Experimental study of carboxylic acid oxidation under Martian conditions: Chemical and isotope characterization

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A series of experiments were performed to better understand the controlling factors of reaction pathways and carbon isotope fractionation during organic matter oxidation processes under shallow subsurface conditions on Mars. Acetic acid, one of the abundant soluble organic compounds observed in carbonaceous chondrites, was the starting material. Hydrogen peroxide (H_2O_2) or magnesium perchlorate ($Mg(ClO_4)_2$) was used in each experiment as the oxidizing agent, with Ni-magnetite being the mineral catalyst.

Time-series measurement of CO_2 generated from experiments has shown that its abundance was always higher with the presence of Ni-magnetite. The carbon isotope fractionation between generated CO_2 and acetic acid (-21.2‰) was 14.3‰ in H_2O_2 experiments with Ni-magnetite after 120 hours, and higher than the theoretical isotope equilibrium prediction value (9.5‰). In experiments without Ni-magnetite, however, CO_2 was depleted in ^{13}C relative to acetic acid.

Oxidation of organic matter is a multistep, kinetic-controlled reaction that proceeds through various reaction pathways and formation of organic intermediates. The selectivity of intermediate, corresponding overall reaction kinetics, and carbon isotope partitioning can be controlled by a number of variables, including oxidizing agent. In this study, the higher $\delta^{13}C$ values of CO_2 in H_2O_2 experiments with Ni-magnetite may be attributed to the formation of hydroxyl radical ($^{\cdot}OH$) via Fenton reaction. With $^{\cdot}OH$ as the ultimate oxidizing agent, the carboxyl (–COOH) functional group in acetic acid would be the precursor of CO_2 generated in the experiments. Carbon isotope measurement of intramolecular distribution of acetic acid has confirmed that the $\delta^{13}C$ values of carboxyl and methyl (–CH_3) groups were -13.4‰ and -29.0‰, respectively. Thus differences in $\delta^{13}C$ of evolved CO_2 could be derived from selective oxidation of the different carbon atoms within the organic molecule.