ISOTOPIC COMPOSITION OF CARBON DIOXIDE RELEASED FROM CONFIDENCE HILLS SEDIMENT AS MEASURED BY THE SAMPLE ANALYSIS AT MARS (SAM) QUADRUPOLE MASS SPECTROMETER. H. B. Franz[1,2], P. R. Mahaffy[1], J. Stern[1], P. Archer, Jr.[4], P. Conrad[1], J. Eigenbrode[1], C. Freissinet[1], D. Glavin[1], J. P. Grotzinger[6], J. Jones[4], D. Ming[4], A. McAdam[1], R. Morris[4], R. Navarro-González[8], T. Owen[9], A. Steele[3], R. Summons[7], B. Sutter[4], C. R. Webster[10], and the MSL Science Team. [1]NASA Goddard Space Flight Center, Code 699, Greenbelt, MD 20771, Heather.B.Franz@nasa.gov, [2]University of Maryland Baltimore County, Baltimore, MD 21228, [3]Carnegie Institute of Washington, Washington, DC 20015, [4]NASA Johnson Space Center, Houston, TX 77058, [5]University of Maryland, College Park, MD 20742, [6]California Institute of Technology, Pasadena, CA 91125, [7]Massachusetts Institute of Technology, Cambridge, MA 02139, [8]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [9]University of Hawaii, Honolulu, HI 96822, [10]Jet Propulsion Laboratory, Pasadena, CA 91009.

Introduction: In October 2014, the Mars Science Laboratory (MSL) "Curiosity" rover drilled into the sediment at the base of Mount Sharp in a location namsed Cionfidence Hills (CH). CH marked the fifth sample pocessed by the Sample Analysis at Mars (SAM) instrument suite since Curiosity arrived in Gale Crater, with previous analyses performed at Rocknest (RN), John Klein (JK), Cumberland (CB), and Windjana (WJ) [1-2]. Evolved gas analysis (EGA) of all samples has indicated H_2O as well as O-, C- and S-bearing phases in the samples, often at abundances that would be below the detection limit of the CheMin instrument. By examining the temperatures at which gases are evolved from samples, SAM EGA data can help provide clues to the mineralogy of volatile-bearing phases when their identities are unclear to CheMin. SAM may also detect gases evolved from amorphous material in solid samples, which is not suitable for analysis by CheMin. Finally, the isotopic composition of these gases may suggest possible formation scenarios and relationships between phases. We will discuss C isotope ratios of CO_2 evolved from the CH sample as measured with SAM's quadrupole mass spectrometer (QMS) and draw comparisons to samples previously analyzed by SAM.

Experimental Methods: In EGA experiments, powdered solid samples are heated in one of SAM's pyrolysis ovens to release volatiles. The samples discussed here were processed through a 150 μm sieve before loading. SAM utilizes He carrier gas to sweep volatiles through the gas manifold and QMS, with nominal pressure and flow rate of ~30 mb and ~0.8 sccm, respectively. The QMS continuously samples the outflow from the pyrolysis oven, scanning over the *m/z* range of interest. Integration of the QMS signal over time for particular *m/z* allows quantitative estimates of chemical and isotopic abundance. A portion of the gas stream, parameterized by a desired range of sample temperature, was also collected during each run for isotopic and abundance analysis of CO_2 and H_2O by the SAM tunable laser spectrometer (TLS).

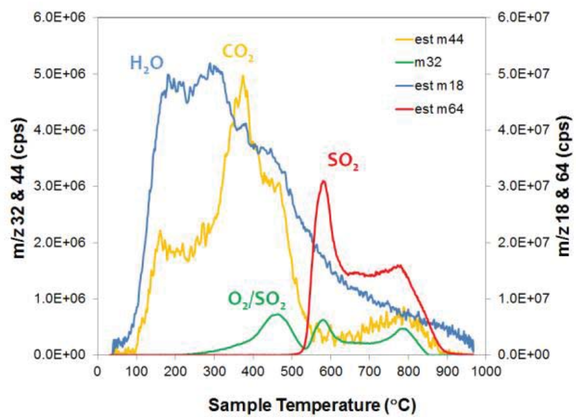

Figure 1. Major volatiles released from the CH drilled sample. The legend indicates the time trace of signal at the *m/z* values shown, e.g., m32 implies *m/z* 32. The abbreviation "est" indicates that the major isotopologue shown saturated the QMS detector, so the signal was estimated from a minor isotopologue for illustrative purposes.

During a nominal experiment, the sample is heated to ~850 °C at a rate of 35 °C/min. The RN experiments revealed an instrument background from products of a derivatization reagent, *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), carried by SAM [3], which has continued to be evident in all subsequent samples. In an effort to deconvolve potential contributions to the CO_2 release, various heating protocols were employed at JK and CB. The first three JK runs included a "boiloff" at the beginning of the experiment, in which the sample was held at a temperature of ~200-300 °C for ~1/2 hour, designed to eliminate instrument background components that would thermally degrade or combust at low temperature before performing the final pyrolysis ramp. Additional measures were taken at CB to reduce adsorption of MTBSTFA to the cup and sample by warming the sample handling system during loading. The science goals at CH included targeted analysis of low-temperature water by the TLS, so no special background strategies were employed.

EGA Results: The H_2O, O_2, CO_2 and SO_2 released by the CH sample are shown in Figure 1. This figure shows the major molecular ion for each species for ease of comparing approximate relative abundances. In cases where the major molecular ion saturated the QMS detector, its value was estimated based from other isotopologues for the purpose of this plot. The volatile of greatest abundance in this sample was H_2O, followed by CO_2 and SO_2.

Carbon isotope ratios: The compound peak shape of the CH CO_2 EGA trace shown in Figure 1 suggest contributions from multiple carbon sources. Candidates for the carbon source include adsorbed CO_2, combusted or decarboxylated organic compounds from background or martian sources, and Fe- or Mg-bearing carbonates. The temperature cut directed to the TLS for analysis was below 160 °C, so the TLS was unable to analyze the isotopic composition of the largest CO_2 peak at ~375 °C. For this reason, we have estimated the isotopic composition of evolved CO_2 from QMS EGA data in an effort to understand the carbon source.

Interference from other compounds at *m/z* 12 and 13 and detector saturation at the major molecular CO_2 ion of *m/z* 44 typically precluded the use of these *m/z* values in determining $\delta^{13}C$ (with respect to V-PDB), which was instead computed from *m/z* 22, 45 and 46. The oxygen isotopic composition ($\delta^{18}O$) of the CO_2 was computed from data at *m/z* 22 and 46, and carbon isotopic composition was computed from data at *m/z* 22 and 45. In addition, $\delta^{13}C$ was also computed from data at *m/z* 45 and 46, using the previously computed $\delta^{18}O$. The CO_2 release likely reflects a mixture of carbon and oxygen from multiple sources. Minimum analytical uncertainties in $\delta^{13}C$ are currently estimated at ± 10‰, based on repeated laboratory EGA analyses [4]. Additional uncertainty arises from background effects and interference from other compounds. We will discuss the resulting $\delta^{18}O$ and $\delta^{13}C$ in light of possible sources that may have contributed to the CO_2 releases.

References: [1] Franz et al. (2013) LPSC XLIV. [2] Franz et al. (2014) LPSC XLV. [3] Glavin et al. (2013) *JGR* 118. [4] Franz et al. (2008) LPSC XXXIX, #2433. [5] Webster et al. (2013) *Science* 341. [6] Mahaffy et al. (2013) *Science* 341.