

**CARBON ISOTOPES OF CO₂ FROM MINERAL CATALYZED ORGANIC OXIDATION
PROCESSES UNDER MARTIAN CONDITIONS**

A Thesis Presented to
the Faculty of the Earth and Atmospheric Sciences Department
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Nikole Constance Haney
May 2016

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ABSTRACT

Organic molecules have not been positively identified by spacecraft missions on Mars. The extent of indigenous or meteoric contributions to organic molecules observed in Martian meteorites is also not well understood. The reason has been mostly attributed to the potential presence of oxidizing agents in Martian soil, degradation, and photocatalytic reactions by UV radiation. Given the presence of strong UV radiation, hydrogen peroxide, perchlorates, and chlorates create an extremely oxidizing environment. It is possible that oxidation reactions have diminished the concentrations of organic molecules, if present, on Martian surface. Oxidation of organic matter can proceed through a series of pathways under different conditions, such as temperature, mineral catalysts, and residence time. Carbon isotope measurement has long been used as an effective tool to identify reaction mechanisms. However, the effects of variables on carbon isotope fractionations between products and reactants during kinetic-controlled oxidation reactions are poorly understood. Previous laboratory experiments on the $\delta^{13}\text{C}$ values of CO_2 generated by hydrogen peroxide reacting with short chain carboxylic acids have shown that organic intermediates and reaction pathways may be different with different mineral catalysts, which control the isotope values of CO_2 . To get a better understanding of the effects of oxidizing agents and mineral catalysts on reaction pathways of organic oxidation reactions and corresponding carbon isotope values of CO_2 , a series of experiments were performed under Martian conditions. The simple carboxylic acid, acetic acid, was used as an organic reactant, with hydrogen

peroxide, which is believed to be present on Martian surface as an oxidizer. The mineral catalysts in each experiment includes magnetite (NiFe_2O_4), hematite (Fe_2O_3), olivine ($[\text{Mg}^{+2}, \text{Fe}^{+2}]_2\text{SiO}_4$), akaganéite ($\text{Fe}^{3+}\text{O}[\text{OH},\text{Cl}]$), and goethite ($\text{FeO}(\text{OH})$). Experiments were conducted at 30 °C with carbon isotope measurements taken at reaction times of 1 hour, 4 hours, 24 hours, 72 hours, and 144 hours. The carbon isotope values obtained from the experiments give insights into reaction mechanisms of organic oxidation processes, provide fundamental data which is critical for understanding the results returned by the Mars Science Laboratory rover and future missions, and help elucidate the origin and evolution of organics, if present, on Mars.

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1. Introduction

Spacecraft missions to Mars have yet to yield positive identification of organic molecules (Benner et al., 2000). The extent of indigenous or meteoric contributions to organic molecules observed in Martian meteorites is also not well understood (Benner et al., 2000). Degradation and photocatalytic reactions by strong UV radiation have been attributed to the potential presence of oxidizing agents in the Martian soil (ten Kate, 2010). As a result of strong UV radiation, hydrogen peroxide, perchlorates, and chlorates, an extremely oxidizing environment exists on Mars (ten Kate, 2010). The UV radiation can cause the cleaving of H₂O into H and [•]OH radicals, which in turn react with organics (Benner, 2000). It is possible that oxidation reactions have diminished the concentrations of organic molecules, if present, on the Martian surface. It is believed that CO₂ gas is then generated from the reaction of hydrogen peroxide with organics in the soil (Kwan et al., 2002).

Carbon isotope measurement has long been used as an effective tool to identify reaction mechanisms. However, the effects of variables on carbon isotope fractionations between products and reactants during kinetic-controlled oxidation reactions are poorly understood. Furthermore, oxidation of organic matter can proceed through a series of pathways under different conditions, such as temperature, mineral catalysts, and reaction time (Fu et al., 2012). Previous laboratory experiments on the δ¹³C values of CO₂ generated by hydrogen peroxide reacting with short chain carboxylic acids have

shown that organic intermediates and reaction pathways may be different with different mineral catalysts, which control the isotope values of CO₂ (Fu et al., 2012).

