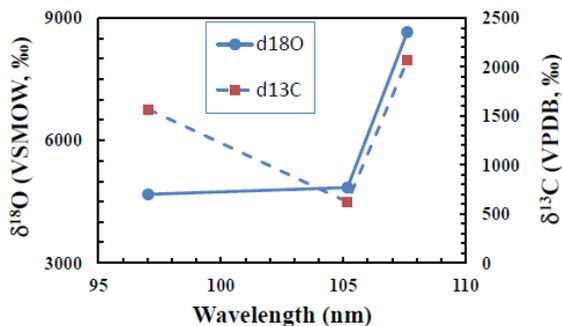




quot of sample) was first measured after cryogenically drying the sample from the photochemically product water using a Finnigan MAT 253 IRMS. In the next step, the product CO<sub>2</sub> was equilibrated in the presence of CuO at 900 °C to erase any mass dependent oxygen isotopic composition and the equilibrated CO<sub>2</sub> was remeasured for the same isotopologue ratios. From the initial and final isotopologue ratios,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and  $\delta^{17}\text{O}$  of photochemically produced CO<sub>2</sub> was determined.

**Results:** Figures 2 and 3 show the carbon and oxygen isotopic composition of the product CO<sub>2</sub>. The oxygen isotopic composition of CO<sub>2</sub> is very different and more enriched from that reported earlier [8] for photodissociation at the same wavelengths at higher temperature (200 K). Interestingly, the slope values in oxygen three isotope plot are also different, where the reported slope values for 105 and 107 nm was 1.4 and a value of 1.0 for 97 nm thus requiring an extraordinary mass independent temperature dependence in the photolysis.

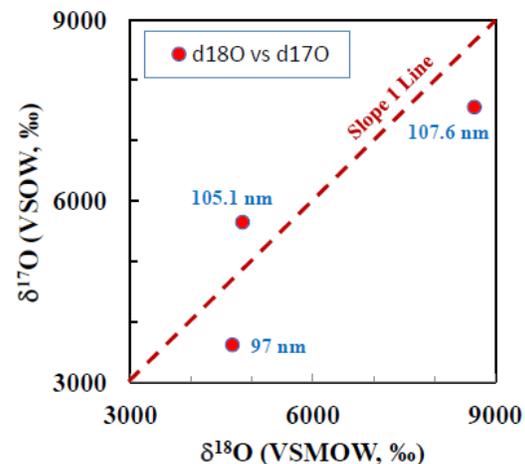


**Figure 2.** Wavelength dependent carbon and oxygen isotopic fractionation in product CO<sub>2</sub>. Along with oxygen isotopes, carbon isotopes are also significantly enriched.

**Discussion:** The line absorption by CO is subject to shielding primarily by absorption of the more abundant <sup>12</sup>C<sup>16</sup>O isotopologue resulting in an enrichment of <sup>13</sup>C, <sup>17</sup>O and <sup>18</sup>O in the dissociation product due to preferential absorption of rarer isotopologues [6, 10]. Isotopic fractionation based on self-shielding models depend on cross-section and column density and does not show a large variation with temperature as measured and compared with reported measurements. The new 80K data firmly establishes the hypothesis that the perturbation dominated state mixing (through overlapping wavefunctions) dynamics determines which isotopologues preferentially dissociate. With lowering of temperatures, the state mixing dynamics change dramatically in localized zones and hence, the measured fractionation.

**Connection to the Solar Nebula:** Through a chemical fractionation model of IS clouds Langer et al. [10] was able to classify carbon bearing species into

three families—CO, HCO<sup>+</sup>, and the “carbon isotope pool”—with distinct isotopic behaviors [11]. The carbon bearing molecules such as HCN, CN, C<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> etc are the members of this pool. The measured carbon isotopic composition from the molecules of giant planets and comets, which show <sup>13</sup>C enrichments compared to the terrestrial planets, belongs to this said pool. <sup>13</sup>C enriched C atoms generated from CO photodissociation may potentially generate the carbon containing molecules of this pool and thus enriched in <sup>13</sup>C. Photodissociation is an inevitable process in the solar nebula and that would generate isotopic enriched molecular pool and potentially can explain the observed (summarized in Figure 1) extreme variation measured in solar system bodies [12].



**Figure 3.** Three isotope plot of oxygen showing the isotopic composition in CO<sub>2</sub> at different wavelengths. The isotopic enrichments in heavy oxygen isotopes are larger by a factor of >2 compared to the compositions measured at higher temperature (200K) photodissociation at the same wavelengths [8].

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