Obtaining carbon isotopic information for organic carbon from Martian sediments has long been a goal of planetary science, as it has the potential to elucidate the origin of such carbon and aspects of Martian carbon cycling. Carbon isotopic values ($\delta^{13}$C$_{\text{VPDB}}$) of the methane released during pyrolysis of 24 powder samples at Gale crater, Mars, show a high degree of variation ($-137 \pm 8\%$ to $+22 \pm 10\%$) when measured by the tunable laser spectrometer portion of the Sample Analysis at Mars instrument suite during evolved gas analysis. Included in these data are 10 measured $\delta^{13}$C values less than $-70\%$ found for six different sampling locations, all potentially associated with a possible paleosurface. There are multiple plausible explanations for the anomalously depleted $\delta^{13}$C observed in evolved methane, but no single explanation can be accepted without further research. Three possible explanations are the photolysis of biological methane released during pyrolysis as observed by the MSL tunable laser spectrometer (TLS) of the Sample Analysis at Mars (SAM) instrument suite (3) from 24 samples from Gale crater, Mars (Table 1) using methods described in this paper’s supplement. The amount of CH$_4$ observed by the TLS-SAM instrument for the TLS temperature cut is also indicated in Table 1. This includes five analyses of the Cumberland (CB) sample drilled in the Sheepbed member of the Bradbury group rocks at Yellowknife Bay, as well as 15 samples from the Mount Sharp group, three from the overlying Stimson formation, and hundreds of meters of stratigraphy in Gale crater that represent conditions of the present Earth.

Results

For evolved gas analysis (EGA) at Gale crater, drilled powder or scooped fines are heated at 35 °C in the oven, in practice, depends on the relative abundances of oxycarbons and reduced minerals in each sample. During EGA, organic material can produce a range of products including CO$_2$, CH$_4$, CO, OCS, CS$_2$, and molecular organic fragments. EGA $\delta^{13}$C CH$_4$ values were measured by the TLS instrument of the SAM suite for 24 samples from Gale crater, Mars (Table 1) including CO$_2$, CH$_4$, CO, OCS, CS$_2$, and molecular organic fragments. The values show remarkable variation indicating different origins for the carbon evolved from different samples. Samples from multiple locations within Gale crater evolved methane with highly fractionated carbon isotopes. We suggest three routes by which highly fractionated carbon could be deposited on Mars, with each suggesting that Martian carbon cycling is quite distinct from that of the present Earth.

Significance

Carbon isotopic analysis is among the most pervasive geochemical approaches because the fractionation of carbon isotopes produces a natural tracer of biological and chemical processes. Rover-based carbon isotopic analyses of sedimentary rocks on Mars have the potential to reveal modes of Martian carbon cycling. We report carbon isotopic values of the methane released during pyrolysis of samples obtained at Gale crater. The authors declare no competing interest.

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one scooped sand sample. Shown in Table 2 are the posterior probabilities of reduced sulfur presence (based on several evolved sulfur gases observed compared to laboratory data) and the δ\(^{34}\)S values calculated from SO\(_2\) evolved between \(\sim 500\) and \(600^\circ\) C during EGA and measured by the SAM quadrupole mass spectrometer (QMS). As seen in Fig. 2, the TLS CH\(_4\) δ\(^{13}\)C values that are highly \(^{13}\)C depleted correspond predominantly with the \(^{34}\)S-depleted δ\(^{34}\)S QMS values observed for evolved SO\(_2\), reported by Franz et al. (4) and Wong (5). Four of the most depleted TLS CH\(_4\) δ\(^{13}\)C values (Table 1) are from samples [CB2, CB3, CB5, and Edinburgh (EB)] that also clearly evolve \(^{34}\)S-depleted SO\(_2\) (Table 2 and Fig. 2). Such δ\(^{34}\)S-depleted SO\(_2\) evolved at mid (500 to 600°C) temperature has been interpreted to indicate Martian sulfides (4). Reduced sulfur has also been inferred based on the evolution of OCS and CS\(_2\) compared to analyses of laboratory sulfur samples (6). Interestingly, 8 out of the 10 samples showing strong TLS δ\(^{13}\)C depletions (i.e., < -70‰) in evolved CH\(_4\) also evolved sulfur gases (OCS and CS\(_2\)) indicative of a reduced sulfur detection based on statistical comparisons to laboratory runs (Table 2). One of the two samples in which the EGA data do not support a reduced sulfur detection is CB6, which had an unusual EGA procedure that prohibited an effective analysis of the sulfur gases. The other is Hutton (HU), which occurs just below the Greenheugh pediment (a gently sloping erosional surface downslope from Gediz Vallis) and the Basal Siccar Point group unconformity. HU shows evidence for geochemical alteration by later fluids flowing near the Basal Siccar Point group unconformity (e.g., ref. 7).

