Geophysical Research Abstracts
Vol. 15, EGU2013-14105, 2013
EGU General Assembly 2013

CO_2 photolysis produces mass independent fractionation and a $^{16}O^{13}C^{18}O$ clumped isotope anomaly

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Carbon dioxide is the main component of the atmospheres of Mars and Venus, and the early Earth. Photochemistry in these atmospheres is based on the UV photolysis of CO_2; fractionation in CO_2 photolysis impacts the isotopic composition of the photoproduct CO and O_2. For the first time, an accurate model of fractionation in CO_2 photolysis has been made, using the time-dependent methodology, yielding the temperature and isotopologue dependent CO_2 absorption cross sections: $^{16}O^{12}C^{16}O$ (626), 627, 628, 636, and the clumped species 638. The calculations reproduce experimental absorption cross sections at low resolution without scaling intensity. The main results are: a) The accurate description of the temperature dependence of the CO_2 UV absorption cross section has a large impact on catalytic HO_x radical concentrations in CO_2 atmospheres. b) CO_2 photolysis in the modern mesosphere has a ^{13}C fractionation exceeding 300 per mil. This, together with CO_2 + O(^1D) exchange, may generate a significant CO_2 clumped isotope anomaly. c) In a CO_2 atmosphere, CO_2 photolysis produces mass independent fractionation (MIF) in the O_x reservoir, as observed via the Martian meteorite ALH84001. This MIF, combined with a sink of oxygen to the surface of Mars or to space, can explain the variable Martian oxygen MIF implied by the 'Black Beauty' meteorite NWA 7034.