(Ca,Mg)-carbonate a nd Mg-carbonate a t t he P hoenix L anding Site: Evaluation of t he Phoenix L ander's Thermal Evolved G as A nalyzer (TEGA) Data Using Laboratory Simulations. B. Sutter[1] , D.W. Ming, W.V. Boynton[3], P.B. Niles[2], and R.V. Morris[2]. [1]Jacobs-ESCG, Houston, TX brad.sutter-2@nasa.gov, [2] NASA-Johnson Space Center, Houston, TX, [3]Univ. Arizona, Tucson, AZ.

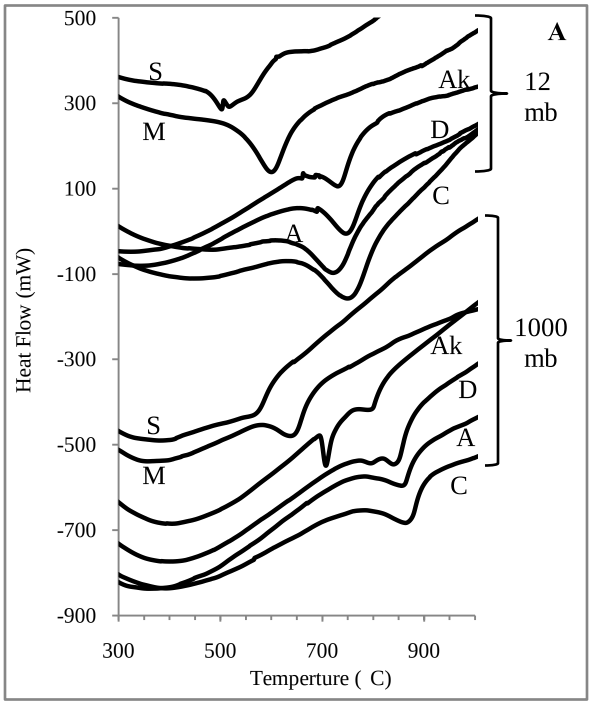
Introduction: Calcium carbonate (4.5 wt. %) was detected in the soil at the Phoenix Landing site by the Phoenix Lander's The Thermal and Evolved Gas Analyzer [1]. TEGA operated at 12 mbar pressure, yet the detection of calcium carbonate is based on interpretations derived from thermal analysis literature of carbonates measured under ambient (1000 mbar) and vacuum (10^{-3} mbar) conditions [2,3] as well as at 100 and 30 mbar [4,5] and one analysis at 12 mbar by the TEGA engineering qualification model (TEGA-EQM)[1]. Thermodynamics ($T_e = \Delta H/\Delta S$) dictate that pressure affects entropy (ΔS) which causes the temperature (T_e) of mineral decomposition at one pressure to differ from T_e obtained at another pressure. Thermal decomposition analyses of Fe-, Mg-, and Ca-bearing carbonates at 12 mbar is required to enhance the understanding of the TEGA results at TEGA operating pressures. The objectives of this work are to (1) evaluate the thermal and evolved gas behavior of a suite of Fe-, Mg-, Ca-carbonate minerals at 1000 and 12 mbar and (2) discuss possible emplacement mechanisms for the Phoenix carbonate.

Materials and Methods: Thermal analyses were performed on a Setaram Ligne 96 laboratory differential scanning calorimeter (DSC) coupled to a Pfeiffer ThermoStar GSD 301 T quadrupole mass spectrometer. The following carbonates were examined: calcite, aragonite, magnesite, siderite ($Fe_{0.65}Mg_{0.35}CO_3$), dolomite and ankerite [$(Ca,Fe_{0.55},Mg_{0.45})(CO_3)_2$]. The thermal analyses were conducted (1) at1000 mb N_2 and 20 sccm flow rate and (2) near TEGA conditions of 12 mbar N_2 and a 1 sccm flow rate with heating from 30 to 1100°C at a temperature ramp rate of 20°C min^{-1}. Simultaneous sampling of the output gas stream for CO_2 and other gases was made by the mass spectrometer. Carbon dioxide counts were recorded as a function of temperature (T_{CO2}). Standard laboratory (1000mbar) data were used to assist the interpretation of the 12 mbar results. T_e and T_{CO2} refer to the temperatures at which endotherm and CO_2 release are first detected, respectively.

Results and Discussion: Carbonate decomposition at 1000 mbar is indicated by a single endothermic peak for calcite, magnesite, aragonite and siderite while two endothermic peaks were observed for ankerite and dolomite (Fig. 1). The T_e and T_{CO2} for carbonate decomposition were lower for the 12 mbar experiments compared to 1000 mbar experiments (Fig. 1). The decrease in T_e and T_{CO2} for the 12 mbar versus 1000 mbar analysis is attributed to increasing entropy at lower pressure. Similar to the 1000 mbar analyses, carbonate decomposition at 12 mbar was indicated by a single endothermic peak for calcite, magnesite, and aragonite (Fig. 1). However, the double endothermic peaks observed for dolomite and ankerite at 1000 mbar are mostly a single endotherm at 12 mbar with minor secondary endothermic and exothermic peaks (Fig. 1). The TEGA instrument does not have the sensitivity to detect these minor secondary peaks. Thermodynamic calculations demonstrate that the difference between carbonate decomposition temperatures (e.g., magnesite vs. calcite) decrease as pressure decreases. This indicates that T_e differences will decrease and thus have the potential to cause multiple peaks to merge into one peak as pressure decreases. The merging of peaks is also enhanced by peak broadening caused by greater peak areas associated with temporary CO_2 accumulation caused by lower flow rate in the 12 mbar (1 sccm) experiments. These factors caused the T_e to be similar for dolomite, ankerite, and calcite at 12 mbar. The single endotherm and similar T_e for dolomite, ankerite, and calcite at 12 mbar suggests that in addition to calcite, ankerite and dolomite are plausible candidates for the high temperature carbonate endotherm obversed in the Wicked Witch soil by TEGA.

