## NANOPHASE CARBONATES ON MARS: IMPLICATIONS FOR CARBONATE FORMATION AND HABITABILITY

P. Douglas Archer, Jr.\*<sup>1</sup>, H. Vern Lauer<sup>2</sup>, Douglas W. Ming<sup>3</sup>, Paul B. Niles<sup>3</sup>, Richard V. Morris<sup>3</sup>, Elizabeth B. Rampe<sup>3</sup>, Brad Sutter<sup>1</sup>, and the MSL Science Team

<sup>1</sup>Jacobs, NASA Johnson Space Center, Houston, TX 77058, USA: <a href="doug.archer@nasa.gov">doug.archer@nasa.gov</a>; <sup>2</sup>Barrios Technology–Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058; <sup>3</sup>NASA Johnson Space Center, Houston, TX 77058, USA.

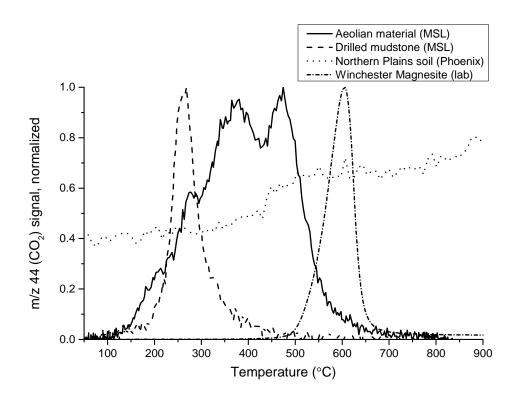
Despite having an atmosphere composed primarily of CO<sub>2</sub> and evidence for abundant water in the past, carbonate minerals have only been discovered in small amounts in martian dust [1], in outcrops of very limited extent [2, 3], in soils in the Northern Plains (the landing site of the 2007 Phoenix Mars Scout Mission) [4] and may have recently been detected in aeolian material and drilled and powdered sedimentary rock in Gale Crater (the Mars Science Laboratory [MSL] landing site) [5]. Thermal analysis of martian soils by instruments on Phoenix and MSL has demonstrated a release of CO<sub>2</sub> at temperatures as low as 250-300 °C, much lower than the traditional decomposition temperatures of calcium or magnesium carbonates. Thermal decomposition temperature can depend on a number of factors such as instrument pressure and ramp rate, and sample particle size [6]. However, if the CO<sub>2</sub> released at low temperatures is from carbonates, small particle size is the only effect that could have such a large impact on decomposition temperature, implying the presence of extremely fine-grained (i.e., "nanophase" or clay-sized) carbonates.

We hypothesize that this lower temperature release is the signature of small particle-sized (clay-sized) carbonates formed by the weathering of primary minerals in dust or soils through interactions with atmospheric water and carbon dioxide and that this process may persist under current martian conditions. Preliminary work has shown that clay-sized carbonate grains can decompose at much lower temperatures than previously thought. The first work took carbonate, decomposed it to CaO, then flowed  $CO_2$  over these samples held at temperatures >100 °C to reform carbonates. Thermal analysis confirmed that carbonates were indeed formed and transmission electron microsopy was used to determine crystal sized were on the order of 10 nm. The next step used minerals such as diopside and wollastonite that were sealed in a glass tube with a  $CO_2$  and  $H_2O$  source. After reacting these materials for a number of hours, thermal analysis demonstrated the formations of carbonates that decomposed at temperatures as low as 500 °C [7].

Further work is underway to carry out the weathering process under more Mars-like conditions (low pressure and low temperature) to determine if the carbonate decomposition temperature can be shifted to even lower temperatures, consistent with what has been detected by thermal analysis instruments on Mars.

- 1. Bandfield, J.L., T.D. Glotch, and P.R. Christensen, *Spectroscopic Identification of Carbonate Minerals in the Martian Dust.* Science, 2003. **301**(5636): p. 1084-1087.
- 2. Ehlmann, B.L., et al., *Orbital Identification of Carbonate-Bearing Rocks on Mars.* Science, 2008. **322**(5909): p. 1828-1832.
- 3. Morris, R.V., et al., *Identification of Carbonate-Rich Outcrops on Mars by the Spirit Rover*. Science, 2010. **329**(5990): p. 421-424.
- 4. Boynton, W.V., et al., Evidence for Calcium Carbonate at the Mars Phoenix Landing Site. Science, 2009. **325**(5936): p. 61-64.
- 5. Leshin, L.A., et al., *Volatile, Isotope, and Organic Analysis of Martian Fines with the Mars Curiosity Rover.* Science, 2013. **341**(6153).
- 6. Archer, P.D., Jr., D.W. Ming, and B. Sutter, *The effects of instrument parameters and sample properties on thermal decomposition: interpreting thermal analysis data from Mars.* Planetary Science, 2013. **2**(1): p. 1-21.
- 7. Lauer, H.V., et al., Thermal and Evolved Gas Analysis of ``Nanophase"

  Carbonates: Implications for Thermal and Evolved Gas Analysis on Mars Missions, in
  43rd Lunar and Planetary Science Conference 2012. p. 2299.



**Figure 1.** Evolved Gas Analysis (EGA) data, m/z 44 ( $CO_2$ ) in particular, for samples analyzed on Mars and in terrestrial labs. The laboratory sample of a Winchester magnesite with particle size <150  $\mu$ m, analyzed under conditions similar to the martian samples, has a peak decomposition temperature of ~600 °C. Martian samples of an aeolian material, a drilled mudstone, and soil from the martian Northern Plains have peak decomposition temperatures of 250 to 550 °C (the northern plains sample has a second peak >1000 °C not shown in this plot). The lower decomposition temperatures of martian samples could be due to the presence of nanophase carbonates, formed at low temperatures from the interaction of  $CO_2$  and water vapor in the martian atmosphere with surface materials.