POSSIBLE CALCITE AND MAGNESIUM PERCHLORATE INTERACTION IN THE MARS PHOENIX THERMAL AND EVOLVED GAS ANALYZER (TEGA). K. M. Cannon[1], B. Sutter[2], D. W. Ming[3], W. V. Boynton[4] and R. C. Quinn[5], [1]Department of Geological Sciences and Geological Engineering, Queen's University, Kingston, Ontario, Canada, K7L 3N6 (cannon@geol.queensu.ca), [2]Jacobs-ESCG, Houston, TX, [3]NASA Johnson Space Center, Houston, TX, [4]Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ. [5]SETI 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 CO_2 release between 400°C and 680°C [1]. Possible explanations given for this lower temperature CO_2 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 CO_2 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 CO_2 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]. $Mg(ClO_4)_2{\bullet}6H_2O$ is the stable phase at ambient martian conditions [6], and breaks down at lower temperatures than carbonates giving off Cl_2 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 $Mg(ClO_4)_2$. They support a two-stage process:

$$(1)\ 2Mg(ClO_4)_2 = [MgO{\bullet}Mg(ClO_4)_2] + Cl_2 + 3.5O_2$$

$$(2)\ [MgO{\bullet}Mg(ClO_4)_2] = 2MgO + Cl_2 + 3.5O_2$$

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 CO_2:

$$(3)\ CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O$$

Other possible perchlorate species, $Ca(ClO_4)_2$, $KClO_4$, and $NaClO_4$ are not likely involved in this reaction because their thermal decomposition does not evolve Cl_2 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 CO_2 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 $CaCO_3$ was held fixed at 0.025 mmol and was mixed with increased amounts of $Mg(ClO_4)_2{\bullet}6H_2O$ (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 N_2 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 N_2 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, $CaCl_2$ formation and calcite decomposition (Fig. 1). Endothermic transitions at 75°C - 250°C (peaks a1, a2, a3, Fig. 1) represent the dehydration of $Mg(ClO_4)_2{\bullet}6H_2O$. The exotherm at 500°C (peak b) is attributed to decomposition of Mg-perchlorate and crystallization of $CaCl_2$. 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 $CaCl_2$ phases, while the endotherm (e) in the TEGA data represents the curie transition temperature of the nickel oven.

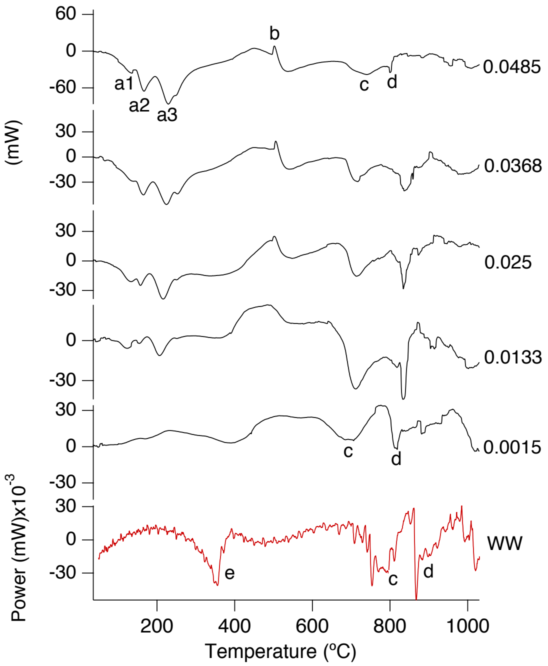

Figure 1. Calorimetric results showing heat flow vs. temperature for laboratory experiments (mmol Mg-perchlorate indicated) and Wicked Witch (WW) TEGA sample. Downward and upward peaks indicate endothermic and exothermic reactions, respectively.

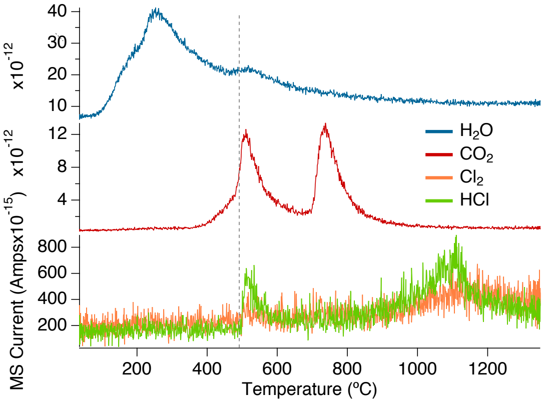

Figure 2. Mass spectrometry data for laboratory experiment with 0.025 mmol $CaCO_3$ and 0.025 mmol $Mg(ClO_4)_2•6H_2O$. H_2O (mass 18), CO_2 (mass 44), Cl_2 (mass 35) and HCl (mass 36) are plotted versus temperature.

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 $Mg(ClO_4)_2•6H_2O$. 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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