**Discussion**

Some of the \(^{13}\)C depletions reported here are anomalously large, especially with respect to the carbon isotopic composition of the Martian atmosphere, whose δ\(^{13}\)C value reported earlier by TLS-SAM is \(\sim 46‰\) (8). This atmospheric value reflects the integrated largescale loss of volatiles from the Martian atmosphere and thus, the δ\(^{13}\)C composition of the atmosphere may have been less \(^{13}\)C enriched when Gale crater sediments were deposited. Because of the magnitude of the \(^{13}\)C depletions observed in CH\(_4\) evolved during EGA runs, the authors have considered potential rover-induced origins for the observations without uncovering any explanation. In fact, the TLS spectra obtained on Mars from evolved CH\(_4\) (SI Appendix, Fig. S1) are exceptionally clean and provide multiple \(^{12}\)C and \(^{13}\)C lines with which to calculate δ\(^{13}\)C values, making it unlikely that the \(^{13}\)C depletions observed are due to an interfering organic molecule. From the repeat CB analyses, it appears that the isotope depletion observed in CH\(_4\) is most pronounced at lower temperatures. This observation suggests that precursors to the evolved CH\(_4\) are relatively volatile organic molecules. However, strong depletions were still observed in several samples using high-temperature cuts (>450°C) in which the temperature cut...
includes a tail of a CH$_4$ release centered at a lower temperature (e.g., SI Appendix, Fig. S2). The CH$_4$ isotopic variation in CB samples, though, are not completely explained by differences in the temperature cut. Additionally, at Yellowknife Bay, the TLS analyses of CB using the 2.78-$\mu$m laser produced highly $^{13}$C-depleted CO$_2$ $^{13}$C values (SI Appendix, Table S1). While these TLS analyses of CB produced CO$_2$ $^{13}$C values that were, in some cases, comparable to CH$_4$ $^{13}$C (SI Appendix, Table S1), such depleted CO$_2$ $^{13}$C values have not been observed in later samples of the mission. In contrast, TLS CH$_4$ $^{13}$C values using the 3.27-$\mu$m laser show strong depletions in multiple different drill samples from vastly different parts of the mission. Because the observation of anomalous $^{13}$C values in evolved CH$_4$ are repeatable with different samples spread out in space and time, we have focused on those values for this study.

We have considered the SAM instrument background of N-tert-butyldimethylsilyl-N-methyl-trifluoroacetamide (MTBSTFA ($^{13}$C = $-35$%$v$; refs. 9 and 10) as a reasonable source of evolved CH$_4$ to consider. Early in the mission, this background was estimated to contribute up to 900 nmol of CO$_2$ during pyrolysis (11). In addition to oxidizing to CO$_2$, MBTSTFA is known to react with water resulting in 1,3-bis(1,1-dimethylethyl)-1,3,3-tetramethyldisiloxane [or bisilylated water (BSW)], which can be monitored by the SAM QMS. Based on the levels of BSW detected, the level of MTBSTFA background has been variable between runs depending on how long it has been since a wet chemistry experiment and, for a few cases in which it was relevant, how long a sample was stored before analysis. For 16 of the samples, the mean of the total BSW observed during the course of the EGA runs was 1.0 nmol with an SD of 1.5 nmol (Table 2). HU had over 22 times this average, and Duluth (DU) had over 30 times more than this average. In the case of DU, the extreme amount of BSW observed was also concurrent with an anomalous amount of total EGA methane (774 nmol) and a TLS CH$_4$ isotopic value ($^{13}$C = $-45$%$v$) similar to MTBSTFA ($^{13}$C = $-35$%$v$), which demonstrated that with elevated levels of MTBSTFA in the SAM background, a portion can end up as evolved CH$_4$. Further, an intramolecular isotopic analysis of methyl-trifluoroacetamide from the hydrolysis of MTBSTFA showed that the types of carbon (methyl-carbon and carbonyl C) most likely to contribute CH$_4$ from the MTBSTFA background were the most $^{13}$C enriched (SI Appendix, Fig. S3), making it unlikely that the observed anomalies stemmed from a site-specific carbon depletion obscured in the bulk $^{13}$C value for MTBSTFA.

Major endmember carbon reservoirs (SI Appendix, Table S4) presently on Mars are the atmospheric CO$_2$ ($^{13}$C = $+46 \pm 4$%$v$; ref. 8) and the igneous carbon ($^{13}$C = $-20 \pm 4$%$v$; ref. 12). TLS $^{13}$C values between $-17 \pm 2$%$v$ and $-57 \pm 2$%$v$ were found for 10 samples including DU. The isotopic composition of the CH$_4$ evolved during pyrolysis of these samples may reflect the MTBSTFA SAM background, Martian igneous carbon, and/or meteoritic infall along with any isotopic fractionations the occur during oven reactions. Laboratory experiments using solid materials were conducted to explore the magnitude of carbon isotopic fractionation possible during pyrolysis under conditions similar to SAM (SI Appendix, Table S2). We found that cleavage and reduction of methyl groups to CH$_4$ as would happen for most CH$_4$ derived from MTBSTFA products, produced little $^{13}$C depletion (0.4 to 4.6%$v$; SI Appendix, Fig. S4). CH$_4$ evolved from recalcitrant sources (graphite and diamond) showed $^{13}$C-depletion of 8 to 21%$v$, CH$_4$ from oxalate/oxamide showed moderate $^{13}$C depletion (25.0 to 25.3%$v$), and bicarbonate reduction showed the largest $^{13}$C depletions (28.5 to 49%$v$). Both our laboratory pyrolysis experiments (SI Appendix, Table S2) and modeling of possible isotopic pseuqeoequilibration during pyrolysis (SI Appendix, Figs. S5–S8 and Table S3) considering several different scenarios suggested that oven processes would typically produce fractionations less than 50%$v$ and, therefore, cannot account for the large $^{13}$C depletions observed in multiple samples at Gale crater. Applying the most extreme oven fractionation imagined to

