

NANOPHASE CARBONATES ON MARS: FORMATION, DETECTION, AND IMPLICATIONS. P. D. Archer, Jr.¹, H. V. Lauer², D. W. Ming³, P. B. Niles³, R. V. Morris³, E. B. Rampe³, B. Sutter¹, and the MSL Science Team,¹Jacobs, NASA Johnson Space Center, Houston, TX 77058 doug.archer@gmail.com, ²Barrios Technology–Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, ³NASA Johnson Space Center, Houston, TX 77058.

Introduction: Despite having an atmosphere composed primarily of CO₂ and evidence for abundant water in the past, carbonate minerals have only been discovered on Mars in small amounts in martian dust [1], in soils in the Northern Plains [2], and in outcrops of limited spatial extent [3, 4]. Recently, carbonates have been identified as the possible source of CO₂ released during thermal analysis of material from an aeolian deposit named Rocknest [5, 6] and drilled sample from the sheepbed mudstone [7], both samples analyzed by the Mars Science Laboratory (MSL) in Gale Crater.

Both the Phoenix lander and MSL carry thermal analysis instruments, the Thermal and Evolved Gas Analyzer (TEGA) on Phoenix and the Sample Analysis at Mars (SAM) instrument on MSL. While thermal analysis does not provide definitive mineralogy, it can detect volatile-bearing minerals present at very low abundance and the temperature profiles of evolved gases can reveal physical properties of the sample. For example, the decomposition temperature of volatile-bearing minerals depends heavily on the particle size of the mineral [8].

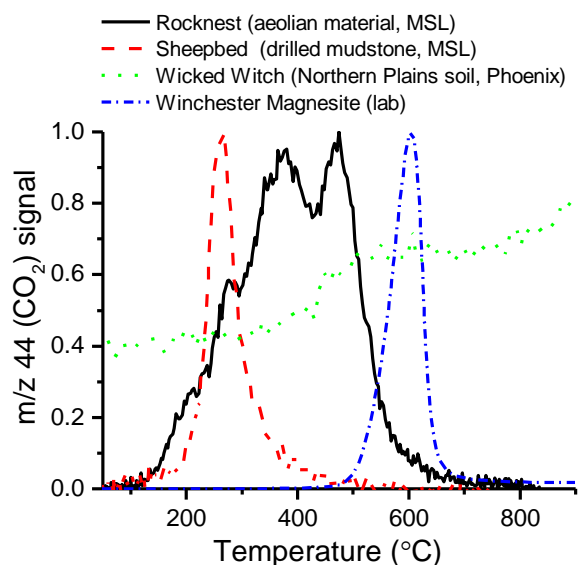


Figure 1 – m/z 44 (CO₂) releases from Rocknest aeolian material (Rocknest 4), drilled samples of Sheepbed mudstone (Cumberland 3), Northern Plains Soil (Wicked Witch), and a <150 μm particle-size portion of terrestrial magnesite. Maximum signal normalized to 1 (max for WW sample was off scale).

The CO₂ releases (indicative of carbonate decomposition) detected by the TEGA and SAM instruments have been at temperatures lower than is seen for carbonate minerals on Earth when run under similar instrumental conditions (Figure 1). The low temperature release of CO₂, if from the decomposition of carbonates, is consistent with very fine-grained particles.

The small particle size inferred from the thermal decomposition measurements is consistent with a carbonate of particles <2 μm. These small particle sizes indicate that carbonate formation is extremely rate-limited, likely by temperature or the availability of water. Carbonate formation through the interaction of thin films of water with primary minerals in a CO₂ atmosphere have been hypothesized in the past [2, 9] and some previous work has been done that has experimentally validated the mechanism [10]. We are continuing this work by investigating how various temperatures and relative humidities affect carbonate formation rates and particle size in order to constrain the formation conditions of nanophase carbonates on Mars. We are coupling this with isotopic analysis in order to determine if there is any isotopic fractionation when carbonates are formed through this process, with the goal of determining whether nanophase carbonates on Mars are being formed under current martian conditions. If we are unable to reproduce the release profile of CO₂ seen in martian samples, this strengthens the case for the other carbon-bearing materials, such as organic molecules or oxalates, that may be present.

Materials and Methods: We have constructed a system that allows us to control the relative humidity, temperature, and partial pressure of CO₂ (pCO₂) to investigate how carbonate formation progresses under different conditions. We use an RH-200 relative humidity generator from L&C Science and Technology to generate RH over a range of 5-95% from -40 to 80 °C. The sample temperature is controlled by immersing the stainless steel tubing containing the sample in a recirculating fluid bath that can be controlled over a temperature range of -30 °C to 100 °C (the sample is isolated from the fluid of the bath by vacuum-tight fittings). A CO₂/N₂/H₂O mixture is flowed through the sample, which is contained between two metal frits, and the pCO₂ can be adjusted from 0 to 500+ mbar. The gas composition is measured by a Hiden HPR-20 Benchtop Gas Analysis System which samples gas

through a capillary line that is then analyzed by a quadrupole mass spectrometer (QMS).

