Investigation of Carbon Dioxide mystery in the atmosphere of Mars using oxygen triple isotope anomaly.

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Abstract and Background

The red planet - Mars, today is a frigid cold desert(frozen CO_2 and H_2O) with thin air (~6mbar). However, the presence of deep channels and weathered rocks documented by various satellite and rovers on Mars serve as evidence that Mars had once experienced liquid water and dense atmosphere. Phoenix data has shown that the heat generated due to a strong UV radiation can trigger huge dust storms and sublimation of CO_2 and H_2O. The interaction of UV light (λ <180nm) with gaseous CO_2 leads to its dissociation into carbon monoxide(CO) and oxygen. Therefore it is expected to see a significant amount of CO in the atmosphere, however the latest Mars space probe MAVEN (Mars Atmosphere and Volatile EvolutioN mission) has not detected even a trace of CO. Therefore the question stands of where does carbon monoxide go?

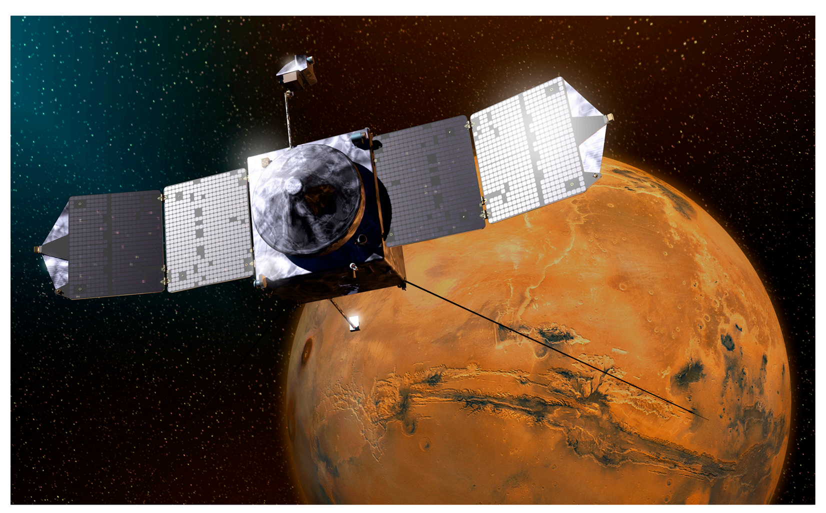
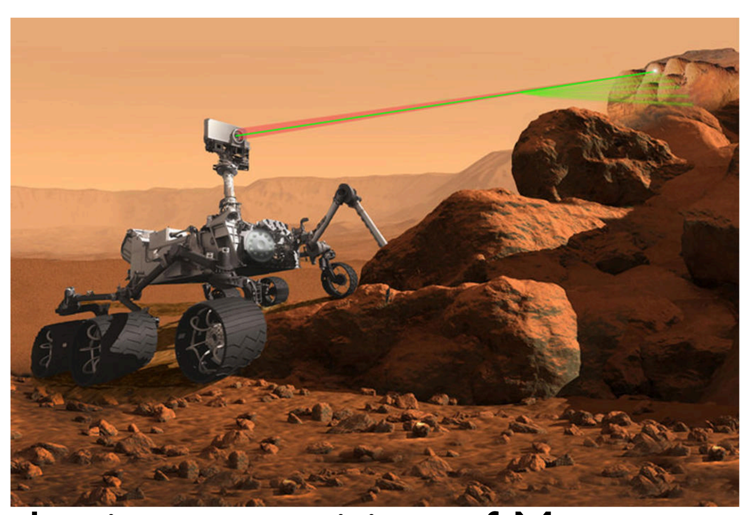



Figure 1a: MAVEN to measure atmospheric composition of Mars
Figure 1b: Curiosity to investigate Martian climate and geology

Method

CO and O_2 of known isotopic composition was used to investigate the formation of CO_2 in the presence of UV light. Two sets of experiments were designed to simulate Mars' present day atmosphere. Water was added in Set 1 to produce OH radicals to simulate summer time gas phase photochemistry:

Set 1: CO, O_2 and H_2O Set 2: CO and O_2

A source of UV light is mercury discharge lamp(λ_1=184nm, λ_2=253nm)

λ=184nm dissociate oxygen and to produce ozone:

$$O_2 \rightarrow O^{\bullet} + O^{\bullet} \quad (1) \qquad O_2 + O \rightarrow O_3^{*} + M \rightarrow O_3 \quad (2)$$

λ=253nm dissociates ozone molecules to $O(^1D)$ which may react with CO to form CO_2.

