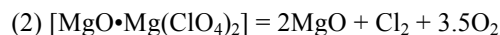


POSSIBLE CALCITE AND MAGNESIUM PERCHLORATE INTERACTION IN THE MARS PHOENIX THERMAL AND EVOLVED GAS ANALYZER (TEGA). K. M. Cannon¹, B. Sutter², D. W. Ming³, W. V. Boynton⁴ and R. C. Quinn⁵, ¹Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada, K7L 3N6 (cannon@geol.queensu.ca), ²Jacobs-ESCG, Houston, TX, ³NASA Johnson Space Center, Houston, TX, ⁴Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ, ⁵SETI Institute, NASA Ames Research Center, Moffett Field, CA.

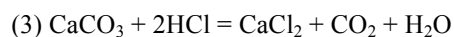
Introduction: The Mars Phoenix Lander's TEGA instrument detected a calcium carbonate phase decomposing at high temperatures (~700°C) from the Wicked Witch soil sample [1]. TEGA also detected a lower temperature CO₂ release between 400°C and 680°C [1]. Possible explanations given for this lower temperature CO₂ release include thermal decomposition of Mg or Fe carbonates, a zeolitic-type desorption reaction, or combustion of organic compounds in the soil [2].

The detection of 0.6 wt % soluble perchlorate by the Wet Chemistry Laboratory (WCL) on Phoenix [3] has implications for the possibility of organic molecules in the soil. Ming *et al.* [4] demonstrated that perchlorates could have oxidized organic compounds to CO₂ in TEGA, preventing detection of their characteristic mass fragments. Here, we propose that a perchlorate salt and calcium carbonate present in martian soil reacted to produce the 400°C - 680°C TEGA CO₂ release.

The parent salts of the perchlorate on Mars are unknown, but geochemical models using WCL data support the possible dominance of Mg-perchlorate salts [5]. Mg(ClO₄)₂•6H₂O is the stable phase at ambient martian conditions [6], and breaks down at lower temperatures than carbonates giving off Cl₂ and HCl gas [7,8]. Devlin and Herley [7] report two exotherms at 410-478°C and 473-533°C which correspond to the decomposition of Mg(ClO₄)₂. They support a two-stage process:



If the chlorine gas produced reacts with moisture in the system or if the magnesium perchlorate has not fully dehydrated, then HCl gas can form and react with a carbonate phase to evolve CO₂:



Other possible perchlorate species, Ca(ClO₄)₂, KClO₄, and NaClO₄ are not likely involved in this reaction because their thermal decomposition does not evolve Cl₂ or HCl [9,10,11]. Calcite is present in higher molar amounts than perchlorate in the Phoenix soil; therefore, it will not completely react and the

remaining calcite will decompose normally at higher temperatures, producing the high temperature CO₂ release seen in the TEGA data. The objectives of this work are to assess the nature of calcite and Mg-perchlorate thermodynamic reactions and associated evolved gas releases using laboratory differential scanning calorimetry/mass spectroscopy (DSC/MS) to simulate the TEGA instrument, and to assess the mineralogical changes that occur during these processes using powder X-ray diffraction (XRD).

Materials and Methods: Calcite (Iceland Spar) and Mg-perchlorate (Baker grade reagent) were crushed and sieved to 53-150 μm particle sizes for DSC/MS experiments, and to <53 μm for the XRD studies. The amount of CaCO₃ was held fixed at 0.025 mmol and was mixed with increased amounts of Mg(ClO₄)₂•6H₂O (0.0015, 0.0133, 0.025, 0.0368 and 0.0485 mmol) for DSC/MS experiments.

DSC/MS experiments were conducted in a Setaram Ligne 96 heat flux differential scanning calorimeter coupled to a Pfeiffer quadrupole mass spectrometer. A 12 mbar N₂ atmosphere with a flow rate of 1 sccm was used to simulate TEGA operating conditions. Samples were heated to 1350°C (20°C min⁻¹). Heated powder XRD was performed on calcite and Mg-perchlorate mixtures with an Anton Paar XRK900 heating chamber in a Panalytical X'pert Pro diffractometer using CoKα radiation. The chamber was held at 12 mbar pressure with a N₂ gas flow rate of 1 sccm. Scans were collected at 25°C intervals between 25°C and 875°C.

Results: The calorimetric analyses of the calcite and Mg-perchlorate mixtures exhibit multiple thermodynamic transitions attributed to Mg-perchlorate dehydration and decomposition, CaCl₂ formation and calcite decomposition (Fig. 1). Endothermic transitions at 75°C - 250°C (peaks a1, a2, a3, Fig. 1) represent the dehydration of Mg(ClO₄)₂•6H₂O. The exotherm at 500°C (peak b) is attributed to decomposition of Mg-perchlorate and crystallization of CaCl₂. The thermal decomposition of calcite (peak c) appears as a broad endothermic transition centered at 715°C. The sharp endotherm (d) is due to decomposition of oxidized CaCl₂ phases, while the endotherm (e) in the TEGA data represents the curie transition temperature of the nickel oven.

