Supporting Information for

Highly enriched carbon and oxygen isotopes in carbonate-derived CO_2 at Gale crater, Mars

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Supplemental Materials

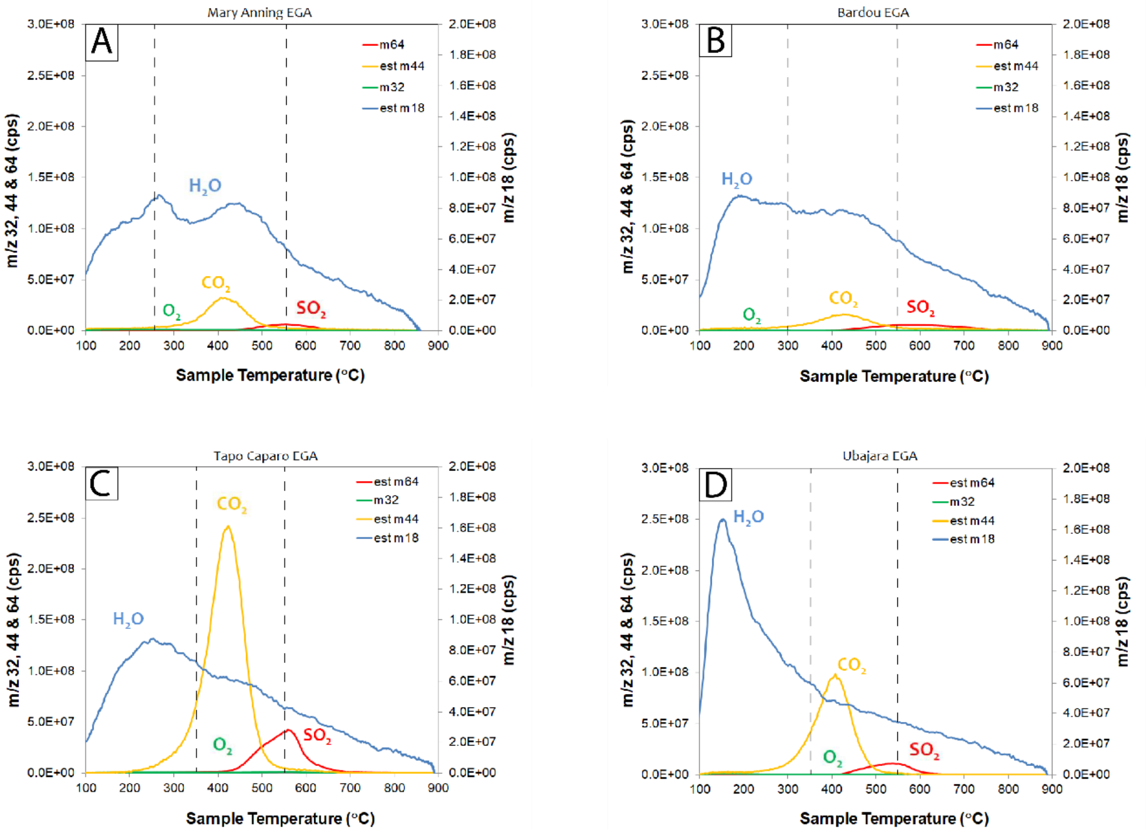

Figure S1: Evolved gas analysis (EGA) data for H_2O, CO_2, SO_2, and O_2 compared with temperature at each of the four sites: A) Mary Anning, B) Bardou, C) Tapo Caparo, and D) Ubajara. The dashed black lines within each panel show the lower and upper bounds, respectively, of the TLS cut within which the carbon and oxygen isotopes of the CO_2 were analyzed. These temperature bounds are as follows in each panel: 265 and 552°C at Mary Anning, 301 and 549°C at Bardou, 353 and 555°C at Tapo Caparo, and 353 and 553°C at Ubajara. The "m" in data labels (e.g., m32) refers to mass while "est" is short for estimated.

