

**THERMAL AND EVOLVED GAS BEHAVIOR OF CALCITE UNDER MARS PHOENIX TEGA OPERATING CONDITIONS.** B. Sutter<sup>1</sup>, H. V. Lauer<sup>2</sup>, D. C. Golden<sup>3</sup>, W. V. Boynton<sup>4</sup>, R. V. Morris<sup>5</sup>, P. B. Niles<sup>5</sup> and D. W. Ming<sup>5</sup>. <sup>1</sup>Jacobs/ESCG, Houston TX, 77058, brad.sutter-2@nasa.gov. <sup>2</sup>ESCG/Barrios Tech., Houston, TX 77058. <sup>3</sup>ESCG/Hamilton Sundstrand, Houston, TX 77058. <sup>4</sup>University of Arizona, Tucson, AZ 85721. <sup>5</sup>NASA Johnson Space Center, Houston, TX 77058.

**Introduction:** The Mars Phoenix Scout Mission with its diverse instrument suite successfully examined several soils on the Northern plains of Mars. The Thermal and Evolved Gas Analyzer (TEGA) was employed to detect organic and inorganic materials by coupling a differential scanning calorimeter (DSC) with a magnetic-sector mass spectrometer (MS). Martian soil was heated up to 1000°C in the DSC ovens and evolved gases from mineral decomposition products were examined with the MS. TEGA's DSC has the capability to detect endothermic and exothermic reactions during heating that are characteristic of minerals present in the Martian soil.

Initial TEGA results indicated the presence of endothermic peaks with onset temperatures that ranged from 675°C to 750°C with corresponding CO<sub>2</sub> release. This result suggests the presence of calcite (CaCO<sub>3</sub> → CaO + CO<sub>2</sub>) [1]. Organic combustion to CO<sub>2</sub> is not likely since this mostly occurs at temperatures below 550°C. Fe-carbonate and Mg-carbonate are not likely because their decomposition temperatures are less than 600°C. TEGA enthalpy determinations suggest that calcite, may occur in the Martian soil in concentrations of ~1 to 5 wt. % [1].

The detection of calcite could be questioned based on previous results that suggest Mars soils are mostly acidic (e.g., [2,3]). However, the Phoenix landing site soil pH was measured at pH 8.3±0.5 [4], which is typical of terrestrial soils where pH is controlled by calcite solubility [5].

The range of onset temperatures and calcite concentration as calculated by TEGA is poorly constrained in part because of limited thermal data of calcite at reduced pressures. TEGA operates at <30 mbar while most calcite literature thermal data was obtained at 1000 mbar or higher pressures.

Past work [6,7,8] has indicated that as total pressure decreases, the onset temperature and enthalpy for endothermic reactions can decrease and increase, respectively. Proper identification of calcite onset temperatures in the TEGA data set requires that laboratory analysis of calcite and other carbonates be evaluated at TEGA operating conditions (e.g., ≤30 mbar, ~1 sccm flow rate). Furthermore, the enthalpy (J/g) of calcite decomposition at ≤30 mbar must be evaluated to ensure accurate calculations of calcite concentrations based on TEGA enthalpies.

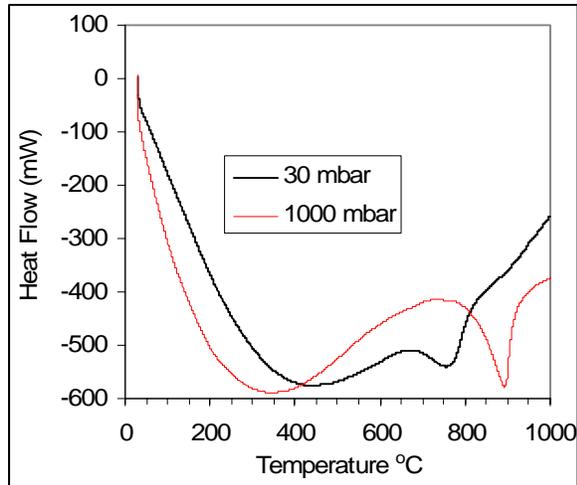
The objectives of this work are to (1) assess the onset temperature and (2) enthalpy of calcite decomposition at TEGA pressures (30 mbar). Results of this work will enhance the ability to assess the true onset temperature and enthalpy of calcite decomposition in the TEGA data sets.

**Materials and Methods:** Iceland Spar calcite was examined in this work. Differential scanning calorimetry analysis was performed with a Setaram Ligne 96. Ten mg samples were heated from 30 to 1100°C at heating rate of 20°C min<sup>-1</sup> at pressure of 30 mbar. All analyses were purged with research grade N<sub>2</sub> at a rate of 4.5 sccm.

**Results and Discussion:** Calcite decomposition onset temperature was 677°C at 30 mbar which is lower than the onset temperatures at 1000 mbar (815°C) (Fig. 1). Calcite decomposition results in CO<sub>2</sub> release, thus lower pressures cause a greater pressure difference between the inner calcite crystal and the surface which facilitates CO<sub>2</sub> diffusion through the calcite lattice [8]. This could have the effect of lowering the temperature required to decompose calcite.

The enthalpy for calcite decomposition was calculated to be 2000 J/g and 1575 J/g at 30 and 1000 mbar, respectively. The enthalpy of calcite decomposition at 30 mbar is much higher than that at 1000 mbar. The higher enthalpy at reduced pressure may be attributed to adiabatically expanding gas that cools the sample holder which results in more heat required to maintain the sample temperature [6]. The higher enthalpy at lower pressure relative to the lower enthalpy determined at higher pressure is important because this affects the calculated concentration of calcite in the Mars soil based on the enthalpy measured by TEGA.

The amount of calcite (g) in the Phoenix soils is estimated by dividing the measured TEGA enthalpy (J) by the enthalpy (2000 J/g) measured at 30 mb in the testbed. Calcite concentrations will be overestimated if the enthalpies (e.g., 1575 J/g) measured at 1000 mb are used to calculate the amount in Phoenix soils. Thus, it is critical that the higher enthalpy determined at reduced pressure be utilized in calculating calcite concentration in the Mars soil.



**Fig. 1. Differential scanning calorimetry of calcite at 30 and 1000 mb N<sub>2</sub> pressure. Calcite onset decomposition at 30 mb was 677°C while the 1000 mb onset temperature was 815°C**

**Conclusions:** Results of this work demonstrate the need to evaluate calcite thermal properties at pressure conditions representative of TEGA operating conditions. Future work will mix calcite with other Mars analog material (e.g., Mars JSC-1) to assess any effects that other materials may have on the thermal properties of calcite. More importantly, calcite will be run in the TEGA engineering qualification model (EQM) to provide the most accurate assessment of thermal properties of calcite as determined by a TEGA-like instrument. Additional work is also required to evaluate the effect of a lower TEGA N<sub>2</sub> purge flow rate (~ 1 sccm) on the onset temperature and enthalpy of calcite decomposition.

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**References:**

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