

**Thermal and Evolved Gas Analysis of “Nanophase” Carbonates: Implications for Thermal and Evolved Gas Analysis on Mars Missions.** H. V. Lauer, Jr.<sup>1</sup>, P. D. Archer, Jr.<sup>2</sup>, B. Sutter<sup>3</sup>, P.B. Niles<sup>2</sup> and D. W. Ming<sup>2</sup>, <sup>1</sup>ESCG/Barrios Technology ([howard.v.lauer@nasa.gov](mailto:howard.v.lauer@nasa.gov)), <sup>2</sup>ARES NASA/JSC, Houston, TX 77058, <sup>3</sup>ESCG/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 CO<sub>2</sub> release while a low temperature (~400-680°C) CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> releases from CO<sub>2</sub> treated CaO samples and (3) examine the secondary CO<sub>2</sub> 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 (CaCO<sub>3</sub>, Chihauhau, Mexico); Winchester Magnesite (MgCO<sub>3</sub>, Winchester, WI); Ledge dolomite [(CaMg(CO<sub>3</sub>)<sub>2</sub>, W. York, PA] and Copper Lake siderite[(Fe<sub>0.65</sub>Mg<sub>0.35</sub>CO<sub>3</sub>), 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 3scm at 30 mb pressure (Sam-like operating conditions) or N<sub>2</sub> carrier gas at 1 scm 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 CO<sub>2</sub> 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 N<sub>2</sub>) 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

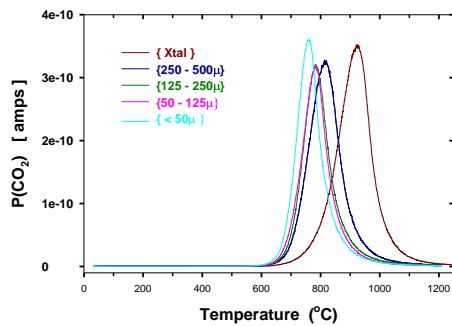
state level. The TA instrument was heated to 1200 °C at 20 °C/min and then cooled back to ambient. The instrument was reheated to 1200 °C and allowed to cool to ambient. During both heatings and cooling cycles, the net heat flow in the sample and the evolved gases from the sample were recorded as a function to the sample temperature. The purpose of the second heating was to measure the thermal heat flow background 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 CO<sub>2</sub> 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 CO<sub>2</sub>. In this experiment ~30 mg of <50µ calcite was analyzed in the TA instrument using the He carrier gas at 30 mb and 3scm. 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 CO<sub>2</sub>. The sample was held at 400 °C in flowing CO<sub>2</sub> 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 CO<sub>2</sub> 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.

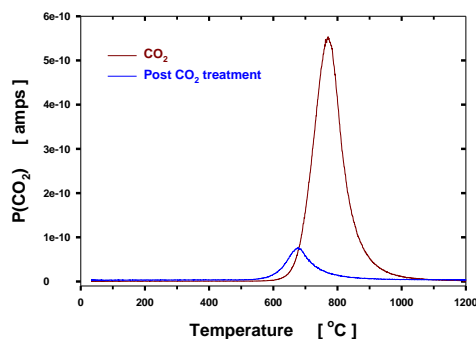
**Table 1: Onset and peak temperatures for the calcite runs shown in Figure 1 {Xtal = single calcite crystal – 31.0 mg}**

Sample ID	Onset Temp.	Peak Temp.
Xtal	798.5	925.1
250 - 500	709.7	813.8
125 - 250	700.8	784.1
50 - 125	695.1	783.3
<50	681.0	758.9



**Figure 1:** Evolved  $\text{CO}_2$  for a 31 mg single crystal of calcite and several particle sizes. These experiments were performed at 30 mb using a He carrier gas at 3 scfm.

Figure 2 shows the results of the calcite ( $\text{CaCO}_3$ ) growth experiment at reduced pressure.



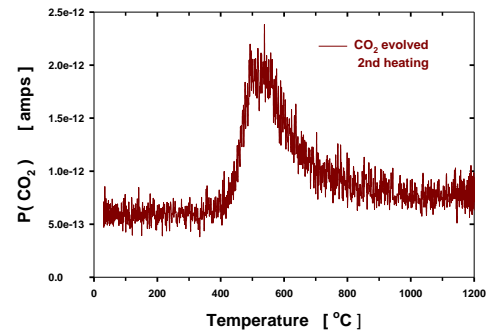
**Figure 2.** Evolved  $\text{CO}_2$  for calcite ( $<50 \mu\text{m}$ ) followed by  $\text{CO}_2$  treatment and reheat twice under SAM-like conditions. The peak shown in red is the initial heating of the calcite converting it to CaO. The  $\text{CO}_2$  peak shown in blue indicates the evolved  $\text{CO}_2$  for the post  $\text{CO}_2$  treated material

The post  $\text{CO}_2$  treated sample clearly shows a temperature peak shift of  $\sim 90^\circ\text{C}$  and an onset temperature shift of  $\sim 75^\circ\text{C}$  to lower temperature than the  $<50 \mu\text{m}$  calcite sample (Fig. 2). These results indicate that the  $\text{CO}_2$  treatment of the CaO formed in the initial calcite analysis resulted in the formation of a finer grain sized calcite. Measurement of the area under the peaks indicates that for the conditions imposed on the material,  $\sim 10\%$  of the sample was reconverted to a finer grain sized calcite. The results presented in Fig. 2 suggest the formation of fine grain calcite from CaO at reduced pressure in the presence of a partial pressure of  $\text{CO}_2$ .

A small  $\text{CO}_2$  release with a peak at  $\sim 520^\circ\text{C}$  and an onset temperature  $\sim 456^\circ\text{C}$  was observed during the second heating. At first thought, it was suspected that this  $\text{CO}_2$  release might have been the result of contamination in the instrument, since the observed peak was at a temperature  $\sim 250^\circ\text{C}$  lower than the  $\text{CO}_2$  evolved the initial heating of the sample. It turns out that contamination was not the source of the second heating  $\text{CO}_2$  release for the calcite samples. Evolved  $\text{CO}_2$  released during the first and second heatings of Copper Lake

Siderite, i.e. an Fe-carbonate; showed no  $\text{CO}_2$  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  $\text{CO}_2$  recorded during the second heating of a  $125\text{-}250\mu\text{m}$  calcite sample.



**Figure 3.** Measured  $\text{CO}_2$  release for the second heating of a  $125\text{-}250\mu\text{m}$  calcite sample.

The data shown in Figure 2 indicate that fine grain calcite formation is possible at reduced pressure with some partial pressure of  $\text{CO}_2$  present. Consequently, the interpretation of the results shown in Figure 3 is that there is a high enough partial pressure of  $\text{CO}_2$  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  $\text{CO}_2$  releases for the first and second heatings indicate the amount of "nanophase" calcite formed is equivalent to  $\sim 1.7\%$  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  $\text{CO}_2$  measured in these experiments was observed at lower temperatures, i.e.  $\sim 340^\circ\text{C}$  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  $\text{CO}_2$  release. "Nanophase" Ca-carbonate might contribute to this  $\text{CO}_2$  release.

**References:**[1] Sutter et. al.(2012) Ms. Ref. # ICARUS-12064R1 in Press.[2] Boynton et. al.(2009) *Science*, 325,61 – 64.[3] Lauer et. al. (2000)a,b *LPSC XXXI*. [4] Sutter et. al. (2009) *LPSC XL*.