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S1. Alternative Mechanisms for ^{13}C and ^{18}O Enrichment

The main manuscript outlines the two preferred mechanisms for producing the high δ^{13} and δ^{18}O values measured in carbonates identified within Gale crater: 1) Rayleigh distillation and evaporation, and 2) kinetic isotope effects associated with cryogenic (≤0°C) precipitation. These two mechanisms are the most consistent with the observed isotope data and provide the simplest explanation. However, there are additional processes that are less likely, but cannot yet be ruled out. These processes include cosmic ray exposure, equilibrium between CO_2 and reduced carbon phases (*e.g.*, CO, CH_4), and photochemical fractionation via interactions with UV radiation. These pathways rarely come into play on Earth given the influences of the thick atmosphere and cycling related to the biosphere. However, without these factors or the planetary-scale recycling from plate tectonics, these processes may become more relevant on Mars. The following three sections discuss these processes and how they might have affected the isotopic balance of chemical species on Mars.

S1.1. Galactic and Solar Cosmic Ray Exposure

Another method of enriching the Martian surface in ^{13}C is via spallation reactions that alter the proton and neutron mass of nuclei. A relatively thin atmosphere and lack of global magnetic field has exposed the Martian surface to galactic and solar cosmic rays (CR) over the last 3.5 billion years[1,2]. Energetic CR particles are a form of ionizing radiation that can cause spallation reactions within oxygen-bearing species at the surface and in the atmosphere, which then produce ^{12}C and ^{13}C via the following reactions[3]:

$$^{16}O+p \rightarrow {}^{12}C+3p+2n \tag{3}$$

$$^{16}O+p \rightarrow {}^{13}C+3p+1n \tag{4}$$

$$^{16}O+n \rightarrow {}^{12}C+2p+3n \tag{5}$$

$$^{16}O + n \rightarrow {}^{13}C+2p+2n \tag{6}$$

Spallation produces ^{12}C and ^{13}C at comparable rates[4]. Therefore, given that ^{13}C is normally far scarcer than ^{12}C, δ^{13}C rises with greater exposure. Pavlov and colleagues[3] estimated the effects of spallation on the carbon and nitrogen isotopic composition in Martian rocks using modern day galactic cosmic ray flux. Assuming a total carbon content of 10 ppm for surface rocks, CR exposure over 3.5 billion years could produce ^{13}C-enrichment of >30‰. This estimate could be even larger, as recent studies found that the solar CR fluxes were ~50 times higher than present in the first billion years of the Solar system[5]. However, these estimates are preliminary as the large enrichments highlighted by Pavlov and colleagues[3] depend on low carbon content. If the total carbon content at the surface is higher, such as that estimated at the Phoenix landing site[6] and via orbital measurements[7], the ^{13}C enrichments from CR exposure will be diluted by the correspondingly larger size of the carbon reservoir. At Gale crater, refractory organic carbon content in a lacustrine sedimentary rock is estimated to be ~700 ppm by weight[8]. While it is possible that CR exposure partially contributed to the enriched δ^{13}C values of the Gale crater carbonates, it is not clear whether the local variability between the carbonates can be explained by this mechanism. Similarly, this mechanism would enrich other carbon reservoirs beyond the carbonates, but this is not born out in the data[8–10].

Future modeling efforts are needed to quantify the CR alteration of nuclei composition and their overall isotopic impact on carbon-bearing species at the Martian surface.

CR exposure can also ionize reduced carbon phases[11,12] (*e.g.*, CH_4, sedimentary organic matter, macromolecular carbon in mafic rocks[13]), water, minerals, and salts. These ionizing reactions can ultimately transform the reduced carbon reservoirs on Mars into more oxidized ones, including CO_2 and other phases relevant to carbonate formation. As such, oxidation via CR exposure represents a reaction pathway that should be considered. However, there are extremely limited constraints on the isotopic composition of the reduced phases, the size of those reservoirs, and the carbon and oxygen isotope fractionation of oxidation associated with CR exposure. While this type of ionization could potentially factor into the isotopic composition of the Gale crater carbonates, it is beyond the scope of the current discussion.