### Table 1. MSL methane isotopic values from EGA

| Label* | Sol | Temperature cut for TLS (°C) | TLS CH$_4$ (nmol) | ±1 SE | TLS CH$_4$ $^{13}$C (%) | ±1 SE |
|--------|-----|------------------------------|-------------------|-------|-------------------------|-------|
| CB1    | 281 | 220–319                      | 5.0               | <0.01 | -133                    | 12    |
| CB2    | 286 | 99–349                       | 5.5               | 0.01  | -115                    | 5     |
| CB3    | 290 | 450–786                      | 2.6               | 0.01  | -96                     | 8     |
| CB5    | 368 | 450–786                      | 1.8               | <0.01 | -75                     | 9     |
| CB6    | 382 | 450–786                      | 1.3               | 0.01  | -71                     | 21    |
| TP     | 928 | 382–614                      | 6.9               | 0.01  | -30                     | 12    |
| BS1    | 1,130 | 639–862                  | 12.1              | 0.01  | -32                     | 9     |
| GH1    | 1,147 | 639–862                 | 7.7               | 0.01  | 11                      | 16    |
| GB2    | 1,237 | 583–770                  | 6.2               | 0.01  | -88                     | 8     |
| OU1    | 1,382 | 347–749                 | 43.8              | 0.03  | -17                     | 2     |
| MB     | 1,443 | 377–771                 | 19.1              | 0.06  | -6                      | 6     |
| DU     | 2,072 | 539–837                | 27.2              | 0.06  | -45                     | 3     |
| ST     | 2,147 | 437–788                 | 45.9              | 0.06  | -31                     | 2     |
| HF     | 2,231 | 167–356                 | 16.3              | 0.02  | -133                    | 4     |
| RH     | 2,281 | 405–572                 | 2.1               | 0.00  | -78                     | 7     |
| KM     | 2,393 | 374–549                 | 14.4              | 0.02  | -35                     | 6     |
| GE1    | 2,497 | 350–600                 | 39.8              | 0.03  | -57                     | 2     |
| GE3    | 2,531 | 355–617                 | 19.3              | 0.04  | -37                     | 5     |
| HU     | 2,576 | 452–785                 | 20.1              | 0.02  | -114                    | 3     |
| EB     | 2,721 | 264–538                 | 8.4               | 0.02  | -137                    | 8     |
| GG     | 2,765 | 270–556                 | 77.9              | 0.68  | 22                      | 10    |
| MA1    | 2,844 | 270–556                 | 34.7              | 0.04  | -29                     | 2     |
| BD     | 3,098 | 220–440                 | 38.9              | 0.05  | -28                     | 2     |
| PT     | 3,176 | 220–440                 | 27.7              | 0.03  | -65                     | 2     |

*Labels refer to Curiosity rover drill holes: Cumberland (CB1, CB2, CB3, CB5, CB6), Telegraph Peak (TP), Big Sky (BS1), Greenhorn (GH1), Gobabeb (GB2), Oudam (OU1), Marimba (MB), Duluth (DU), Stoer (ST), Highfield (HF), Rockhall (RH), Kilmarie (KM), Glen Etive (GE1, GE3), Hutton (HU), Edinburgh (EB), Glasgow (GG), Mary Anning (MA1), Bardou (BD), and Pontours (PT).

SE = SE at 67% CI.
these carbon reservoirs results in CH₄ with δ¹³C values of about −5 to −70‰. CB (CB1, CB2, CB3, CB5, CB6), Globabeb (GB2), Highfield (HF), Rock Hall (RH), Hutton (HU), and EB showed TLS CH₄ values more ¹³C depleted than this range, indicating that even reactions are not likely to be causing their anomalous ¹³C-depleted values observed in evolved CH₄.

It may be notable that the highly depleted ¹³C values for evolved CH₄ have so far been found in five distinct locations at Gale crater, Mars (Table 2 and Fig. 1 A–F). The highly ¹³C-depleted signal was first seen in the mudstones of Yellowknife Bay on the crater floor (Fig. 1F) in a location where high thermal inertia values were measured from orbit and have been potentially attributed to secondary alteration at the end of the Peace Vallis fan (13). Next, highly ¹³C-depleted methane values were observed in a sample of the sand from the Bagnold dunes (GB2), a modern dune field of basaltic sand (Fig. 1F). Next, the depleted values were observed at the top of the Vera Rubin ridge (VRR) in mudstone samples of the red and gray Jura member of the Murray formation (RH and HF, respectively). Finally, the highly ¹³C-depleted values were observed just below the Basal Sicc Point group unconformity (HU; Fig. 1C) and in the overlying Stimson formation sandstone that forms the cap rock of the current Greenheugh pediment morphological feature (EB; Fig. 1B). These different locations include a variety of lithologies (mudstone, sand, and sandstone) and are temporally spread throughout the mission operations to date.

One potential connection between these evolved methane samples depleted in ¹³C is that they might all represent samples associated with a paleosurface (Figs. 3 and 4). The locations of the samples yielding depleted ¹³C methane along with their elevations are shown in Fig. 3 for illustration of this paleosurface possibility. Yellowknife Bay may have been weathered by flow out of Peace Vallis. The Bagnold dunes represent sand from, in part, a recently eroded local sandstone. The VRR is a resistant topographic ridge relatively higher than other samples of the Murray formation mudstone with a unique diagenetic history (14) that may include weathering from the outflow of the Gediz Vallis (6). Finally, the Greenheugh pediment is presently a large geomorphic surface and represents the remains of a larger paleosurface that would have extended downslope toward the crater floor (15). The HU sample, which shows the strongly ¹³C-depleted signature, is just below the Greenheugh pediment and is believed to have been exposed to fluid migration near the Basal Sicc Point group unconformity (7). Similar to the HU sample, Pontours (PT) is in the Carolyn Shoemaker formation below the Greenheugh pediment and, therefore, has likely been exposed to fluids during erosion of the pediment. PT is actually at a higher elevation than the EB sample because of the lateral slope of the pediment, and, interestingly, the TLS CH₄ ³⁴S value for PT is intermediate between what is expected for SAM’s MTBSTFA background carbon and the highly ¹³C-depleted values (i.e., <−70‰) found for 10 of the Gale crater samples.

