CARBON ISOTOPE FRACTIONATION ASSOCIATED WITH ADSORPTION OF CO₂ ON MINERAL SUBSTRATES AND ITS RELEVANCE TO THE STUDY OF MARS.  T. Rahn and J. M. Êiller, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125. eiler@gps.caltech.edu

Introduction: Volatile compounds (i.e., CO₂, H₂O, N₂, Ar, Xe) on Mars are likely adsorbed on dust and fine components of the regolith [1-4]; these adsorbed reservoirs may have played an important role in mitigating isotopic fractionations associated with escape of atmospheric compounds to space [4,5]. The geochemistry of adsorption is not well understood at conditions relevant to Mars and thus it is not obvious what other consequences may arise from such processes; in particular, it is not clear what geochemical record may be found in the Martian surface environment documenting variations in size of an adsorbed reservoir. We present here an experimental study of carbon isotope fractionations caused by adsorption of CO₂ onto mineral substrates (data for oxygen isotope fractionations gathered as part of the same experiments are more complex and will be discussed separately).

Methods: We conducted a series of experiments in which CO₂ vapor in a room-temperature, glass vacuum line was exposed to a cold trap containing ~2 grams of powdered mineral or rock held at a constant temperature between 190 and 230 K for periods of up to ten hours; substrates used in experiments described here include crushed natural basalt and natural kaolinite. Following exposure of CO₂ to the cold mineral substrate, vapor was sampled, the substrate was warmed to room temperature, and desorbed vapor was collected separately; both fractions were analyzed by isotope ratio mass spectrometry using a Finnigan 251. Experiments typically consisted of a period of ~20 minutes during which pressure in the vacuum line gradually decreased due to adsorption of CO₂, followed by a period of stable pressure during the remainder of the experiment. Quantities of CO₂ adsorbed on mineral substrates are comparable to those previously documented by [1-3]. Other technical details of these experiments are similar to those given in reference [6], which describes experiments on isotopic fractionations in the CO₂ ice/vapor system. Control experiments were conducted by following the protocol described above but omitting the mineral substrate from the trap; these controls resulted in no measurable loss of CO₂ vapor to a condensed phase (i.e., ice or adsorbate) and no isotopic fractionation between vapor inside and outside of the trap; we therefore conclude that our experimental results described below reflect interactions between CO₂ vapor and chilled mineral substrates.

Results: Carbon isotope fractionations between vapor and adsorbed CO₂ are observed in all experiments lasting greater than ten minutes (comparably to the time required to reach a stable vapor pressure), increase gradually over a period of ~1 hour, and are time invariant within the reproducibility of our experiments after approximately two hours. Analogous experiments conducted by exposing vapors strongly different in isotopic composition from previously prepared, adsorbed CO₂ demonstrate that the fractionations we observe are reversible. Time-invariance and reversibility are generally taken as evidence for attainment of isotopic exchange equilibrium in experiments of this type and we treat our results as equilibrium fractionation factors in the following discussion. However, to our knowledge these experiments are the first documenting stable isotope fractionations between vapor and adsorbed phases and thus this interpretation must be considered provisional until further experience with such systems has been accumulated.

Figure 1: ¹³C/¹²C fractionations between CO₂ vapor and condensed CO₂ (liquid, unfilled squares; ice, filled squares; adsorbate, circles—gray for basalt substrate, unfilled for kaolinite substrate). Conversion to δ notation (left vertical axis) assumes a vapor having the ¹³C/¹²C ratio of PDB.
strength of inter-molecular bonds involving CO$_2$ on isotopic substitution of carbon [7].

**Discussion:** Our results constrain the effect of CO$_2$ adsorption on the $^{13}$C/$^{12}$C ratio of the Martian atmosphere or reservoirs with which the atmosphere undergoes isotopic exchange. This constraint is significant for two issues: 1) explaining subtle differences in $^{13}$C/$^{12}$C between the Earth and Mars, and 2) guiding future measurements to examine the role of adsorption in atmospheric dynamics over climatic, seasonal, or diurnal time scales.

$^{13}$C enrichment in the Martian atmosphere: Several elements in the Martian atmosphere (H, N, the noble gases) are enriched in heavy stable isotopes by 10’s of percent to factors of several relative to those elements in the Earth’s atmosphere; this phenomenon is widely attributed to preferential loss from Mars of light isotopes of these elements during atmospheric escape [5]. Studies of the SNC meteorites suggest that carbon in the Martian atmosphere may be $^{13}$C enriched by tens of per mil relative to bulk terrestrial carbon; this phenomenon has been previously explained as a subtle consequence of heavy-isotope enrichment during atmospheric escape, in part because of the lack of plausible alternative explanations [5]. Our results suggest that adsorption preferentially removes $^{12}$C from CO$_2$ vapor and thus could also generate subtle (per mil to percent level) $^{13}$C enrichments in the Martian atmosphere. The magnitude of $^{13}$C enrichments that are possible by this mechanism depend upon the mode of adsorption (i.e., Rayleigh distillation vs. batch removal) and the size of the substrate reservoir. Our results suggest that adsorption could generate $^{13}$C enrichments of tens of per mil if the current Martian atmosphere is residual to almost quantitative distillative adsorption (down to 1 part in $10^3$). This is an extreme and perhaps implausible requirement, although we note that it is consistent with the proportion of CO$_2$ ‘missing’ from the known surface inventory of Martian volatiles, (assuming Mars formed with a volatile budget comparable to that of the Earth; e.g., [8]), and that it is within the limits (albeit, poorly known) of the capacity of the Martian regolith for CO$_2$ adsorption [3]. We conclude that this explanation of $^{13}$C enrichment in the Martian atmosphere (and the apparent need for a ‘sink’ of CO$_2$ on Mars) is contrary to common models of these phenomena but cannot be strictly disproved given current information. We also note that fractionations by adsorption and by atmospheric escape are not mutually exclusive and therefore both may have contributed to $^{13}$C enrichment of Martian atmospheric carbon.

Studies of atmospheric dynamics: The evolution of the Martian atmosphere over climatic time-scales may be dominated by uptake and release of CO$_2$ from an adsorbed reservoir in response to changes in the radiative balance of the Martian surface [3]. In addition, adsorption may play a role in shorter time scale (i.e., seasonal or daily) variations in the pressure of the Martian atmosphere [9]. Our experiments suggest that such processes likely effect the carbon isotope composition of the residual atmosphere and that these effects are isotopically distinct from that of the seasonal cycle of growth and sublimation of CO$_2$ ice (which is expected to be isotopically non-fractionating; Figure 1). Direct measurements of the variation with time of $^{13}$C/$^{12}$C in the Martian atmosphere and of the composition of volatiles released from the soil were to be attempted as part of the failed Mars Polar Lander; our results suggest that measurements of this type have the potential to identify the sizes of adsorbed reservoirs and the means by which they interact with the atmosphere, and thus are an appropriate goal for future exploration of Mars. Such studies will require per mil level precision for measurements of the $^{13}$C/$^{12}$C ratio and thus would require significant advances over previous in situ measurements.