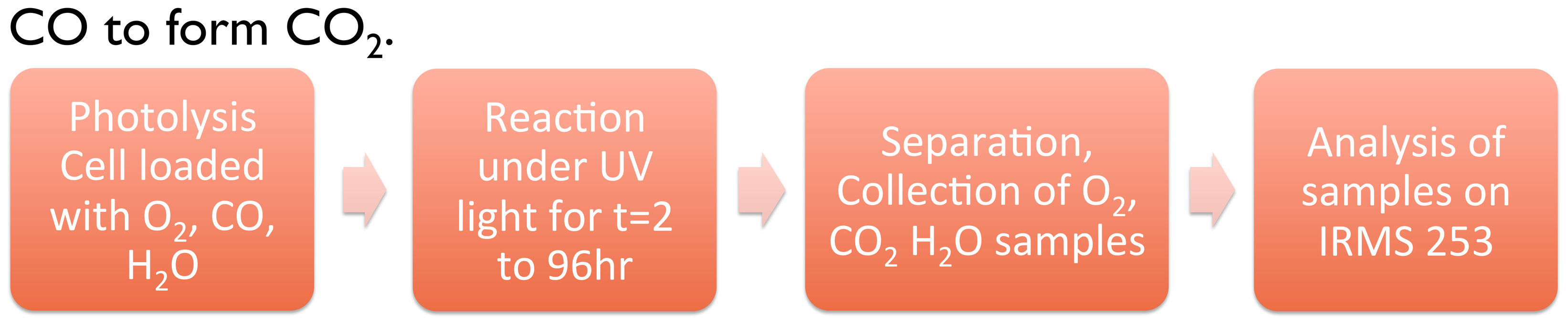


Figure 2: Schematic of the general workflow of the experiment

Many process such diffusion, evaporation follow mass dependent fractionation. The commonly used delta(δ) value denote the isotope ratios $^{17}O/^{16}O(^{17}R)$ and $^{18}O/^{16}O(^{18}R)$.