While this distribution of samples yielding a strongly ¹³C-depleted signature may be a coincidence, it could be explained if the signature relates to a process that primarily impacted a paleosurface associated with outflow from Gediz Vallis and Peace Vallis that included the Greenheugh pediment capping unit, the topographic high represented by the VRR, and the crater floor at Yellowknife Bay. Given this distribution of samples yielding isotopically anomalous methane, we have considered multiple phenomena that have the potential to explain the results. These phenomena are not presented in order of preference, but rather are treated equally, starting with the canonical explanation for when this type of geochemical signature is found on Earth and moving to possible processes that would be increasingly specific to Mars.

**Martian Methanotrophy?** The observed ¹³C-depleted EGA CH₄ was presumably released from organic materials in the solid sample during pyrolysis. The canonical explanation on Earth for highly depleted carbon associated with a paleosurface would be microbial methanotroph converting methane into biomass when the methane was already ¹³C depleted because of its biological production during methanogenesis (e.g., ref. 16). The Archean Tumbiana Formation has highly ¹³C-depleted biomass preserved along with abundant lacustrine stromatolites (e.g., refs. 17 and 18). The bulk biomass found in the Tumbiana Formation has δ¹³C values as low as −60‰ (19), the origin of which is often attributed to widespread methanotrophy during a period of abundant methane in the Earth’s atmosphere and shallow basins (16, 20). Highly depleted biomass is also found in some sediments in and around active modern marine methane seeps (e.g., refs. 21–24), and there are several examples of highly ¹³C-depleted biomass preserved in paleo seeps deposits (25, 26).

Because of both the overall oxidizing state of the Martian atmosphere and the presence of ferric iron and sulfate minerals, during times of large methane releases, methanotrophy would be energetically favorable. Based on observations of apparent methane plumes from the Martian interior and the growing understanding of the ways methane can be microbiologically oxidized on Earth, microbial methanotroph has been proposed as a possible metabolism for recent and ancient Mars (27, 28). This explanation would also potentially explain the observation of reduced sulfur in many of the same samples in which negative δ³⁴S values were found (29) because marine methane oxidation is coupled to sulfate reduction. If the highly ¹³C-depleted carbon and reduced sulfur are indeed found predominantly together on a paleosurface, the co-occurrence could result from the coproduction of ¹³C-depleted microbial biomass and sulfides during the microbial anaerobic oxidation of methane based on sulfate as an electron acceptor.

In order to get the observed magnitude of ¹³C depletion in the observed EGA methane released from organic materials, the CH₄ that was originally consumed by microorganisms in this model would need to already be highly ¹³C depleted.
(perhaps $-40$ to $-100\%e$) because the observed depletion on Earth during anaerobic methanotrophy is on the order of about $30\%e$ (30), assuming fractionations associated with possible Martian metabolisms are similar to those observed on Earth. Therefore, this explanation requires multiple steps with the CH$_4$ consumed by the methanotrophs to be biological CH$_4$ from microbial methanogenesis. Furthermore, the inorganic CO$_2$ fueling this microbial ecosystem would need to have a $\delta^{13}C$ composition similar to Martian magmatic carbon ($-20\%e$; refs. 12 and 31) rather than the highly $^{13}C$-enriched values observed in the present Martian atmosphere ($+46\%e$; ref. 8).

For this model to work, either the deposition of the $^{13}C$-depleted carbon would have needed to occur before the loss of significant carbon from the Martian atmosphere or there would need to have been CO$_2$ reservoirs in the Martian subsurface that were isolated from the atmosphere. In either scenario, the

Table 2. Relevant results from the MSL QMS during EGA and informal stratigraphic units for samples

| Label | BSW (nmol) | Reduced S PP* (%) | SO$_2$ $\delta^{34}S$† (%) | ±1 SE | Stratigraphy                     |
|-------|------------|-------------------|-----------------------------|-------|---------------------------------|
| CB1   | 3          | >99               | -21                         | 36    | Sheepbed, Bradbury group        |
| CB2   | 1.8        | 89                | -28                         | 14    |                                 |
| CB3   | 1.3        | 89                | -47                         | 14    |                                 |
| CB5   | 0.2        | 84                | -40                         | 10    |                                 |
| CB6   | 0.1        | ND                | ND                          | ND    |                                 |
| TP    | 0.2        | <1                | 6                           | 7     |                                 |
| BS1   | 0.4        | 78                | 3                           | 6     | Stimson formation               |
| GH1   | 0.2        | <1, 60            | 28                          | 7     |                                 |
| GB2   | 0.1        | 86, 57            | ND                          | ND    | Bagnold dunes                   |
| OU1   | 0.6        | 16                | -31                         | 9     | Hartmann’s†                     |
| MB    | 0.2        | 74                | ND                          | ND    | Karasburg†                      |
| DU    | 31.2       | 2                 | ND                          | ND    | Blunts Point†                   |
| ST    | 2.9        | 4                 | ND                          | ND    | Pettegrov Point†                 |
| HF    | 3.5        | 93                | -18                         | 40    |                                 |
| RH    | 0.3        | 93                | -21                         | 19    |                                 |
| KM    | 0.4        | 97                | 20                          | 4     | Knockfarril Hill§               |
| GE1   | 0.6        | 7                 | 20                          | 5     |                                 |
| GE3   | 0.2        | 9                 | -14                         | 5     |                                 |
| HU    | 12.7       | 11                | 18                          | 6     |                                 |
| EB    | 5          | 73                | -27                         | 7     |                                 |
| GG    | 1.2        | 1                 | 5                           | 9     |                                 |
| MA1   | 0.3        | 1                 | 8                           | 5     |                                 |
| BD    | 0.5        | 6                 | -9                          | 6     |                                 |
| PT    | 0.3        | 1                 | 1                           | 3     |                                 |

