible for the lower O_2 evolution temperatures observed from the wind-blown deposit. However, when comparing the catalytic tendencies of these iron bearing minerals to the evolved O_2 release found by SAM none of the crystalline components in the investigated minerals resulted in similar O_2 release temperature. The amorphous HWMK919 mixture did not yield an exact O_2 peak temperature match, but its overall O_2 temperature release did span most of the Rocknest O_2 release temperature range. Since its O_2 release did span across the SAM's observed O_2 release more work evaluating amorphous Fe phase mixtures is needed.

Evolved chlorinated species were only detected during analysis of the HWMK919, fayalite and pyrite mixtures indicating that Fe-phases may have a role in releasing the HCl phases detected in Rocknest. Future work will evaluate magnesium and sodium perchlorate/chlorates mixed with Fe phases as potential sources of evolved O_2 and HCl from Rocknest.

References: [1] Leshin et al. (2013) *Science*, 341, 1238937. [2] Glavin et al. (2013), *JGR*, 118, 1955. [3] Rao B., et al. (2010), *Environ. Sci. Technol.*, 44, 8429. [4] Furuichi (1974), *J. Therm. Anal.*, 6, 305. [5] Lee et al. (2001), *Thermochimica Acta*, 367. [6] Meyer et al. (1965), *J. Phys.Chem*, 69, 1114. [7] Morris et al. (2000) *JGR*, 105, 1757. [8] Morris et al. (2001), *JGR*, 106, 5057. [9] Bish et al. (2013), *Science*, 341, 1238932. [10] Vanimen et al. (2013) *Science*, 1243480. [11] Migdal-Mikuli (2008), *J. Therm. Anal. Calor.*, 91, 529.