To get a better understanding of the effects of oxidizing agents and mineral catalysts on reaction pathways of organic oxidation reactions and corresponding carbon isotope values of CO₂, experiments have been conducted on the effects of mineral catalysts on oxidation of organic molecules under Martian conditions (Fu et al., 2012; Mujib et al., 2015). Both studies utilized the Finnigan GasBench II in combination with the Thermo MAT 253 Isotope Ratio Mass Spectrometer (IRMS) for carbon isotope measurement of CO₂ generated from oxidation experiments of carboxylic acids. Experimental conditions consisted of a constant temperature of 30 °C and varying reaction times.

2. Experimental & Procedure

Experiments that are designed to simulate organic oxidation processes under Martian conditions were performed using three components: an organic material, a mineral catalyst, and an oxidizing agent. A carboxylic acid, acetic acid, was used as an organic reactant. Previous studies have shown that Martian soil contains hematite (Fe₂O₃) (Benner, 2000), Ni-magnetite (NiFe₂O₄) (Huguenin et al., 1979), olivine ((Mg⁺², Fe⁺²)₂SiO₄) (Huguenin et al., 1979), akaganéite (Fe³⁺O(OH,Cl)) (Carter, 2014), and goethite (FeO(OH)) (Benner, 2000). These are the mineral catalysts used in the experiments. The oxidizing agent for the reactions is hydrogen peroxide (H₂O₂, 50 wt%). Experimental conditions are summarized in Table 1.

Table 1

Experimental Conditions for the oxidation of acetic acid with hydrogen peroxide in the presence of a mineral catalyst.

<i>Experimental Conditions</i>	
Temperature	30°C
Time(s)	1, 4, 24, 72, and 144 Hours
Reactant	Acetic Acid (CH ₃ COOH)
Oxidizing Agent	Hydrogen Peroxide (H ₂ O ₂)
Mineral Catalyst(s)	Ni-magnetite, Hematite, Goethite, Akaganéite, and Olivine

Two types of experiments were conducted. The first experiment, called the overnight experiments, involved reacting hydrogen peroxide with a mineral catalyst overnight before the addition of acetic acid. The next experiment, referred to as the immediate experiments, was the immediate addition of hydrogen peroxide and acetic acid to the mineral catalyst. In both the overnight and immediate experiments, 0.1 g of each of the mineral catalysts was added to 12 mL septum capped vials as pictured in Figure 1.



FIGURE 1. Septum capped vials (12 mL) with a mineral catalyst and hydrogen peroxide.

From left to right: Ni-magnetite, goethite, hematite, akaganéite, and olivine.

In each septum-capped vial, 0.1 mL of the oxidizing agent, hydrogen peroxide (H₂O₂, 50%), was injected. After flushing the vials with He, the carboxylic acid (CH₃COOH, 1 ml) was injected into the septum capped vial following the overnight reaction of hydrogen peroxide with a mineral catalyst. In the immediate experiments, the carboxylic acid is added to the He flushed mineral catalyst immediately followed by the oxidizing agent. Experimental conditions include maintaining a reaction temperature of 30 °C.

2.1 Isotope Fractionation of CO₂ and Acetic Acid

Stable isotope reactions can reach equilibrium. The following equation represents equilibrium reaction:



Kinetic isotope reactions do not reach an equilibrium point and are characterized by fluctuations in value.

The isotope value for carbon is calculated as such:

$$R_x = \frac{X^{n_1}}{X^{n_2}} \quad (\text{Eq. 2})$$

$$\delta_x = \left(\frac{R_x - R_{std}}{R_{std}} \right) \times 1000 \quad (\text{Eq. 3})$$

Where X is an element, carbon for the purposes of these experiments, n₁ and n₂ are the stable isotopes of X, R is the isotope ratio, and R_{std} is a standard in (‰, read “per mil”) to which all measurements are compared.