ND, not determined.

*PP, posterior probability; Wong (5); Wong et al. (6).
†Franz et al. (4); Wong (5).
‡Members of Murray formation.
§Members of Carolyn Shoemaker formation.

Fig. 3. (A) Map of the northwest portion of Gale crater with annotations showing Peace Vallis and the alluvial fan leading toward the high thermal inertia region (High TI) in Aeolis Palus. Gediz Vallis is labeled to the south of the MSL traverse. The MSL traverse through sol 3192 is shown in red. The red rectangle outlines the region shown in B. Dashed line represents the profile in C. Base map is a mosaic from Calef and Parker (84). (B) Map of the MSL-specific study area and rover traverse through sol 3192. Samples analyzed by TLS with highly depleted $^{13}C$ values are labeled along the traverse. Dashed line corresponds to the elevation profile shown in D. Base map is a HiRISE mosaic from the Planetary Data System (PDS) PLACES archive. (C) Profile from A to A’ in A showing the change in elevation from the lower end of Peace Vallis to Yellowknife Bay. (D) Elevation profile from B to B’ to B” shown in B. Drill samples with highly depleted $^{13}C$ values are labeled with approximate elevations.
initial carbon could have had an isotopic composition down to $\delta^{13}C = -20\%_o$. The first option, however, appears inconsistent with Gale crater sedimentology, given the relatively late emplacement of the Stimson formation that is cut by the paleosurface of interest here. The other option is possible, but it is hard to evaluate with our limited knowledge of the hydrodynamics of subsurface Mars. Potentially supporting this model is the observation of long, straight alkanes in the CB sample (32). Overall, there is, however, no supporting sedimentological evidence for microbial methanotrophy on the paleosurface discussed here. This is in sharp contrast to analog methanotrophic environments on Earth, for which there is often plenty of textural evidence for microbial processes in deposited layers. It is plausible that such evidence once existed at Gale crater as an authigenic carbonate (e.g., refs. 33 and 34) that was later dissolved by acidic fluids. While sedimentary structures may be destroyed by dissolution, dissolution can concentrate molecular biosignatures. The Curiosity rover will again encounter the Stimson formation sandstone on the Greenheugh pediment, providing an opportunity to search for specific organic molecules (e.g., refs. 35 and 36) in this rock unit. The lack of sedimentary evidence for microbial surface activity and the need to avoid influence from a $^{13}C$-enriched Martian atmosphere cast enough doubt on this biological explanation of surface methanotrophy to tentatively dismiss it pending further exploration for either evidence of surface-associated microbial activity or microbial-influenced sediments whose organic material could have been redeposited to the paleosurface.

**Interstellar Dust?** The solar system passes through an average-sized giant molecular cloud (GMC) once every 100 million years, providing a mechanism for triggering cooling events on terrestrial planets through the influx of particles to planetary atmospheres that is substantially higher (20 to 100 times) than the ongoing flux of interplanetary dust (37). The solar system passing through a dense molecular cloud would inevitably also result in an influx of $^{13}C$-depleted carbonaceous dust particles (38), as about 1% of such interstellar clouds is dust (39). The $\delta^{13}C$ value for interstellar dust in the Allende meteorite has been shown to be as low as $-260\%_o$ (40), demonstrating that interstellar dust is a potential source of highly depleted carbon for periodic deposition on the surface of Mars. It is also plausible, but presently uncertain, that these particles would similarly be associated with sulfides having negative $\delta^{34}S$ values, as observed in the Curiosity data. The flux of such particles would be quite low and typically diluted by other sources of carbon. However, because the arrival of such particles is predicted to trigger a global cooling event, it is reasonable that particles would accumulate on the surface of glacial ice largely absent of typical sedimentary carbon. Glacial melt during the glacial period and ice retreat after should leave the interstellar dust particles on the glacial geomorphological surface. The existing sedimentological evidence for the paleosurface that has cut the Stimson formation does not rule out glacial processes, with Curiosity having only visited the Greenheugh pediment surface briefly at EB, and some studies across Mars support such an interpretation for similar outflow channels (41–44).

This explanation of interstellar dust as a source of the observed $^{13}C$-depleted values at Gale crater largely fits the observations if the isotopic signatures are not diluted by other geological processes and with the understanding that this explanation relies on a rare event, making it perhaps coincidental that the mission should find this signature preserved. Finally, the SAM results presented here suggest that the most $^{13}C$-depleted values are liberated during relatively low oven temperatures, with the high-temperature examples typically being tails of lower-temperature methane release. These observations might be understood to indicate that the organic precursor molecules being converted into methane in the SAM oven are not recalci-trant kerogen-like molecules, as pyrolysis of kerogen usually occurs at a higher temperature. If this interpretation is correct, then this constraint can be consistent with an interstellar dust origin, as there are a wide variety of known interstellar molecules, including many that are highly volatile (45). Overall, this explanation is plausible, but it requires additional research outside the scope of this report to verify, including the $\delta^{34}S$ values and the nature and relative amounts of carbon forms in GMC dust.

