TITLE: The Role of $\delta^{13}C$ in the Search for Reduced Organics on the Surface of Mars

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ABSTRACT BODY: The capabilities of the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) to detect trace amounts of organic carbon compounds are unprecedented, and MSL may be the first mission to reveal the presence of organic carbon on Mars. The search for reduced organic carbon on Mars is inextricably tied to: a) the preservation potential of the environment from which we take a solid sample, and b) the evolved gas analysis (EGA) techniques used by SAM to release volatiles from this solid sample.

Several prospective targets have been identified for sample analysis at Gale Crater. Stratigraphic sequences of phyllosilicates and sulfates at Gale are thought to represent a period of global climate transition from a moderate pH lacustrine environment to an evaporitic environment, both of which could sequester organic carbon (Thomson et al. 2011). The sediment mound in Gale Crater contains a range of lithologies suggesting changes in redox conditions, and evidence of both lacustrine and fluvial depositional processes, which may have transported organic carbon from the layer in which it formed and resulted in its preservation elsewhere within the crater (Anderson and Bell, 2010). Inverted channel fills suggest erosion resistant material that could serve to preserve organics originally deposited in a low energy aqueous environment.

The lithology sampled will affect not only the preservation of organics, but also our ability to detect organics during our evolved gas analysis, based on the sample matrix. For example, reduced organics may be trapped in the mineral structure, and thermal evolution of these organics will occur during thermal decomposition of the host mineral. If organics are occluded in minerals that have very high thermal decomposition temperatures, they may be, in effect, "too well preserved," and difficult to detect during EGA.

Alternatively, the possible presence of perchlorate, or other strong oxidants in surface regolith, may result in destruction of structural information identifying organic molecules before reaching the QMS on SAM via oxidation to CO_2 during heating. If this is the case, the stable carbon isotopic composition ($\delta^{13}C$) of the CO_2 evolved and measured by the Tunable Laser Spectrometer (TLS) on SAM may help identify the presence of organics. On Earth, biological activity can cause large fractionations of $^{13}C/^{12}C$, which can preserved in sedimentary deposits and distinguish the organic products of biotic processes from inorganic atmospheric and geological reservoirs. It is plausible that similar fractionations could occur on Mars and be preserved in reduced organic matter in sediments.

Bulk $\delta^{13}C$ measurements alone may not reveal a signature of trace organic carbon that may be present along with inorganic carbon. If both organic and inorganic carbon compounds are present, it may be possible to detect the organic carbon by comparing the $\delta^{13}C$ of pyrolysis and combustion experiments. The TLS on SAM is capable of obtaining high precision measurements of $\delta^{13}C$ from CO_2 evolved during pyrolysis and combustion of solid regolith samples. Because carbonates are expected to be present at abundances of 0.1-1 % in Martian soil, and organics in the ppb range (Webster and Mahaffy, 2011), analog samples

must represent this mix of reduced organic carbon and carbonate. The work presented here will examine the use of $\delta^{13}C$ of CO_2 produced during combustion of bulk Mars analog samples as a proxy for detection of reduced organic carbon.