

Organic Combustion in the Presence of Ca-Carbonate and Mg-Perchlorate: A Possible Source for the Low Temperature CO₂ release seen in Mars Phoenix Thermal and Evolved Gas Analyzer Data

Two of the most important discoveries of the Phoenix Lander were the detection of ~0.6% perchlorate [1] and 3-5% carbonate [2] in landing site soils. The Thermal and Evolved Gas Analyzer (TEGA) instrument on the Phoenix lander could heat samples up to ~1000 °C and monitor evolved gases with a mass spectrometer. TEGA detected a low (~350 °C) and high (~750 °C) temperature CO₂ release. The high temp release was attributed to the thermal decomposition of Ca-carbonate (calcite). The low temperature CO₂ release could be due to desorption of CO₂, decomposition of a different carbonate mineral, or the combustion of organic material. A new hypothesis has also been proposed that the low temperature CO₂ release could be due to the early breakdown of calcite in the presence of the decomposition products of certain perchlorate salts [3]. We have investigated whether or not this new hypothesis is also compatible with organic combustion.

Magnesium perchlorate is stable as Mg(ClO₄)₂·6H₂O on the martian surface [4]. During thermal decomposition, this perchlorate salt releases H₂O, Cl₂, and O₂ gases. The Cl₂ can react with water to form HCl which then reacts with calcite, releasing CO₂ below the standard thermal decomposition temperature of calcite. However, when using concentrations of perchlorate and calcite similar to what was detected by Phoenix, the ratio of high:low temperature CO₂ evolved is much larger in the lab, indicating that although this process might contribute to the low temp CO₂ release, it cannot account for all of it.

While H₂O and Cl₂ cause calcite decomposition, the O₂ evolved during perchlorate decomposition can lead to the combustion of any reduced carbon present in the sample [5]. We investigate the possible contribution of organic molecules to the low temperature CO₂ release seen on Mars.

To perform these analyses, Iceland spar calcite (5%) and Mg(ClO₄)₂·6H₂O (1%) are mixed into a corundum powder (94%) which had been heated to 1100 °C in air to remove any organic contaminants. This was the base material into which organics were added. 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 meteoritically delivered organic material that has been oxidized to various levels by surface processes on Mars [6, 7].

Organics are mixed into the calcite-perchlorate-corundum material with a mortar and pestle to concentration of 1, 0.5, 0.1, and 0.05%. ~100 mg of sample is placed into a sample crucible and loaded into a Setaram Ligne 96 differential scanning calorimeter. Samples are heated up to 1350 °C at 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. All samples are run at least twice and the results are checked for consistency.

The presence of organic molecules increases the amount of low temperature CO₂ released, coincident with the early decomposition of calcite caused by perchlorate decomposition. However, the very high concentration of organics needed to match the TEGA data suggests that organics cannot be the sole source of the observed CO₂ released.

[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. [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.