Thermal and Evolved Gas Analysis of “Nanophase” Carbonates: Implications for Thermal and Evolved Gas Analysis on Mars Missions. H. V. Lauer, Jr.1, P. D. Archer, Jr.2, B. Sutter1, P.B. Niles2 and D. W. Ming3, 1ESCG/Barrios Technology (howard.v.lauer@nasa.gov) , 2ARES NASA/JSC, Houston, TX 77058, 3ESCG/Jacobs Technology

Introduction: Data collected by the Mars Phoenix Lander’s Thermal and Evolved Gas Analyzer (TEGA) suggested the presence of calcium-rich carbonates as indicated by a high temperature CO2 release while a low temperature (~400-680°C) CO2 release suggested possible Mg- and/or Fe- carbonates [1,2]. Interpretations of the data collected by Mars remote instruments is done by comparing the mission data to a database on the thermal properties of well-characterized Martian analog materials collected under reduced and Earth ambient pressures [3,4]. We are proposing that “nanophase” carbonates may also be contributing to the low temperature CO2 release. The objectives of this paper is to (1) characterize the thermal and evolved gas properties of carbonates of varying particle size, (2) evaluate the CO2 releases from CO2 treated CaO samples and (3) examine the secondary CO2 release from reheated calcite of varying particle size.

Materials and Methods: The following well characterized carbonates were analyzed in a laboratory thermal analyzer (TA) intergrated with a quadrupole mass spectrometer (QMS) that mimicked the operating conditions for the MSL Sample Analysis at Mars (SAM) and the Phoenix TEGA instruments: Iceland Spar calcite (CaCO3, Chihauhau, Mexico); Winchester Magnesite (MgCO3, Winchester, WI); Ledge dolomite [(CaMg(CO3)2], W. York, PA] and Copper Lake siderite[(Fe0.65Mg0.35CO3), Copper Lake Nova Scotia, Canada]. The calcite experiments were performed using samples ground and sieved in ethanol to produce a starting material of known particle size, whereas the other experiments were conducted on unsieved finely ground starting material. The analyses were performed with He carrier gas at 3sccm at 30 mb pressure (SAM-like operating conditions) or N2 carrier gas at 1 sccm and 12 mb system pressure (TEGA-like operating conditions).

The calcite experiments were done using different grain size starting material (<50μm, 50-125μm, 125-250μm, 250-500μm and a single crystal ~2-3 mm/side) to quantify the affect of particle size on the temperature of the CO2 release. Samples were weighed in previously baked out (1000 °C in air) alumina crucibles and then placed in the sample holder of the TA. The instrument was evacuated and back filled with the specified carrier gas (He or N2) three times. The system was then allowed to equilibrate until all of the gas masses to be measured with the QMS have reached their steady state level. The TA instrument was heated to 1200 °C at 20 °C/min and then cooled back to ambient. The instrument was reheated to 1200 °C and allowed to cool to ambient. During both heatings and cooling cycles, the net heat flow in the sample and the evolved gases from the sample were recorded as a function to the sample temperature. The purpose of the second heating was to measure the thermal heat flow backround signal for the sample being analyzed. The results from experiments using SAM-like or TEGA-like operating conditions are very similar. Since a much larger set of experiments dealing with grain-size effects have been completed using SAM-like conditions, only these experiments will be presented. In addition because of space limitations, detailed results will only be presented for the calcite portion of this study.

In addition to reporting the evolved CO2 gas results as a function of grain size, an experiment was done to show the ability of fine grain carbonates to form from oxides at reduced pressure with an elevated partial pressure of CO2. In this experiment ~30 mg of <50μ calcite was analyzed in the TA instrument using the He carrier gas at 30 mb and 3sccm. The sample was heated to 1250 °C as previously described. The cool down process was halted and the sample temperature held at 400 °C at which point the carrier gas was switched to CO2. The sample was held at 400 °C in flowing CO2 for 6 hrs. The sample was then allowed to cool down to ambient. The system/sample was then treated as though it was a new sample.

Results: Figure 1 presents the evolved CO2 from calcite as a function of temperature for several different particle sizes using SAM-like conditions. The results obtained for TEGA-like conditions were similar.

Table 1: Onset and peak temperatures for the calcite runs shown in Figure 1 {Xtal = single calcite crystal – 31.0 mg}
Siderite, i.e. an Fe-carbonate; showed no CO$_2$ release during the second heating. The clean second heating for siderite indicates that the calcite second heating detection is a real signal and not the result of contamination. Figure 3 reports the measured CO$_2$ recorded during the second heating of a 125-250µm calcite sample.

The data shown in Figure 2 indicate that fine grain calcite formation is possible at reduced pressure with some partial pressure of CO$_2$ present. Consequently, the interpretation of the results shown in Figure 3 is that there is a high enough partial pressure of CO$_2$ in the He carrier gas in the TA instrument that during the cool down of the sample from the first heating and the equilibration time before the second heating, a very fine grained calcite forms. Areas under the CO$_2$ releases for the first and second heatings indicate the amount of “nanophase” calcite formed is equivalent to ~ 1.7% of the original calcite. In the future, we will attempt to produce higher yields of the “nanophase” calcite such that it can be characterized via other techniques (e.g. TEM).

Similar results were observed for other non iron bearing carbonates. The “nanophase” evolved CO$_2$ measured in these experiments was observed at lower temperatures, i.e.~ 340 °C for magnesite.

**Conclusions:** The results we have presented indicates that “nanophase” carbonates or at least very very fine grain carbonates exist and could be in the martian soil at substantial levels. The Phoenix TEGA results [1,2] show a low temperature CO$_2$ release. “Nanophase” Ca-carbonate might contribute to this CO$_2$ release.