The fractionation factor (α) is found by:

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (\text{Eq. 4})$$

Where R_A and R_B are isotope ratios, and is related to the δ_x values by:

$$\alpha_{A-B} = \frac{1000 + \delta_A}{1000 + \delta_B} \quad (\text{Eq. 5})$$

The fractionation (ϵ_C) between CO_2 and acetic acid was determined by the following equation:

$$\epsilon_C = \delta_{\text{CO}_2} - \delta_{\text{acetic acid}} \quad (\text{Eq. 6})$$

In which A is the measured carbon isotope value (‰) and B is the initial value of acetic acid, which is approximately -21.2 ‰ (Socki et al., 2011).

In the thermal decomposition of stearic acid with clay minerals, the formation of the hydrocarbons depended on the mineral structure (Heller-Kallai et al., 1984). This suggests that the minerals present could determine the products produced by the oxidation of an acid.

2.2 Instrumentation

The Thermo MAT 253 Isotope Ratio Mass Spectrometer (IRMS) was used in conjunction with the Finnigan GasBench II to measure the $\delta^{13}\text{C}$ values of generated CO_2 from the oxidation reaction, as pictured in Figure 2. A series of carbon isotope measurements of CO_2 were performed after the following time intervals: 1 h, 4 h, 24 h, 72 h, and 144 h. The IRMS has an average uncertainty in $\delta^{13}\text{C}$ of ± 0.5 ‰. The measurements yielded carbon isotope values of CO_2 for the oxidizing agent and organic material, which were

compared to the carbon isotope values of the same experiments but in the presence of a mineral catalyst. Carbon dioxide reference gas measurements were conducted before every experiment to ensure accurate isotope values.

Each reported value represents three measurements of three identical samples of each experimental trial. This means that each value is an overall average of nine injections to minimize error.



FIGURE 2. The instrument setup at NASA Johnson Space Center. The instruments used were the following: 1) Thermo Trace GC (gas chromatograph) Ultra, 2) Thermo MAT 253 IRMS (isotope ratio mass spectrometer), and 3) Finnigan GasBench II.

2.3 Reference Samples

The absolute value of the reference gas was determined by referencing the CO₂ gas used in the experiments with a known CO₂ reference gas. A measurement of the reference gas ESCG-1441C with a confirmed $\delta^{13}\text{C}$ value of -3.61‰ (PDB) was conducted. The CO₂ reference gas was then compared to ESCG-1441C and was found to be at a $\delta^{13}\text{C}$ value of -39.925‰ (PDB). This was the reference value used in all of the experiments. The isotope value of acetic acid was determined to be -21.2‰ from the measurements of -29‰ for methyl ($\delta^{13}\text{C}_{\text{methyl}}$) and -13.4‰ for carboxyl ($\delta^{13}\text{C}_{\text{carboxyl}}$) (Yamada et al., 2002; Fu et al., 2012).

2.4 Akaganéite Synthesis

Akaganéite was synthesized as outlined (Stahl et al., 2003) with modifications. The synthesized mineral catalyst was produced from a 0.2 M FeCl₃ solution. The solution was baked at 90 ° C for 5 h. The solution was then centrifuged at 4000 rpm for 5 m or until the product had solidified at the bottom of the 50 mL Falcon tube. The resulting solid was then washed 3 times with approximately 35 mL per wash of DI water. The washed solid was then dried at 70 ° C for 15 h. A 1 L solution of 0.2M FeCl₃ produced 1.3 g of akaganéite.

2.5 Olivine

The olivine samples used in this experiment were from San Carlos, Arizona, USA. The approximately 1 mm fresh grains were ground to a fine powder using a marble mortar and pestle.

3. Results

3.1 Relative CO₂ Abundance

Semi-quantitative data gained from the mass 44 peak of CO₂ shows that the CO₂ abundance is higher in experiments containing a mineral catalyst than without with the experiments containing akaganéite and olivine as exceptions. Different experiments with catalysts produced more CO₂ gas than others. There was not a pattern as to how much CO₂ gas was produced as a function of time before 48 hours. The production of CO₂ slowed after 48 hours for all experiments.