**Abiotic Reduction of CO₂?** There is growing recognition of the possible abiotic production of organic carbon on Mars through either electrochemical reduction (46) or photochemical reduction (10). In both cases, CO₂ would be converted into organic material abiotically and therefore could, in principle, lead to $^{13}C$-depleted organic material associated with a paleosurface. For electrochemical reduction, sulfides are one of the various reduced minerals that thermodynamically drive such carbon fixation reactions, and, similarly, sulfides are possible mineral catalysts that can promote photochemical reduction of CO₂. Thus, if abiotic reduction of CO₂ is an important process on Mars, it is likely to be associated with reduced sulfur, as observed at Gale crater. The present atmosphere of Mars, as previously noted, is highly enriched in $^{13}C$ (+46‰), and so either the abiotic reduction would need to have been occurring in subsurface environments (which does not match our observations) or would need to have occurred prior to the loss of much of the Martian atmosphere (which appears somewhat inconsistent with the timing of the erosional paleosurface with which the depleted carbon appears to be associated). While the timing of the erosional

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**Fig. 4.** Notional geologic history for Gale crater progressing from left to right starting with (A) a lacustrine environment. (B) After deposition, the lacustrine mudstones and sandstones were later exposed and eroded to produce the unconformity between the Mount Sharp group rocks (Murray and Carolyn Shoemaker formations) and the Stimson formation. (C and D) The Stimson sandstone has also been eroded to produce a paleosurface (and later the present landscape of ridges, buttes, and a pediment).
paleosurface is poorly constrained to the Hesperian, deuterium enrichment of clays at Gale crater indicated significant loss of atmospheric volatiles by this time (47), and the implications of that loss for the overall history of Martian volatile loss is an area of active research (48). Overall, though, the carbon isotopic fractionations expected during abiotic reduction are likely similar to those measured for abiotic hydrothermal reduction (up to ~50‰; SI Appendix, Fig. S9B). Fractionation of this magnitude would not produce organic material as depleted as the observed TLS values for the EGA methane reported in Table 1, and therefore, this explanation does not appear to explain the observations of highly 13C-depleted evolved methane during pyrolysis of samples at Gale crater. However, carbon isotopic fractionation during photochemical reduction of CO2 on a mineral surface has not been experimentally evaluated, and so, further research is needed before we can fully evaluate the abiotic reduction as the source of the highly 13C-depleted carbon isotopic values reported here. To be clear, there are a number of other CH4 isotope values reported in Table 1 that could reflect the reduction of CO2 on the Martian surface, including the most 13C-enriched values (~1 ± 6‰ to +22 ± 10‰). These 13C-enriched results match what would be expected for processes, biotic or abiotic, that produce organic material from the modern Martian atmosphere, for example.

**Photoysis of CH4 or CO and SO2?** Photochemical reactions are attractive as a source for the observed phenomenon because photochemical reactions are known to have influenced Mars’s volatiles, including the sulfur isotopic values found in Martian meteorites (49-52). Also, the fallout of products from atmospheric photochemistry might be expected to accumulate on an erosional surface, such as the proposed paleosurface discussed throughout this paper. There are several different overall schemes by which photochemistry in the Martian atmosphere might result in the large δ13C depletions observed by the MSL-TLS component of the SAM instrument.

A growing number of studies have reported variable CH4 abundances in the Martian atmosphere (53-55), including recent reports of seasonal and diurnal variation (56, 57) and plumes (55) detectable on the surface at Gale crater. The photoysis of atmospheric CH4 in a relatively dry, anaerobic atmosphere can produce organic aerosols and particles (e.g., Ref. 58). Perhaps when the postulated paleosurface was exposed, CH4 photoysis resulted in the deposition of such organic material. This model would explain why the highly depleted δ13C values seem to be associated with a possible paleosurface, similar to a model proposed for the Late-Archean Earth (59). Further, the model could potentially also explain the observation of 34S-depleted reduced sulfur in the same deposits if there was also SO2 photoysis along with the CH4 photochemistry producing sulfur-containing organic molecules. For example, Haley (60) suggested that photoexcitation of SO2 can lead to the production of methanesulfonic acid on the Archean Earth. Additional work is needed to explore the possibility that CH4 photoysis during Martain plume events would deposit 34S-depleted sulfur-containing organic material. However, past studies indicate that the magnitude of carbon isotopic fractionation during CH4 photoysis is relatively small (<15‰; refs. 61–63). Fractionation during CH4 photoysis appears insufficient to produce δ13C values as depleted as some of those observed at Gale crater even when starting from bulk Mars δ13C values (~20‰) representative of carbon from the interior of Mars. In order to produce organic material that is highly 13C depleted (considerably more depleted than ~70‰), another step with significant δ13C fractionation would need to have occurred during the formation of the methane. In principle, this could be abiogenic CH4 reduction in the Martian crust during serpentization or microbial methanogenesis. As noted previously, the abiogenic reduction of CO2 results in ~50‰ 13C depletion. If the source CO2 had a δ13C composition of ~20‰, subsequent abiogenic reduction to CH4, and subsequent photochemistry, then the resultant organic material deposited could be as depleted as perhaps ~85‰, a value that does not adequately include all of the values observed at Gale crater. If microbial methanogenesis were producing the observed atmospheric CH4, photoysis of the biologically produced CH4 would result in isotopic compositions consistent with the strongly depleted 13C values observed. At a minimum, however, new observations would be needed to confirm a biological origin for Mars CH4 plumes before this explanation can be accepted.