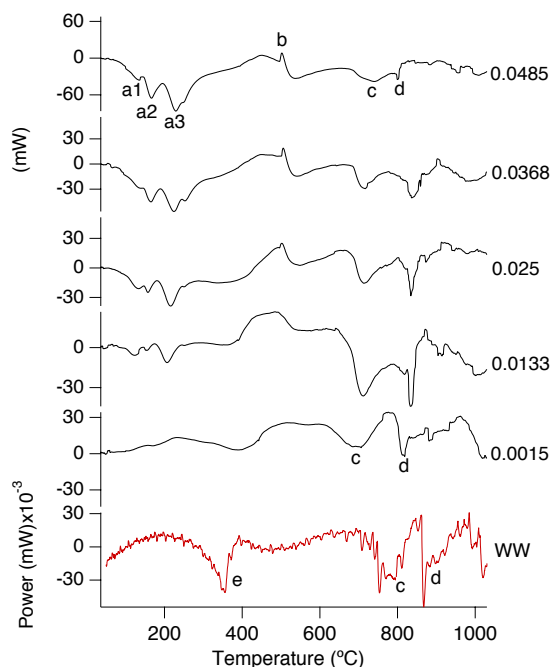


Figure 1. Calorimetric results showing heat flow vs. temperature for laboratory experiments (mmol Mg-perchlorate indicated) and Wicked Witch (WW) TEGA sample. Downward and upward peaks indicate endothermic and exothermic reactions, respectively.

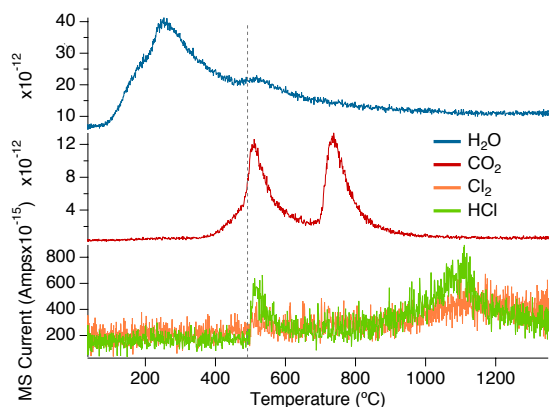


Figure 2. Mass spectrometry data for laboratory experiment with 0.025 mmol CaCO_3 and 0.025 mmol $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. H_2O (mass 18), CO_2 (mass 44), Cl_2 (mass 35) and HCl (mass 36) are plotted versus temperature.

Two CO_2 releases were observed in the laboratory analyses; one low temperature release attributed to an inorganic reaction between HCl gas and calcite and a higher temperature CO_2 release due to the thermal decomposition of calcite. The low temperature CO_2 release was closely associated with the detection of Cl_2 and HCl (Fig. 2) which further demonstrated that HCl was causing CaCO_3 decomposition and CO_2 release. The amount of CO_2 in the low temperature release increased while that of the high temperature

release decreased with the addition of more perchlorate. Heated powder XRD also demonstrated that a reaction between calcite and Mg-perchlorate contributed to the low temperature CO_2 release through the identification of CaCl_2 forming at 390°C .

In addition to a reaction between HCl and CaCO_3 , the mass spectrometry data suggest that heated H_2O vapor appears to be lowering the onset temperature for calcite decomposition [12] to contribute to the low temperature CO_2 release in our experiments. The low temperature CO_2 release observed in TEGA is consistent with that in the laboratory results, but the ratio of CO_2 evolved at high temperatures to low temperatures is much less. This discrepancy can be accounted for if there is an additional source of water in the soil such as hydrated minerals (e.g., epsomite).

Conclusions: The detection of HCl gas released from the thermal decomposition of Mg-perchlorate, and its reaction with calcite to produce CaCl_2 and release CO_2 is a clear demonstration of the thermal interaction between CaCO_3 and $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Inorganic reactions involving calcite, Mg-perchlorate and an additional source of water vapor can account for all CO_2 releases detected by TEGA. Since there is evidence for all these components being in the soil, we propose that this interaction of phases account for the CO_2 releases observed by TEGA.

Results from this work will have implications for the Sample Analysis at Mars (SAM) experiments on the Mars Science Laboratory Curiosity rover when it searches for organics in Gale crater. A similar low temperature CO_2 release could be misinterpreted as evidence for organics at the surface. Therefore, detection of organic fragments themselves, and not their possible oxidation products, should be used as definitive evidence for organics on Mars.

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