3.2 Acetic Acid and H₂O₂ Reaction without a Mineral

The reaction of acetic acid and hydrogen peroxide without a mineral catalyst produced progressively depleted isotope ratio values and leveled out after 48 hours as seen in Figure 3. The measured CO₂ at 1 h was -32.8 ‰ and was measured to be -65.4 ‰ at 144 h (see Table 2). The isotope ratio values decreases rapidly within the first 24 h of

reaction and slowly increased after 24 h. The fractionation values, as seen in Table 3, decrease within the first 24 h and increase from 24 h until 144 h.

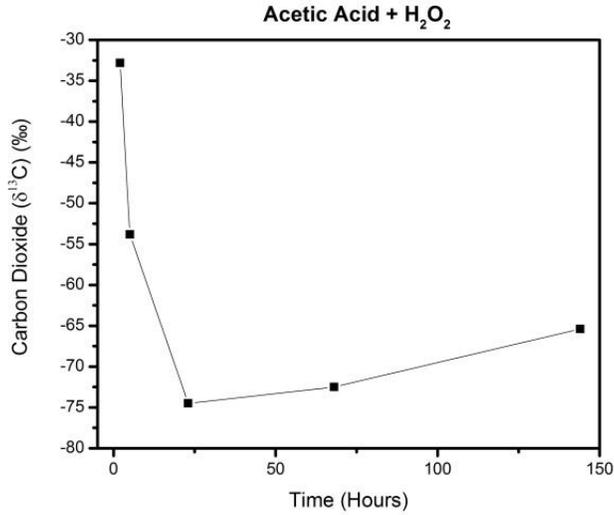


FIGURE 3. Carbon isotope values of carbon dioxide generated from acetic acid and hydrogen peroxide over time.

Table 2

Carbon isotope values ($\delta^{13}\text{C}$) for overnight experiments (Experiment 1) and immediate addition of acetic acid and hydrogen peroxide (Experiment 2). All values are given in (‰) and time (T) in hours.

<i>T</i>	<i>Ni-magnetite</i>		<i>Goethite</i>		<i>Hematite</i>		<i>Akaganéite</i>		<i>Olivine</i>		<i>No Mineral</i>	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2
1	-8.2	-42.4	-19.6	-64.5	-19.0	-41.3	-26.8	-42.0	-45.5	-52.7	-32.8	-32.8
4	-5.2	-51.5	-47.6	-75.3	-55.1	-66.0	-25.8	-42.7	-68.1	-73.3	-53.8	-53.8
24	-1.9	-46.1	-73.8	-73.2	-77.6	-75.1	-31.8	-40.8	-63.2	-65.8	-74.5	-74.5
72	-13.7	-46.2	-71.6	-76.2	-77.7	-74.1	-30.4	-47.4	-56.5	-53.1	-72.5	-72.5
144	-14.3	-44.9	-68.0	-73.3	-73.0	-73.0	-35.7	-50.1	-53.6	-50.4	-65.4	-65.4

Table 3

Carbon isotope fractionations between CO₂ and acetic acid for overnight experiments (Exp. 1) and immediate addition of acetic acid and hydrogen peroxide (Exp. 2). All values are given in (‰) and time (T) is in hours.

<i>T</i>	<i>Ni-magnetite</i>		<i>Goethite</i>		<i>Hematite</i>		<i>Akaganéite</i>		<i>Olivine</i>		<i>No Mineral</i>	
	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2	Exp. 1	Exp. 2
1	13.0	-21.2	1.6	-43.3	2.2	-20.1	-5.6	-20.8	-24.3	-31.5	-11.6	-11.6
4	16.0	-30.3	-26.4	-54.1	-33.9	-44.8	-4.6	-21.5	-46.9	-52.1	-32.6	-32.6
24	19.3	-24.9	-52.6	-52.0	-56.4	-53.9	-10.6	-19.6	-42.0	-44.6	-53.3	-53.3
72	7.5	-25.0	-50.4	-55.0	-56.5	-52.9	-9.2	-26.2	-35.3	-31.9	-51.3	-51.3
144	6.9	-23.7	-46.8	-52.1	-51.8	-51.8	-14.5	-28.9	-32.4	-29.2	-44.2	-44.2

3.3 Overnight Reactions

3.3.1 $\delta^{13}\text{C}$ for the Overnight Experiments

Most experiments, in which hydrogen peroxide and a mineral catalyst were allowed to react overnight prior to the addition of acetic acid the next day, followed the same trend of depletion within the first 24 h as the standard hydrogen peroxide and acetic acid results. The exceptions were Akaganéite and Ni-magnetite. All experiments showed a decrease in CO₂ production as time increased demonstrating a kinetically controlled reaction.

