Thermal and Evolved Gas Analysis of "Nanophase" Carbonates:Implications for Thermal and Evolved Gas Analysis on Mars Missions.

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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_2 release while a low temperature (~400-680^{o}C) CO_2 release suggested possible Mg- and/or Fe- carbonates [1,2]. Interpertations 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_2 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_2 releases from CO_2 treated CaO samples and (3) examine the secondary CO_2 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 ($CaCO_3$, Chihauhau, Mexico); Winchester Magnesite ($MgCO_3$, Winchester, WI); Ledge dolomite [($CaMg(CO_3)_2$, W. York, PA] and Copper Lake siderite[($Fe_{0.65}Mg_{0.35}CO_3$), 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 N_2 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 CO_2 release. Samples were weighed in previously baked out (1000 ^{o}C in air) aluminia 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_2) 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 ^{o}C at 20 ^{o}C/min and then cooled back to ambient. The instrument was reheated to 1200 ^{o}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_2 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_2. 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 ^{o}C as previously described. The cool down process was halted and the sample temperature held at 400 ^{o}C at which point the carrier gas was switched to CO_2. The sample was held at 400 ^{o}C in flowing CO_2 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_2 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

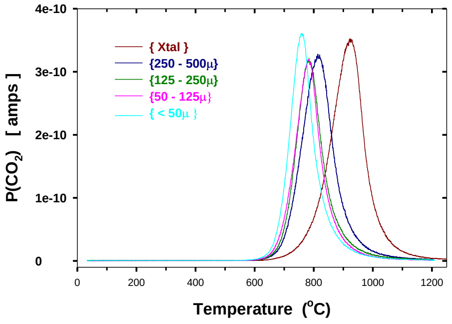

Figure 1: Evolved CO_2 for a 31 mg single crystal of calcite and several particle sizes. These experiments were performed at 30 mb using a He carrier gas at 3 sccm.

Figure 2 shows the results of the calcite ($CaCO_3$) growth experiment at reduced pressure.

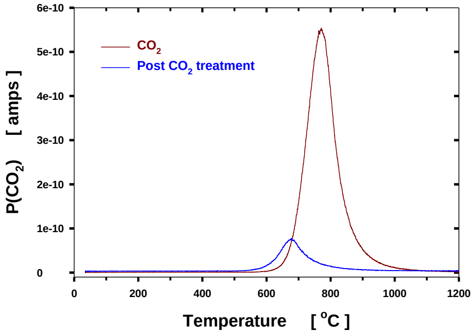

Figure 2. Evolved CO_2 for calcite (<50 μm) followed by CO_2 treatment and reheat twice under SAM-like conditions. The peak shown in red is the initial heating of the calcite converting it to CaO. The CO_2 peak shown in blue indicates the evolved CO_2 for the post CO_2 treated material

The post CO_2 treated sample clearly shows a temperature peak shift of ~ 90 °C and an onset temperature shift of ~ 75 °C to lower temperature than the <50 μm calcite sample (Fig. 2) These results indicate that the 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, ~ 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 CO_2.

A small CO_2 release with a peak at ~ 520 °C and an onset temperature ~ 456 °C was observed during the second heating. At first thought, it was suspected that this CO_2 release might have been the result of contamination in the instrument, since the observed peak was at a temperature ~ 250 °C lower than the CO_2 evolved the initial heating of the sample. It turns out that contamination was not the source of the second heating CO_2 release for the calcite samples. Evolved CO_2 released during the first and second heatings of Copper Lake 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.

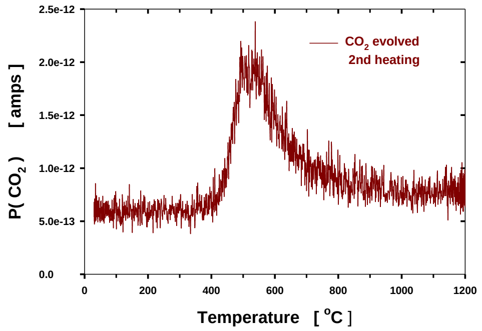

Figure 3. Measured CO_2 release for the second heating of a 125-250μm calcite sample.

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.

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.**