The samples produced by this process will be analyzed by a Netzsch STA 449 F1 Jupiter with simultaneous thermal gravimetry (TG)/differential scanning calorimetry (DSC) capability that is coupled to a Pfeiffer ThermoStar GSD 320 with a 1-200 AMU range quadrupole mass spectrometer. These instruments can be run as analogs to either the TEGA instrument on Phoenix or the SAM instrument on MSL, allowing direct comparison of our results to samples analyzed on Mars. We will also analyze the samples produced by X-ray diffraction (XRD) and transmission electron microscopy (TEM) to verify the mineralogy and particle size of the carbonates produced. Isotope extractions will be performed on the Thermo Gasbench II by standard orthophosphoric reaction techniques. The Gasbench II is interfaced with a Thermo Finnigan MAT 253 mass spectrometer operating in continuous flow mode.

Work is currently underway using synthetic CaO as a starting material for carbonate formation. Our next step is to use San Carlos olivine and an anorthite sample as Ca and Mg endmembers of primary minerals similar to those found on Mars.

Preliminary work has also been done using sealed-tube experiments. This work was done as a proof-of-concept, demonstrating the formation of small-particle-size carbonates through the interaction of CO₂ and water vapor with primary minerals, but was not done under martian conditions. The sealed tube experiments were conducted using minerals that release water (goethite) and CO₂ (silver carbonate) when heated to relatively low temperatures (<400 °C). These minerals were sealed into a glass tube with a primary mineral (e.g. wollastonite) and were heated for ~100 hours. The minerals were physically separated so that only thin film/gas phase reactions were possible. Samples were analyzed as described above.

Results: The results of the sealed tube experiments demonstrate that carbonate formation through gas-phase reactions results in carbonates with small particle size and that the particle size and amount formed depends on sample temperature (Figure 2). The particle size difference is evident by the different release temperatures of CO₂ seen in the two cases and the increasing amount formed at higher temperature is clear from the ~2 orders of magnitude higher intensity of the CO₂ release from the sample heated at 375 °C. The decomposition temperature of these carbonates is >100 °C lower than Iceland spar calcite sieved to contain particle sizes between 53 and 125 μm.

Sealed Tube Experiments

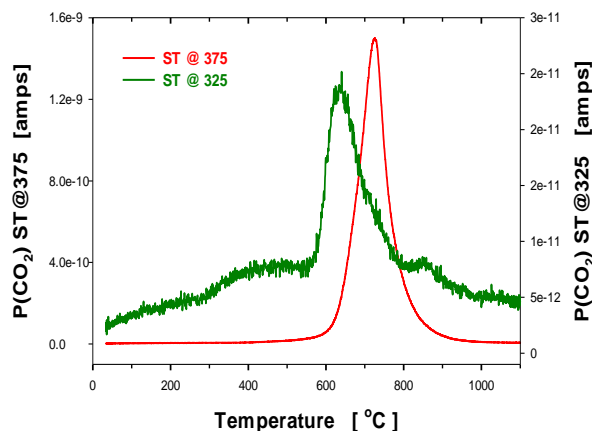


Figure 2 - CO₂ signal vs. temperature for wollastonite samples run in sealed tube experiments. Thermal analysis of two samples are shown, both heated for 120 hours, one to 325 °C (green) and the other to 375 °C (red).

Conclusions: The low temperature releases of CO₂ during thermal analysis of martian samples may be consistent with the presence of nanophase carbonates. Weathering of primary minerals to carbonates through CO₂/H₂O interactions under current Mars conditions might produce carbonates with particle-sizes small enough to explain the low CO₂ release temperatures. Constraining the formation conditions that can create these nanophase carbonates answers important questions about Mars' past climate and addresses whether carbonate formation on Mars is occurring under present-day conditions. Finally, if we are unable to reproduce the low-temperature CO₂ signals seen in analysis of martian samples, we can rule carbonates out as a source of the CO₂, strengthening arguments for other CO₂ sources such as decomposition of refractory organics, combustion of organic material, or decomposition of oxalates.

References: [1] Bandfield, J.L., et al., (2003) *Science*, 301, 5636: p. 1084-1087. [2] Boynton, W.V., et al., (2009) *Science*, 325, 5936: p. 61-64. [3] Morris, R.V., et al., (2010) *Science*, 329, 5990: p. 421-424. [4] Ehlmann, B.L., et al., (2008) *Science*, 322, 5909: p. 1828-1832. [5] Leshin, L.A., et al., (2013) *Science*, 341, 6153. [6] Archer, P.D., Jr., et al., (2014): p. 2013JE004493. [7] Ming, D.W., et al., (2014) *Science*, 343, 6169. [8] Archer, P.D., Jr., et al., (2013) *Planet. Sci.*, 2, 1: p. 1-21. [9] Pollack, J.B., et al., (1990) *JGR*, 95. [10] Stephens, S.K., (1995), *PhD Thesis*.