

## CO<sub>2</sub> photolysis produces mass independent fractionation and a <sup>16</sup>O<sup>13</sup>C<sup>18</sup>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<sub>2</sub>; fractionation in CO<sub>2</sub> photolysis impacts the isotopic composition of the photoproduct CO and O<sub>2</sub>. For the first time, an accurate model of fractionation in CO<sub>2</sub> photolysis has been made, using the time-dependent methodology, yielding the temperature and isotopologue dependent CO<sub>2</sub> absorption cross sections: <sup>16</sup>O<sup>12</sup>C<sup>16</sup>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<sub>2</sub> UV absorption cross section has a large impact on catalytic HOx radical concentrations in CO<sub>2</sub> atmospheres. b) CO<sub>2</sub> photolysis in the modern mesosphere has a <sup>13</sup>C fractionation exceeding 300 per mil. This, together with CO<sub>2</sub> + O(<sup>1</sup>D) exchange, may generate a significant CO<sub>2</sub> clumped isotope anomaly. c) In a CO<sub>2</sub> atmosphere, CO<sub>2</sub> photolysis produces mass independent fractionation (MIF) in the Ox reservoir. This, combined with a sink of oxygen to the surface of Mars and/or space, may impact the oxygen isotope distributions found in the Martian meteorite ALH84001 and the 'Black Beauty' meteorite NWA 7034.

## Composition, formation, and role of the Si-rich surface layer during olivine dissolution

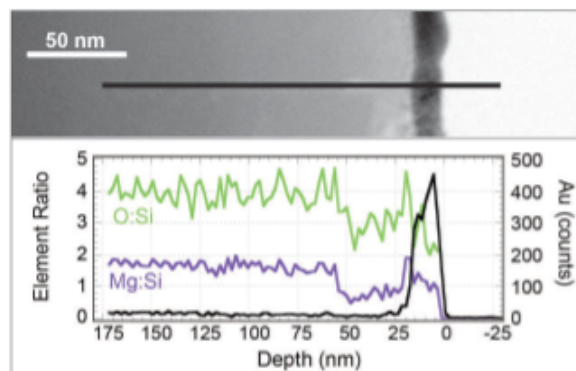
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Olivine ((Mg,Fe)<sub>2</sub>SiO<sub>4</sub>) dissolution in the presence of water and supercritical CO<sub>2</sub> results in the formation of a Mg-depleted, Si-rich surface layer. The Si-rich layer may play a role in limiting olivine carbonation kinetics, but little is known about its mechanism of formation and chemical composition. This study probes the Si-rich layer by reacting olivine with a <sup>29</sup>Si-spiked CO<sub>2</sub>-containing aqueous solution at 60°C and 100 bar, followed by analysis of the mineral products using ion microprobe depth profiling and TEM imaging of cross-sections. After 19 days of unmixed reaction, TEM imaging coupled with energy dispersive spectroscopy (EDS) revealed an amorphous Si-rich layer, 30-40 nm thick, with an average composition of MgSiO<sub>3</sub> [Figure 1]. The location of the Si-rich layer is visible in the image as a vertical stripe slightly lighter in color and in the plot as sharp drops in both the Mg:Si and O:Si ratios. Depth-profiling with the ion microprobe indicates that <sup>29</sup>Si penetrates >100 nm into the mineral surface. Combined TEM and SIMS results suggest that, under these conditions, the Si-rich layer forms due to a dissolution/precipitation mechanism.



**Figure 1:** Scanning transmission electron microscopy image and results from an EDS line scan (location of scan marked by black line on image). Gold (black line in plot) was used to protect the mineral surface during cross section preparation.