

A POSSIBLE ORGANIC CONTRIBUTION TO THE LOW TEMPERATURE CO₂ RELEASE SEEN IN MARS PHOENIX THERMAL AND EVOLVED GAS ANALYZER DATA. P. D. Archer, Jr.¹, H. V. Lauer, Jr.², B. Sutter³, D. W. Ming¹, P. B. Niles¹, and W. V. Boynton⁴, ¹NASA Johnson Space Center, 2101 NASA Parkway, Building 31 Mail Code KX, Houston, TX 77058, doug.archer@gmail.com. ²ESCG/Barrios Technology, Houston, TX 77058, ³Jacobs-ESCG, Houston, TX 77058, ⁴Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721.

Introduction: Two of the most important discoveries of the Phoenix Mars Lander were the discovery of ~0.6% perchlorate [1] and 3-5% carbonate [2] in the soils at the landing site in the martian northern plains. The Thermal and Evolved Gas Analyzer (TEGA) instrument was one of the tools that made this discovery. After soil samples were delivered to TEGA and transferred into small ovens, the samples could be heated up to ~1000 °C and the gases that evolved during heating were monitored by a mass spectrometer. A CO₂ signal was detected at high temperature (~750 °C) that has been attributed to calcium carbonate decomposition. In addition to this CO₂ release, a lower temperature signal was seen. This lower temperature CO₂ release was postulated to be one of three things: 1) desorption of CO₂, 2) decomposition of a different carbonate mineral, or 3) CO₂ released due to organic combustion. Cannon et al. [3] present another novel hypothesis involving the interaction of decomposition products of a perchlorate salt and calcium carbonate.

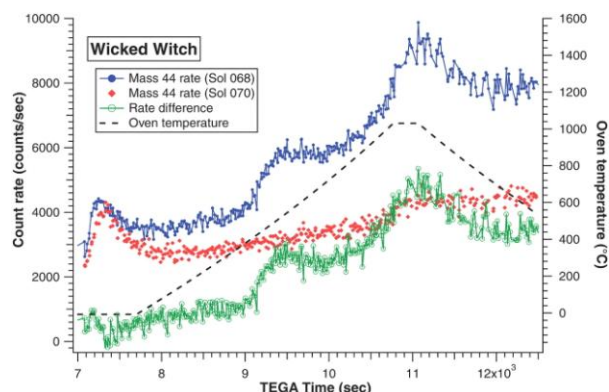


Figure 1 – Mass 44 vs time data from thermal analysis of the soil sample Wicked Witch at the Mars Phoenix landing site. The green curve (signal-background) is the difference between the day 1 and day 2 measurement. Two distinct CO₂ releases are seen, the first at ~400 °C, the second at ~750 °C.

If the perchlorate detected on Mars is magnesium perchlorate, the stable form on the surface is magnesium perchlorate hexahydrate (Mg(ClO₄)₂•6H₂O) [4]. When this perchlorate decomposes at ~400 °C, a lot of gas is released, primarily H₂O, Cl₂, and O₂. The water and Cl₂ can then react to form HCl which can start decomposing calcite well below its standard decomposition temperature of >700 °C. This early decomposition

of calcite could explain the lower temperature CO₂ release seen by the TEGA instrument.

One caveat with regards to the work of Cannon et al. is that, although the timing of the low temperature peak coincides well with the CO₂ release seen in the TEGA data, the relative intensities of the peak do not match when a calcite:perchlorate ratio consistent with Phoenix results is used. Integrating the area under the CO₂ peaks in the TEGA data gives a ratio of ~2.5 for the high/low releases. Thermal analysis on a sample containing reported amounts of perchlorate (0.6 wt%) and calcite (5 wt%) gives a ratio of ~14. This discrepancy leaves room for another CO₂ source.

As stated previously, the decomposition of perchlorate yields O₂ as well as H₂O and Cl₂. This oxygen has been shown to combust reduced carbon compounds during pyrolysis [5] and would coincide with HCl-aided decomposition of carbonate. This work investigates the possible contribution of organic molecules to the low temperature CO₂ release seen on Mars.

Materials and Methods: First, a base mixture of calcite + perchlorate was produced. A sample of Iceland spar calcite was ground in ethanol and sieved to <50 μm. This sample was then sonicated in ethanol to suspend the clay-sized particles (<2 μm). The liquid was then poured off and the process was repeated two more times. The calcite was then mixed in a mortar and pestle with a corundum powder that had been baked at 1100 °C in air for more than 24 hours to remove any organic contamination. Magnesium perchlorate hexahydrate was also added so that the final mixture was 5% CaCO₃, 1% Mg(ClO₄)₂•6H₂O, and the rest purified corundum. This was the basic mixture that was used as a control and in all subsequent runs.

Three different organic molecules were selected for this study: coronene, a polycyclic aromatic hydrocarbon (C₂₄H₁₂), naphthalene-1,4-dicarboxylic acid (C₁₂H₈O₄), and mellitic acid (C₁₂H₆O₁₂). These organics are consistent with meteorically delivered organic material that has been oxidized to various levels by surface processes on Mars [6, 7]. All the organics used have a low vapor pressure so that they don't sublime under low pressure, and also have a relatively high melting point so that the sample is not entirely driven off before the perchlorate decomposition temperature.

Organics are mixed into the calcite-perchlorate-corundum material with a mortar and pestle. An initial organic concentration of 1% is used, and then a portion of that material is diluted down to 0.1%. ~100 mg of sample is placed into a sample crucible and loaded into a Setaram Ligne 96 differential scanning calorimeter (DSC). Samples are heated up to 1350 °C at a rate of 20 °C/minute in a sample chamber at 12mbar pressure, using N₂ as a carrier gas with a flow rate of 1sccm. The exhaust line of the DSC is connected to a Pfeiffer quadrupole mass spectrometer to measure the evolved gases between 1-200 AMU. All samples are run at least twice and the results are checked for consistency.