$$\delta^{17}O \text{ permil} = (^{17}R_{sample}/(^{16}R_{standard}-1))*1000$$

$$\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$$

Experimental Set Up

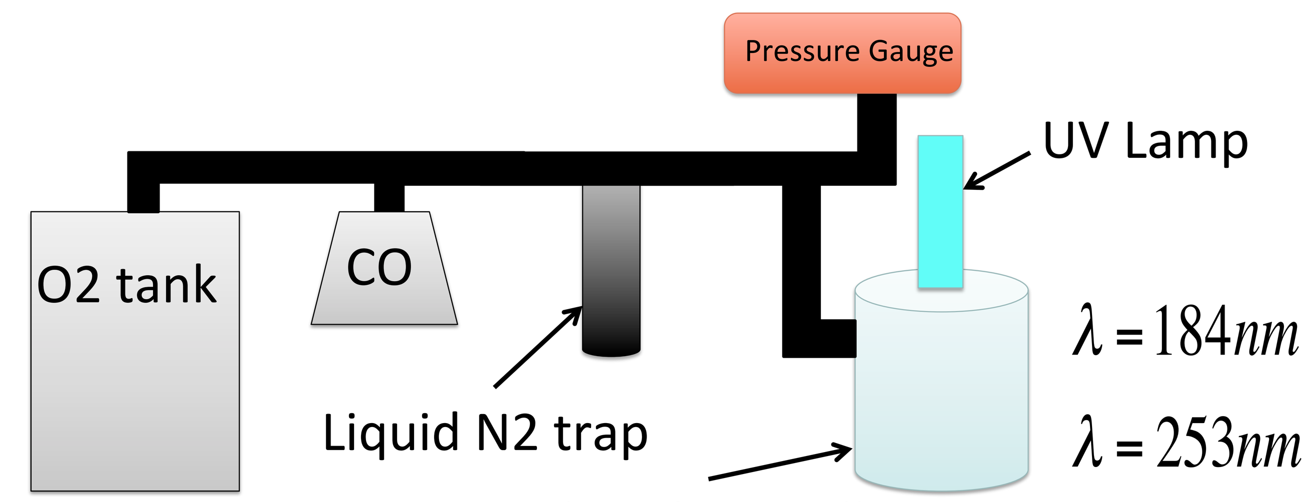
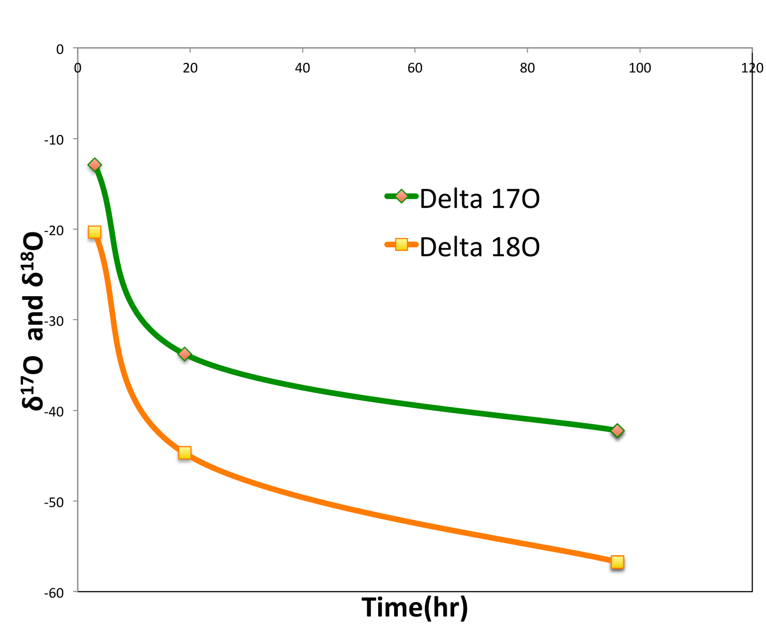


Figure 2: Visual graphic of the experimental set up

Results

The reaction of CO with O_2 in the presence of H_2O (Set 1 experiments) indicated depletion in the oxygen isotopes with time in product CO_2 and O_2(Fig. 4a). In Set 2 CO_2 got lighter, no significant change in O_2. A comparison between Set 1 and Set 2 indicated that O_2 exchange isotopically with H_2O through hydroxyl radicals (eq. 4-8). The trend suggests presence of enriched intermediate species(O_2H and H_2O_2). In the presence of UV light peroxide dissociate quickly and therefore the tiny amount present at steady state cannot be analyzed.