Reactions with Ni-magnetite yielded a value of -8.2 ‰ at 1 h, became more enriched, and then became more depleted at a value of -14.3 ‰ after 144 h, as shown in Figure 4(A). After 72 h, the isotope ratio seems to stabilize. The seemingly stabilized isotope values run parallel and are close in value to the theoretical isotope equilibrium between

carbon dioxide and acetic acid, which is -9.5 ‰ (Galimov, 1975). Reactions with Goethite produced a starting value at -19.6 ‰ and rapidly decreased to -68.0 ‰ (Figure 4(B)). The results follow the predicted trend displayed by the acetic acid and hydrogen peroxide reaction as seen in Figure 3. The experiments with Hematite as the catalyst had a 1 h value of -19.0 ‰ and decreased to -73.1 ‰ after 144 h. The isotope value trend as seen in Figure 4(C) is almost identical to that of goethite in shape and value. The results for hematite also follow the trend as predicted by the acetic acid and hydrogen peroxide experiment. Akaganéite reactions with hydrogen peroxide then acetic acid yielded a beginning value of -26.8 ‰ and ended at -35.7 ‰ at a measurement time of 144 h (Figure 4(D)). The experiments involving Olivine produced a starting isotope ratio of -45.5 ‰ and became more depleted at -53.6 ‰ at 144 h (Figure 4(E)). All values for this experiment can be seen in Table 2.

3.3.2 Fractionations for the Overnight Experiments

The fractionations for the measured CO₂ from the reaction of hydrogen peroxide and acetic acid and the initial value of acetic acid were compared to the reactions containing a mineral catalyst. The theoretical equilibrium of acetic acid and carbon dioxide valued at -9.5 ‰ is included for comparison (Galimov, 1975).

The experiment without a mineral catalyst preserved its downward trend for the calculated fractionation values. The reaction with Ni-magnetite is unique in that it is the only reaction that produced values close to the theoretical equilibrium. It parallels the

equilibrium constant after 72 h but remains slightly depleted in comparison. Goethite produced fractionation values almost identical to the reaction without a mineral catalyst. Its initial value at 1 h was more enriched than the acetic acid and hydrogen peroxide reaction. Hematite follows much the same trend for fractionation as Goethite. Akaganéite produced a similar but shifted fractionation trend. Olivine produced a fractionation curve somewhat similar to the acetic acid and hydrogen peroxide fractionation trend. The fractionations for the overnight experiments can be found in Figure 5 and the numerical values in Table 3.

3.4 Immediate Reactions

3.4.1 $\delta^{13}\text{C}$ for the Immediate Experiments

The experiments in which acetic acid was added to the mineral catalyst prior to the oxidizing agent generated more isotopically lighter $\delta^{13}\text{C}$ values than the overnight experiments. The difference in values and overall trends indicates that the length of oxidation time has an effect on the isotope ratios of generated CO_2 .

Ni-magnetite reactions with hydrogen peroxide then acetic acid yielded a beginning value of -42.4 ‰ and ended at -44.9 ‰ at a measurement time of 144 h (Figure 6(A)). After 4 h of reaction, the sample became more depleted then somewhat stabilized. The trend for Ni-magnetite is opposite from its overnight counterpart; it became depleted then enriched before stabilizing. The experiments with goethite as the catalyst had a 1 h value of -64.5 ‰ and decreased to -73.3 ‰ after 144 h (Figure 6(B)).