Results: The presence of organic molecules can greatly increased the release of low temperature CO₂.

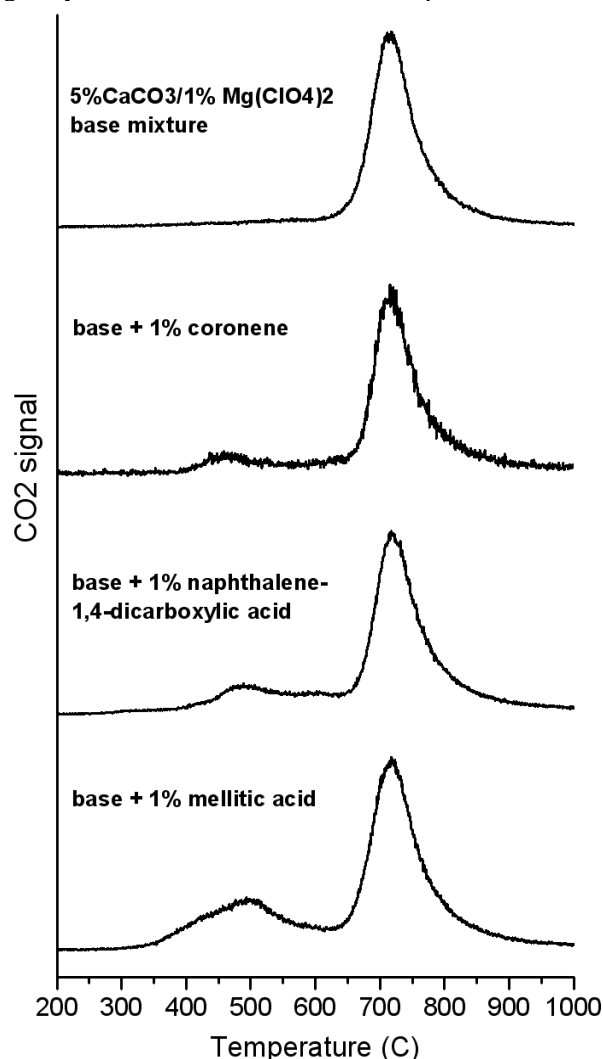


Figure 2. CO₂ signal vs. temperature for the base mixture, then for the three with organics added. The intensity of the low temperature CO₂ release increases with the oxidation state of the organic molecule used. Note that there is a CO₂ release at low temperatures for the base mixture (with a 14:1 high to low CO₂ ratio), but it is difficult to see on this scale.

At high organic concentrations (1%), the amount of CO₂ released increases with increasing oxidation level of the organic used, with the coronene-doped sample giving off the least amount of CO₂ and the mellitic acid containing sample releasing the most (Figure 2). However, when plotting the ratio of the high:low temperature CO₂ released, curious behavior is seen. Again, the ratio of high:low CO₂ released is lowest for the most oxidized organics in the 1% sample (more low temperature CO₂ is released, making the ratio smaller). For samples with lower organic concentrations (0.1%), the order of organics is reversed, with the coronene sample having the lowest ratio and mellitic acid the highest. This behavior is not yet understood and will be investigated further.

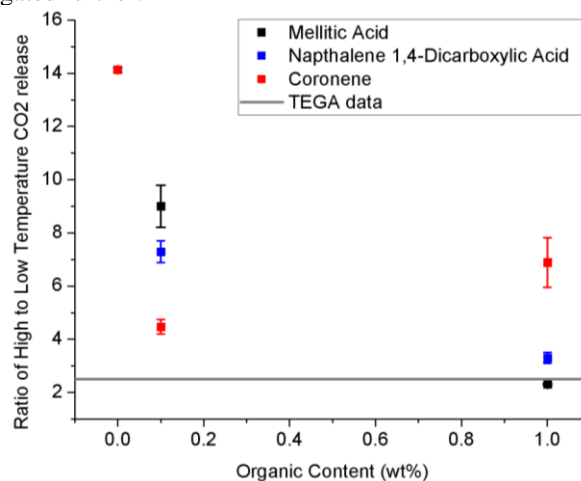


Figure 3. The ratio of high:low temperature CO₂ released vs. organic content. The value seen in Phoenix soils is shown by the gray line at ~2.5. Each point is the average of multiple runs and the error bars are the standard deviation of the average values, not the measurement uncertainty.

Conclusions: The combustion of organic material by oxygen released during perchlorate decomposition is coincident with the early decomposition of calcite also caused by perchlorate decomposition. However, the very high concentration of organics needed to produce the observed CO₂ released suggests that the signal could not be due entirely to organic combustion, but that it could certainly contribute to the detected signal.

References: [1] Hecht M. H. et al. (2009) *Science*, 325, 64-67 (1997) *JGR*, 90, 1151-1154. [2] Boynton W. V. et al. (2009) *Science*, 325, 61-64. [3] Cannon K. M. et al., *LPSC XLIII, this volume*. [4] Besley L. M. and Bottomley G. A (1969) *J. Chem. Thermodyn*, 1, 13-19. [5] Ming D. W. et al. (2009) *LPS XL*, Abstract #2241. [6] Benner S.A. et al. (2000) *PNAS*, 97, 2425-2430. [7] Pizzarello S. (2004) *Origins Life Evol B*, 34, 25-34.