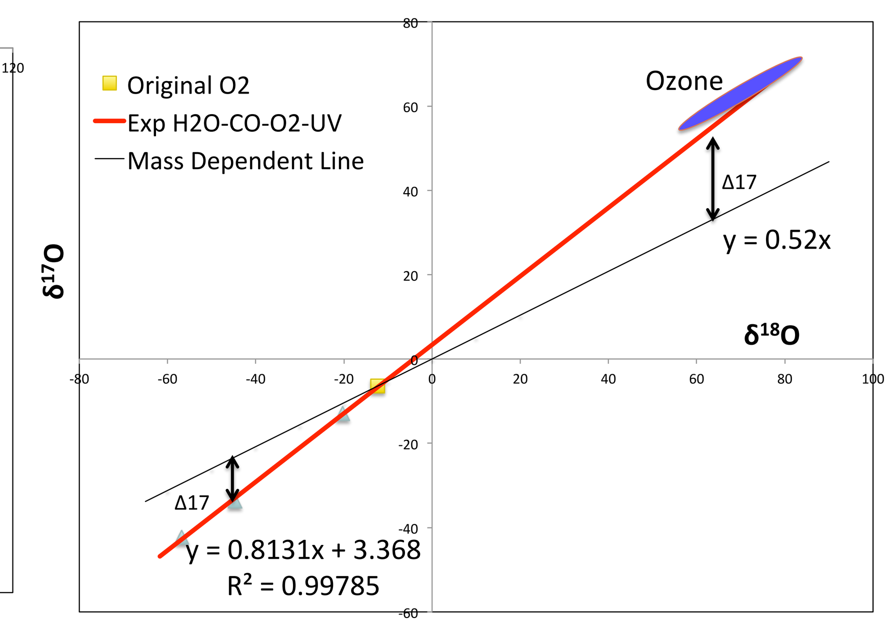


Figure 4a: Graph of $\delta^{17}O$ and $\delta^{18}O$ change with time
Figure 4b: Graph of O_2 fractionation during H_2O-CO-O_2-UV Exp.

Currently we know that the $CO_2 \rightarrow CO + O$ (3) reaction occurs on Mars when UV light of wavelength less than 180 nm hits abundant CO_2 particles in the atmosphere however as there is no build up of CO detected, it has to quickly transform back into CO_2.

Mechanism 1

$$H_2O + Q^1D \rightarrow Q^{\bullet}H + OH \quad (4)$$

$$Q^{\bullet}H + O_2 \rightarrow OQH + O \quad (5)$$

$$OQH + OOH \rightarrow H_2O_2 + OQ \quad (6)$$

There are two ways CO can then proceed to CO_2

$$CO + QH \rightarrow COQ + H^{\bullet} \quad (7) \quad CO + OQH \rightarrow CO_2 + QH^{\bullet} \quad (8)$$

Mechanism 2:

$$OOQ \rightarrow Q(^1D) + O_2$$

$$OOQ \rightarrow OQ + O(^1D) \quad (9) \qquad O(^3P) + CO \rightarrow CO_2 \quad (10)$$

$$O(^1D) + CO \rightarrow CO_2$$

Discussion

Most of the minerals in meteorites from Mars showed oxygen isotope anomaly in $\Delta^{17}O_{carbonates}$ = 0.6–0.9‰ and $\Delta^{17}O_{silicates}$= 0.2–0.4‰ (Farquhar, Thiemens 2000). Here I have shown that CO_2 exchange isotopically with oxygen and hydroxyl radicals and this isotopic signature can be preserved in the carbonate product from anomalous CO_2 and H_2O. The oxygen isotope anomaly is derived from ozone. The ozone molecule is a natural trace with highest enrichment and large oxygen isotope anomaly (30-40‰) which depends on temperature and pressure (Thiemens, Heidenreich 1983). Large isotope anomalies has been observed in other oxygen carrying molecules in the atmosphere of earth such as CO_2, SO_4, NO_3 and H_2O_2 (Thiemens, Shaheen 2014). For Mechanism 2 the experiments have already been completed, however the data is still being worked on to fluorinate the samples of CO_2 to find the Delta17O values. Data collected so far is presented in the table below.

Experiment #	Time(hr)	Ratio of O_2 to CO_2	$\delta^{13}C$	$\delta^{18}O$
Initial	0	0	-43.00	51.00
1	2	19.38	-36.485	20.996
2	2	29.08	-34.542	19.066
3	2	63.33	-33.654	13.933

Table 1: Changes in the oxygen isotopic composition of CO2 with ratio of O_2 to CO_2

In my experiment ozone was formed due to presence of UV light and by looking what isotope numbers are of resulting species I can say that, if the original CO was reacting with $O(^1D)$ from ozone it should move up the line, however as shown in the table 1, δ18O isotope numbers in CO_2 are decreasing which predicts that CO_2 was formed by the reaction with $O(^3P)$ instead.

References

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