Introduction: The Mars Science Laboratory (MSL) is scheduled for launch in 2011. The science objectives for MSL are to assess the past or present biological potential, to characterize the geology, and to investigate other planetary processes that influence habitability at the landing site. The Sample Analysis at Mars (SAM) is a key instrument on the MSL payload that will explore the potential habitability at the landing site [1]. In addition to searching for organic compounds, SAM will have the capability to characterized evolved gases as a function of increasing temperature and provide information on the mineralogy of volatile-bearing phases such as carbonates, sulfates, phyllosilicates, and Fe-oxhydroxides. The operating conditions in SAM ovens will be maintained at 30 mb pressure with a He carrier gas flowing at 1 sccm.

We have previously characterized the thermal and evolved gas behaviors of volatile-bearing species under reduced pressure conditions that simulated operating conditions of the Thermal and Evolved Gas Analyzer (TEGA) that was onboard the 2007 Mars Phoenix Scout Mission [e.g., 2-8]. TEGA ovens operated at 12 mb pressure with a N$_2$ carrier gas flowing at 0.04 sccm. Another key difference between SAM and TEGA is that TEGA was able to perform differential scanning calorimetry whereas SAM only has a pyrolysis oven.

The operating conditions for TEGA and SAM have several key parameter differences including operating pressure (12 vs 30 mb), carrier gas (N$_2$ vs. He), and carrier gas flow rate (0.04 vs 1 sccm). The objectives of this study are to characterize the thermal and evolved gas analysis of calcite under SAM operating conditions and then compare it to calcite thermal and evolved gas analysis under TEGA operating conditions.

Materials and Methods: Iceland Spar calcite ground to 150 μm was used as a test mineral to compare thermal and evolved gases analyses under SAM- and TEGA-like operating conditions.

The thermal and evolved gas laboratory testbed consisted of a Setaram Ligne 96 differential scanning calorimeter (DSC) integrated with a Pfeiffer quadruple mass spectrometer (300 AMU range). The DSC has an operating temperature range from ambient to 1500°C. Research grade N$_2$ and He were used as carrier gases. Sub-ambient pressures were obtained by using the mass spectrometer coupled with an oil-free vacuum pump controlled by microvalves. The mass spectrometer data was collected for a predetermined set of individual masses (<45) and recorded as a function of time rather than a full range mass scan. The carrier gas was allowed to flow through the system for approximately one hour before starting the oven ramp to reach a steady gas state and remove any trace gas contaminants. Experiments were run from ambient temperature to 1200°C at 20°C/min temperature ramp rate. Variables include operating pressure (12 and 30 mb), carrier gas (N$_2$ and He), and carrier gas flow rate (1 sccm) [note: the 1 sccm carrier gas flow rate simulates the TEGA flow rates in our system due to geometrical and volume differences between systems]. Samples were reheated after the initial temperature ramp to 1200°C to establish the baseline data for the DSC and evolved gases.

Results and Discussion: The type of carrier gas does have an impact on the thermal analysis of calcite at 12 mb pressure (Fig. 1). Peak temperatures for the thermal decomposition of calcite were higher (by about 18°C) with the He carrier gas. The peak temperatures were 756 and 774°C for N$_2$ and He carrier gases, respectively. Heat capacities of the two gases are likely responsible for the differences in peak temperature.

![Calcite: Heat Flow 12 mb 1 sccm (He; N$_2$)](image)

Figure 1: Effect of carrier gas (N$_2$ vs He) on thermal analysis of calcite at 12 mb pressure with a carrier gas flow rate of 1 sccm.

Peak temperatures for evolved CO$_2$ were similar for the two carrier gases at 12 mb pressure (Fig. 2). The peak temperatures for N$_2$ and He carrier gases were 785°C and 793°C, respectively. Calcite thermal and evolved gas analysis under SAM-like operating conditions is shown in Figure 3. The onset temperature for thermal decomposition occurs at 668°C. Peak temperatures for the thermal analysis and evolved CO$_2$ were 788°C and 824°C,
respectively. The onset temperature for calcite thermal decomposition under SAM-like operating conditions is considerably lower than calcite decomposition under atmospheric conditions, which occurs at 815°C [3]. The decrease in onset temperature at reduced pressure is attributed to an increase in entropy ($\Delta S$).

The onset temperature for calcite thermal decomposition occurred at a higher temperature under SAM-like operating conditions compared to TEGA-like operating conditions (Fig. 4). The onset temperatures under TEGA- and SAM-like operating conditions were 661°C and 668°C, respectively. The lower onset temperature under TEGA-like operating conditions is expected due to an increase in entropy compared to SAM-like operating conditions.

Evolved CO$_2$ during thermal decomposition of calcite occurred at a higher peak temperature (~22°C higher) under SAM-like operating conditions (Fig. 5). Peak temperatures for evolved CO$_2$ were 802°C and 824°C, respectively, for experiments under TEGA-like and SAM-like operating conditions, respectively.

**Implications for MSL SAM.** Operating pressure and carrier gas have an effect on the thermal and evolved gas behaviors of volatile-bearing phases. This study illustrates that volatile-bearing phases such as calcite will have slightly higher thermal decomposition onset temperatures in SAM compared to TEGA. Although, a large number of volatile-bearing phases have been analyzed at reduced pressures under TEGA operating conditions [2-8], candidate volatile-bearing phases will have to be characterized under SAM-like operating conditions to characterize evolved gas analysis mineralogy on MSL.

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