The Wicked Witch low temperture (400°C) CO_2 release could be attributed to Fe and/or Mg carbonates. Siderite and magnestite T_{CO2} at 12 mb occurred in the 325 to 363°C range (Fig. 1) which are the closest of all the carbonate species examined by the laboratory instrument to the Wicked Witch low-temperature (400°C) CO_2 release. However, there was no obvious siderite and magnesite endothermic transition in the Wicked Witch data that corresponded with laboratory siderite and magnesite endothermic T_e (475-534°C). The amount of Wicked Witch CO_2 released at 400°C was lower than the amount of higher temperature CO_2 released that was associated with the Ca-bearing carbonate endotherm [5]. This suggests the siderite and/or magnesite levels in the Phoenix soil that released CO_2 detectable by TEGA's mass spectrometer are likely too low to be detected by TEGA's calorimeter.

Results from these laboratory studies suggest Fe-bearing carbonates, siderite, may explain the low temperature CO_2 release while ankerite may explain the high temperature endotherm and associated CO_2 release in the Wicked Witch soil. However, the oxidizing nature of the atmosphere as indicated by soil perchlorate [6] and the predominance of surface Fe^{3+} species [7] suggests that reducing conditions are not favorable for Fe^{2+} bearing carbonate formation. Thus, magnesite becomes the most likely candidate



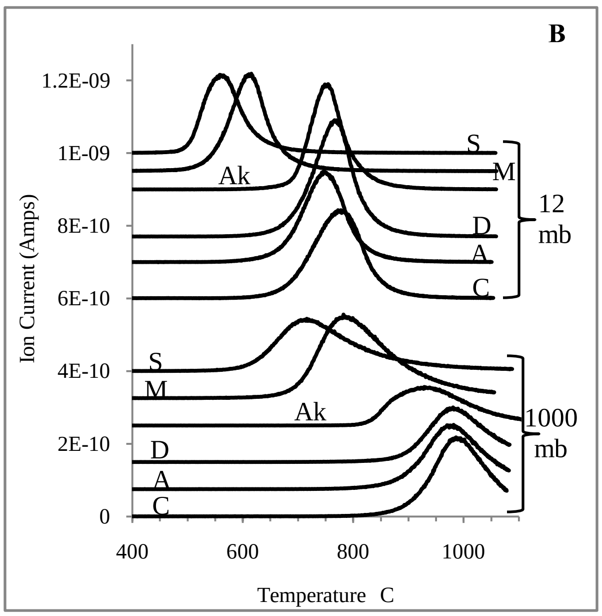


Fig. 1. 1000 and 12 mbar laboratory thermal and evolved CO_2 analysis for calcite (C), aragonite (A), ankerite (AK), dolomite (D) and siderite (S): a) thermal data (mW) and b) carbon dioxide release.

carbonate that could be responsible for the low temperature CO_2 release. The high temperature endotherm and corresponding CO_2 release is attributed to a Ca-rich carbonate such as calcite, aragonite, and/or dolomite. Equilibrium calculations indicated magnesite, dolomite, and calcite would be stable in the Phoenix soils [8].

Phoenix carbonates could be inherited from aqueous activity associated with the deposition of the mid to late Hesperian Vastitas Borealis (VB) and/or early Amazonian Scandia materials (scenario 1). Another possibility (scenario 2) is that Phoenix carbonates were emplaced through deposition of atmospheric dust containing magnesite[9], followed by thin-film water activity [10,11] that dissolved Ca-silicates and some magnesite followed by precipitation as Ca-rich carbonate that ranged from Mg-calcite to dolomite. The presence of pedogenic dolomite in olivine-bearing Hawaiian soils [12] suggests low temperature formation of dolomite is plausible in the Phoenix soils. Thermal calculations indicate that (Ca,Mg)-carbonate concentration could range from 4.5 (no Mg) to 5.4 (dolomite) wt. %.

Scenarios 1 and 2 are both viable processes that could yield $MgCO_3$, $CaCO_3$ and/or $(CaMg)(CO_3)_2$. Scenario 1 suggests that for carbonate deposition with the Vastitas Borealis (VB) and Scandia materials; deposition solutions were alkaline from the mid to late Hesperian and into the early Amazonian. Acid solutions may have dominated elsewhere on Mars during these time frames [13] but the VB and Scandia waters would have been alkaline. Scenario 2 indicates that pedogenic carbonate formation may be ongoing due to water thin-films sourced from the ice table below. Viking soil pH estimates (7.4-8.7) [14] suggest that soil carbonate could be buffering the Viking soil pH as in the Phoenix soil. Soil carbonates at the Phoenix and possibly the Viking Landing sites suggest that moderately alkaline soil pH may occur throughout the northern plains.

Soil carbonate persistence, in at least the northern plains, indicates that moderately alkaline soils may be more prevalent and acid deposits (e.g., Meridiani) are less extensive across Mars. Widespread and moderately alkaline soil pHs would enhance the habitability on Mars for microbial life that may have existed in the past.

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