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ISOTOPIC COMPOSITION OF CARBON DIOXIDE RELEASED FROM GALE CRATER SEDIMENTS THROUGH GLEN TORRIDON AND BEYOND AS MEASURED BY THE SAM QMS.

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Introduction: In early 2019, the Mars Science Laboratory (MSL) Curiosity rover entered a region showing a high abundance of phyllosilicate minerals as observed from orbit, now known as “Glen Torridon” (GT). The presence of these phyllosilicate-rich sedimentary layers and sulfate-rich layers that overlie them was a key driver in the selection of Gale crater as Curiosity’s landing site, since they are expected to contain evidence of a global-scale environmental shift that occurred on Mars [1]. GT was also a high-priority exploration zone due to the close association of organic material with phyllosilicates on Earth. Curiosity acquired several samples drilled from mudstones and sandstones in the GT region and the transition zone from GT into the sulfate-rich unit that were analyzed by the Sample Analysis at Mars (SAM) instrument suite. Evolved gas analysis (EGA) of these samples indicated variable abundances of C,O-bearing species, identified by the release of CO₂ during pyrolysis (Fig. 1). The temperatures at which gases are evolved from samples during SAM EGA provide clues to the sources of volatile-bearing phases, which is particularly helpful when their identities are unclear to the Chemistry and Mineralogy (CheMin) instrument. In addition, the isotopic composition of these gases may suggest possible formation scenarios and relationships between phases. We will discuss C and O isotope ratios of CO₂ evolved from samples of GT and the transition zone into the sulfate-rich unit 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 utilized particles < 150 μm in size. 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. During a nominal experiment, the sample is heated to ~850 °C at a rate of 35 °C/min. 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.

All SAM EGA experiments show evidence for an instrument background from products of a derivatiza-

tion reagent, *N*-methyl-*N*-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA), carried by SAM [2]. Some ionization fragments of these compounds produce isobaric interferences with QMS measurements of CO₂ isotopologues at *m/z* 45 and 46, which are used to calculate C and O isotope ratios, requiring data corrections before isotope ratios are determined [3].

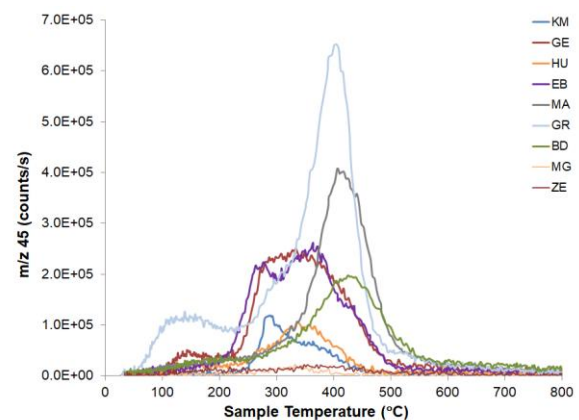


Figure 1. CO₂ released from the samples drilled in the GT region and the transition zone from GT to the sulfate unit, shown as the QMS signal at the *m/z* isotopologue. Abbreviations in the legend indicate sample names: KM = Kilmarie; GE = Glen Etive; HU = Hutton; EB = Edinburgh; MA = Mary Anning; GR = Groken; BD = Bardou; MG = Maria Gordon; ZE = Zechstein. The low-temperature peak (~130 °C) at GR is likely from oxidized SAM background compounds.

EGA Results: The CO₂ released by the samples from the GT and transition zone is shown in Fig. 1. This figure shows the observed signal at the minor isotopologue *m/z* 45 because the major molecular ion (*m/z* 44) saturated the QMS detector. Although the samples were nominally of similar masses, mass estimates with the current drilling technique are not well-constrained, so some differences may exist. However, the range of CO₂ abundances shown in Fig. 1 generally serves as a direct indicator of variability in the contents of C,O-bearing species in the samples. The samples depicted in the figure released enough CO₂ to calculate isotope ratios of at least carbon. Samples acquired by Curiosity and analyzed by SAM from this region of Gale crater that are not shown released too little CO₂

for QMS isotopic calculations.

The largest CO₂ releases were seen at the Mary Anning (MA) and Groken (GR) samples. MA was acquired from the Knockfarril Hill member (KHm) of the Carolyn Shoemaker formation (CSf). GR, of interest due to unusual diagenetic features, was obtained from a site ~1 m from MA [4]. Lesser amounts of CO₂ were released from samples of Kilmarie (KM) of the Jura member of the Murray formation, Glen Etive (GE) of KHm, Hutton (HU) of the Glasgow member of CSf, Edinburgh (EB) of the Stimson formation, and Bardou (BD), drilled from the top of Mont Mercou, located at the border between the GT region and the clay-sulfate transition zone. The smallest CO₂ releases were observed during analyses of the Maria Gordon (MG) and Zechstein (ZE) samples, obtained from the transition zone.

The pattern of CO₂ peak temperatures produced by these samples differs from that of mudstone and sandstone samples acquired from stratigraphically lower sediments in the Murray formation and Yellowknife Bay (YKB). The lower Murray and YKB samples produced CO₂ peaks predominantly between 200-350 °C [3]. Although the EB and KM samples produced peaks within that range, CO₂ was released from the GT and transition zone samples predominantly at temperatures approaching 400 °C and above. This suggests that the C,O-bearing phases in these samples reflect different carbon sources than those from sediments below. Peak temperatures are consistent with various oxalates and acetates [3,5-6], which may be produced as metastable intermediate compounds in UV degradation of organic compounds [7], or possibly fine-grained Fe-carbonates above 400 °C [8].

Isotope ratios: CO₂ released from GT and transition zone samples was broadly more enriched in both ¹⁸O and ¹³C compared to those from most stratigraphically lower samples [3]. This is consistent with oxalates or other salts of organic acids containing carbon from different sources than those that supplied the lower sediments. Alternatively, isotopically enriched CO₂ evolved at temperatures above 400 °C could reflect the presence of carbonates, which would be expected to carry ¹⁸O and ¹³C enrichments if formed in equilibrium with the martian atmosphere after significant escape of early atmospheric gases to space had occurred [3, 9]. Exceptions could be found in carbonates formed from partially a frozen lake, in which the water had been depleted in ¹⁸O by Rayleigh distillation, producing carbonates with lower values of $\delta^{18}\text{O}$ than expected for equilibrium formation conditions [3]. The MA and GR samples were unique among those of the GT and transition zone samples shown here in producing CO₂ with

$\delta^{18}\text{O}$ close to zero or much less enriched than the other samples from this area. If the prominent CO₂ peaks produced by MA and GR do reflect the presence of carbonates, this could indicate deposition during an episode characterized by colder temperatures than experienced by the other GT and transition zone sites represented by this sample set.

References: [1] Milliken et al. (2010) *GRL* 37. [2] Glavin et al. (2013) *JGR* 118. [3] Franz et al. (2020) *Nature Astron.* 4. [4] Gasda et al., in prep. [5] Lewis et al. (2021) *JGR* 126. [6] Applin et al. (2015) *EPSL* 420. [7] Benner et al. (2000) *PNAS* 97. [8] Sutter et al. (2017) *JGR* 122. [9] Mahaffy et al. (2013) *Science* 341.