Alternatively, photochemical reduction of CO2 to formaldehyde (CH2O) via CO as an intermediate (e.g., ref. 64) might be responsible for producing a 13C-depleted organic material because the photochemical partitioning of CO2 and CO can lead to 13C depletion in the CO relative to CO2 (65-67). However, most past studies have considered Martian CO to be isotopically similar to CO2 with any 13C depletion relative to CO2 to be on the order of about 30‰ (68). Recently, however, photodissociation of CO has been shown to yield hundreds of per mil 13C enrichments in the resultant CO2 at 70 K using vacuum ultraviolet (VUV) radiation around 100 nm from a synchrotron source (69), while photodissociation of CO2 has been shown to yield tens of per mil 13C enrichments in the resultant CO (70, 71). While these experiments use too different ultraviolet (UV) wavelengths and different temperatures, together they illustrate how photochemical partitioning in the Martian atmosphere might result in anomalously 13C-depleted CO that could influence geochemistry observed at the Martian surface (72). In fact, CO photoysis has been calculated to have large carbon isotopic fractionation (with a fractionation factor of 0.6) at the top of the Martian atmosphere (73). VUV radiation would interact with the upper Martian atmosphere, and the presence of CO in the Martian atmosphere is maintained by CO2 photoysis. If Martian photochemistry resulted in 13C-depleted CO throughout the atmosphere in the past, photoproduction of formaldehyde and other organics from CO could have accumulated on the exposed surface at Gale crater, resulting in the isotope results reported here (67, 74). Obstacles to the deposition of organic material from the photoysis of CO2 have been the low yield and photochemical instability of the formaldehyde produced (75). Photochemically produced formaldehyde would react quickly with SO2 to yield hydroxymethanesulfonate, protecting it from photolysis back to CO (76), and it is plausible that elevated levels of atmospheric SO2 would directly shield formaldehyde because of the spectral overlap of SO2 and CH2O photoabsorption cross sections combined with the greater strength of SO2 absorption (77, 78). After major eruptions, when there were higher levels of CO, SO2, and H2, the deposition of organics should be maximized, including perhaps formaldehyde, hydroxymethanesulfonate, carbonyl sulfide (79), and thioformaldehyde (80). Because of a relatively long photochemical equilibrium lifetime of SO2 of ~1 Mars year (75, 81) and photodissociative shielding of CH2O afforded by SO2, the likelihood of such reactions increases. Incorporation of 13C-depleted organics into frost or glacial ice at the Martian surface could also concentrate these photochemical products and lead to their preservation in the local soil, protected from further UV reactions. However, the VUV wavelength radiation shown to produce large fractionation is too short for most of the Martian atmosphere and has yet to be explored at various temperatures, limiting any conclusions that can be drawn here. Also, direct observation of CO in the Martian atmosphere by spectroscopy from Earth has not revealed a large 13C depletion in CO, with the results appearing to be within 250‰ of the telluric value (82) and probably slightly 13C enriched relative to Earth (66, 68). Without further information with which to deconvolve the details of where and how carbon was fractionated, we can conclude the photochemical production of organic material from 13C-depleted CO is a possible scenario on Mars.
deposition of highly depleted organic material on to an exposed surface (74) that should not be rejected without further investigation of Martian CO and the photochemical processes that influence its carbon isotopic composition.

Conclusions

There are multiple plausible explanations for anomalously 13C-depleted methane observed by the TLS portion of the SAM instrument suite during EGA of samples from multiple sedimentary horizons at Gale crater, Mars. With present knowledge, there are three options that are consistent with the isotopic values and geology observed. These consistent explanations include the photolysis of biological methane by UV (UV) to methanotrophy, with homogeneity and any organic carbon associated with it. Similarly, the association of the observed anomalous isotopic values with such an ancient erosion surface provides guidance for NASA’s Perseverance rover team for targeting samples that could provide additional insight into the Martian processes responsible for this isotopic fractionation.

Methods

Samples. The first drilled MSL samples were collected from the Sheepbed member mudstones in Yellowknife Bay. The Yellowknife Bay region in Gale includes portions of high thermal inertia rocks toward the distal end of the alluvial fan from Peace Valley. The first and second samples of Sheepbed mudstones—John Klein and CB, respectively—were taken to investigate rocks deposited in this fluvial-lacustrine context. Analyses of these samples indicated the presence of an ancient habitable environment on Mars (2). After analysis of the Sheepbed mudstones, the rover continued its traverse through Aeolis Palus and then began its ascent of Mt. Sharp. Starting in September 2014, the rover transitioned from Bradbury group rocks to Mt. Sharp group rocks, which consist of hundreds of meters of sedimentary stratigraphy subdivided into the Murray formation and the Carolyn Shoemaker formation.