S1.2. CO, CH_4 Equilibrium with CO_2

Evidence for reducing capacity both in the mantle[14] and at the surface[15,16] early in the history of Mars suggests that a significant change was required to reach the current oxidizing environment on Mars. Furthermore, alternating layers of oxidized and reduced species throughout Gale crater point towards fluctuating redox conditions[17,18]. This begs the question: could episodic changes in redox conditions facilitate ^{13}C- and ^{18}O-enrichment of oxidized carbon species? Theoretical studies of carbon isotope exchange between CH_4 and CO_2 demonstrate that the fractionation factor favors ^{13}C-enrichment of the CO_2 ($1000\ln^{13}\alpha_{CO2\text{-}CH4} = 77.6‰$ at 0°C [19]). The same has been shown for CO, which has a fractionation of $1000\ln^{13}\alpha_{CO2\text{-}CO} = 92.6‰$. Magnitudes of fractionation >70‰ are sufficient to bridge the gap between modern atmospheric CO_2 $\delta^{13}C$ and the carbonate $\delta^{13}C$. However, while the theoretical fractionation factors are large enough, experimental studies quantifying CO_2-CH_4 isotope exchange are limited to temperatures >150°C[20]. Experiments by [21] quantified the carbon isotope fractionation in the CO_2-CO-CH_4 system from 200-1200°C in the presence of a nickel catalyst. Extrapolating these fractionation trends to 0°C gives $1000\ln^{13}\alpha_{CO2\text{-}CH4} = 85.06‰$ and $1000\ln^{13}\alpha_{CO2\text{-}CO} = 96.68‰$, which broadly corroborate the theoretical predictions. The rates of these reactions must also be considered. While the experiments were conducted at temperatures > 200°C, a study by Giggenbach[22] predicts that this exchange would be exceedingly slow at lower temperatures (extrapolated rate constant = 4.33×10^{-12} at 0°C). This type of exchange would also require significantly more reduced carbon than is currently present in the atmosphere ($CO < 1.0 \cdot 10^{-3}$ by volume mixing ratio[23], $CH_4 = 0.41$ ppbv[24]). Without those higher concentrations, any isotopic fractionations related to CO_2-CH_4 equilibration would be overprinted by the larger carbon reservoir. As such, equilibrium exchange between CO_2 and CH_4 remains a possible explanation albeit a less likely one with a relatively slow reaction rate.

S1.3. Photochemical Fractionation via UV Radiation

Recent measurements by the Nadir and Occultation for MArs Discovery (NOMAD) spectrometer on the ExoMars Trace Gas Orbiter (TGO) find that CO in Mars' atmosphere is isotopically light (δ^{13}C = -263 ± 132‰[25], or δ^{13}C = −160 ± 90‰[26]). The magnitude of this depletion can be explained using a 1-D model[27]. The offset between the δ^{13}C of CO and that of CO_2 has almost no direct effect on the δ^{13}C of modern atmospheric CO_2 (on << 1 Gyr timescales), as CO makes up <0.1% of the modern Mars atmosphere by volume[23]. This is too small a fraction to induce a measurable isotopic shift in the dominant species, CO_2.

However, the δ^{13}C of atmospheric CO_2 would be greatly elevated by CO-CO_2 isotopic fractionation if the CO mixing ratio with CO_2 rises above ~0.2. CO mixing ratios >0.2 are predicted by photochemical models of Mars-like CO_2-dominated atmospheres when the rate of reducing volcanism is >0.1 km^3 yr^{-1} [28], or if the atmospheric H_2O mixing ratio falls below 10^{-6} [29]. The atmosphere H_2O mixing ratio is currently on the order of 10^{-5}, so this would occur only if the atmosphere is thicker than present and/or is cold enough for H_2O to be efficiently cold-trapped[30]. If CO mixing ratios >0.2 occurred, mass balance would assure that the δ^{13}C of atmospheric CO_2 would rise by tens of ‰, potentially explaining some of the observations discussed here.

This explanation has weaknesses. First, it does not immediately explain the δ^{18}O enrichments that are observed (in the modern atmosphere, the δ^{18}O effect of photochemical fractionation between CO and CO_2 is poorly constrained, $\delta^{18}O_{CO} = -20 \pm 110$‰). Second, the temperatures that are needed for high CO mixing ratios in the absence of reducing volcanism are too low to allow for surface liquid water at Gale crater[30]. Therefore, if this explanation is correct, then either climate cycles, >0.1 km^3 yr^{-1} of reducing volcanism, or both, would be needed to reconcile the sedimentary evidence for surface liquid water at Gale crater with the isotopic data.

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