The Murray formation comprises the basal unit of Mt. Sharp and is divided among several distinct lithologic members dominated by mudstones. The Carolyn Shoemaker formation conformably overlies the Murray formation and has prominent sandstone lithology. To date, more than 20 drilled samples of Mt. Sharp group rocks have been collected and analyzed from the various members. Included among these samples are analyses of regions that show unique properties from orbit such as the VRR, the Glen Torridon region, and the lower sulfate-bearing unit. VRR is a prominent topographic high on lower Mount Sharp that had orbital evidence for elevated hematite and was determined to have formed from several diagenetic events (14). South of the ridge is the Glen Torridon region, which was notable for its elevated orbital spectral signature of phyllosilicates. The most recent samples (as of July 2021) have been documenting the transition from clays to hydrated sulfates.

In a few locations along the rover’s traverse, samples have been taken from the Siccarr Point group, which is comprised of the Stimson formation sandstones. The Stimson formation unconformably overlies the Mt. Sharp group and represents the remnants of an ancient, lithified dune field. The first four samples of Stimson formation rocks were taken to study both the parent rock and areas of localized alteration. The fifth sample of Stimson formation was taken some time in the mission, during the Glen Torridon campaign, when the rover ascended the Greenheugh pediment.

In addition to the drilled samples, MSL has analyzed scooped samples of sand. The fine sand-sized GB and Ogunquit Beach samples were taken from the active Bagnold Dune field and represent local modern aeolian processes.

MSL EGA and MSL Carbon Isotopic Analysis. The SAM consists of a suite of instruments including two pyrolysis ovens, a QMS, six gas chromatography columns, and a TLS (3). Together, SAM can measure the volatile composition of solid samples on Mars through thermal decomposition experiments. EGA-mass spectrometry (EGA-MS) heats samples to ~850 °C and sends evolved volatiles directly to the QMS for identification with a constant flow of He. In this paper, QMS was used for the quantification of sulfur gases, as well as BSW (see SI Appendix, Supplementary Text for additional details). As explained further in the supplement, quadratic discriminant analyses of the QMS gas results provided posterior probabilities for whether each drill sample contained reduced sulfur (6). Gases during EGA can be sampled by the TLS within a specified temperature range. The TLS uses several specific infrared wavelengths to quantify H2O, CO2, and CH4 as well as the isotopes of these gases when present in great enough abundance.

For SAM EGA runs, the solid sample is contained in an oven whose temperature is increased at 35 °C/min to ~850 °C while helium (0.8 scm, 25 mbar) is flowed through the pyrolysis oven. After evaporation of the TLS sample (Herriott) cell to record empty cell values, the TLS cell is opened to receive a “temperature cut” ingest (e.g., 200 to 350 °C) during EGA that introduces He and evolved volatiles into the cell, which is then sealed off for analysis. Typically, empty-cell methane abundances are extremely low (parts per billion by volume) compared to the full-cell EGA values (tens of parts per million by volume (ppmv)) so that empty-cell corrections are not needed. Full-cell pressures (mainly helium) are typically 5 to 15 mbar.

As further discussed in the supplement, three strong 12CH4 lines and four strong 13CH4 CH4 lines are identified in the recorded TLS spectra, although only two of the 13CH4 lines are chosen for analysis to minimize water interferences (SI Appendix, Fig. S1). With the cell closed, the laser scans over the methane lines every second, and on-board, TLS captures average spectra over sequential 2.7-min periods that are downloaded. Analysis of each of these 2.7-min spectra is done on a line-by-line basis through comparison with HITRAN 2016 calculations (that employ terrestrial δ13C values, so that volume mixing ratios in ppmv are retrieved for each of the 12CH4 and two 13CH4 lines. In some cases of very high mixing ratios, the strongest 12CH4 is very deep and not resolved. Then, the average values of the retrieved volume mixing ratios for 12CH4 and for 13CH4 are calculated from each of the 2.7-min spectra. During the run, 26 full-cell spectra are recorded, so that 26 average abundance values can be statistically analyzed to find the mean value with SEs of either 67% CI or 95% CI. Ratiointo the 13CH4 mean abundance with that determined for 12CH4 provides the δ13C values reported here normalized to the terrestrial PDB reference expectation such that

\[
\delta^{13}C = \frac{\text{13C Sample}}{\text{12C PDB std}} - 1 \times 1000
\]

where PDB std. is Pee Dee Belemnite standard, which is equal to 0.0112372.

Supporting Laboratory Analyses. As discussed in the SI Appendix, Supplementary Text, laboratory analyses were conducted (SI Appendix, Figs. S3 and S4, and Table S2) in support of this paper, including an NMR-based investigation (83).

Fig. 5. Three possible scenarios for the origin of the depleted carbon isotopes observed by the SAM TLS. Shown in blue, biologically produced methane from the Martian interior could result in deposition of 13C-depleted organic material after photolysis. While deposition of the depleted organics could also be due to methanotrophy, the paleosurface has not yet provided any evidence for the Martian processes responsible for this isotopic fractionation.
of the intramolecular isotopes of methyl-trifluoracetamide, part of the MBTSEA molecule. Laboratory studies were also used to study carbon isotope fractionation during pyrolysis to CH$_4$ under conditions similar to that of the SAM instrument. Various carbon-containing materials were placed in silver boats and dropped into an oven at 400 °C under flowing helium. The oven temperature then increased to >850 °C, and evolved gases, including CH$_4$, were trapped out of the He flow between 455 °C and 755 °C to simulate a high-temperature TLS cut.

Data Availability. All MSL SAM data are available at the Geosciences Node of NASA’s Planetary Data System (https://pds-geosciences.wustl.edu/missions/msl/sam.htm). All study data are included in the article and/or SI Appendix.
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