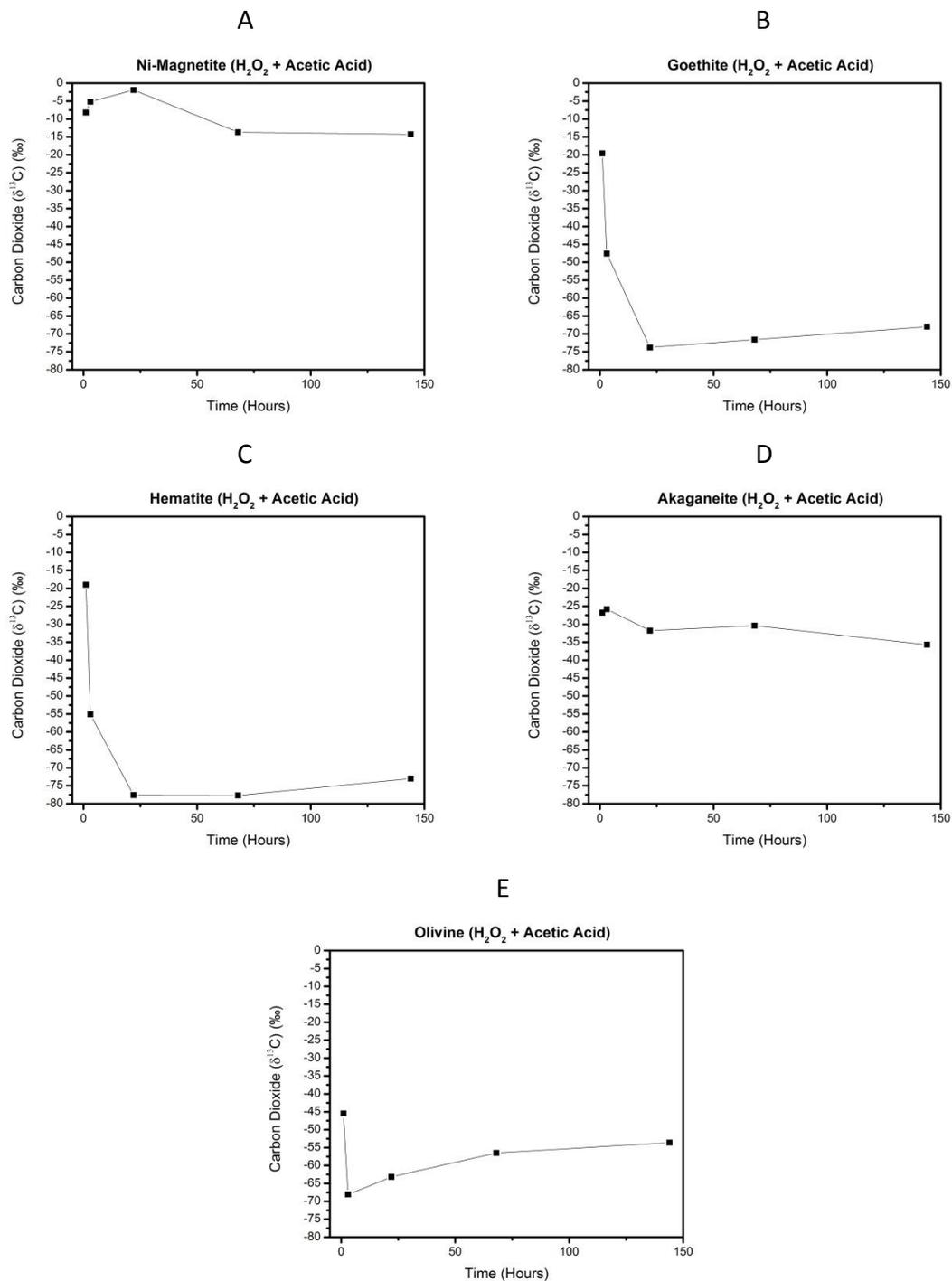


FIGURE 4. Carbon isotope values of carbon dioxide generated from a mineral catalyst A) Ni-magnetite ($NiFe_2O_4$), B) goethite ($FeO(OH)$), C) hematite (Fe_2O_3), D) akaganéite ($Fe^{3+}O(OH,Cl)$), and E) olivine ($(Mg^{+2}, Fe^{+2})_2SiO_4$) reacted overnight with hydrogen peroxide and then reacted with acetic acid.

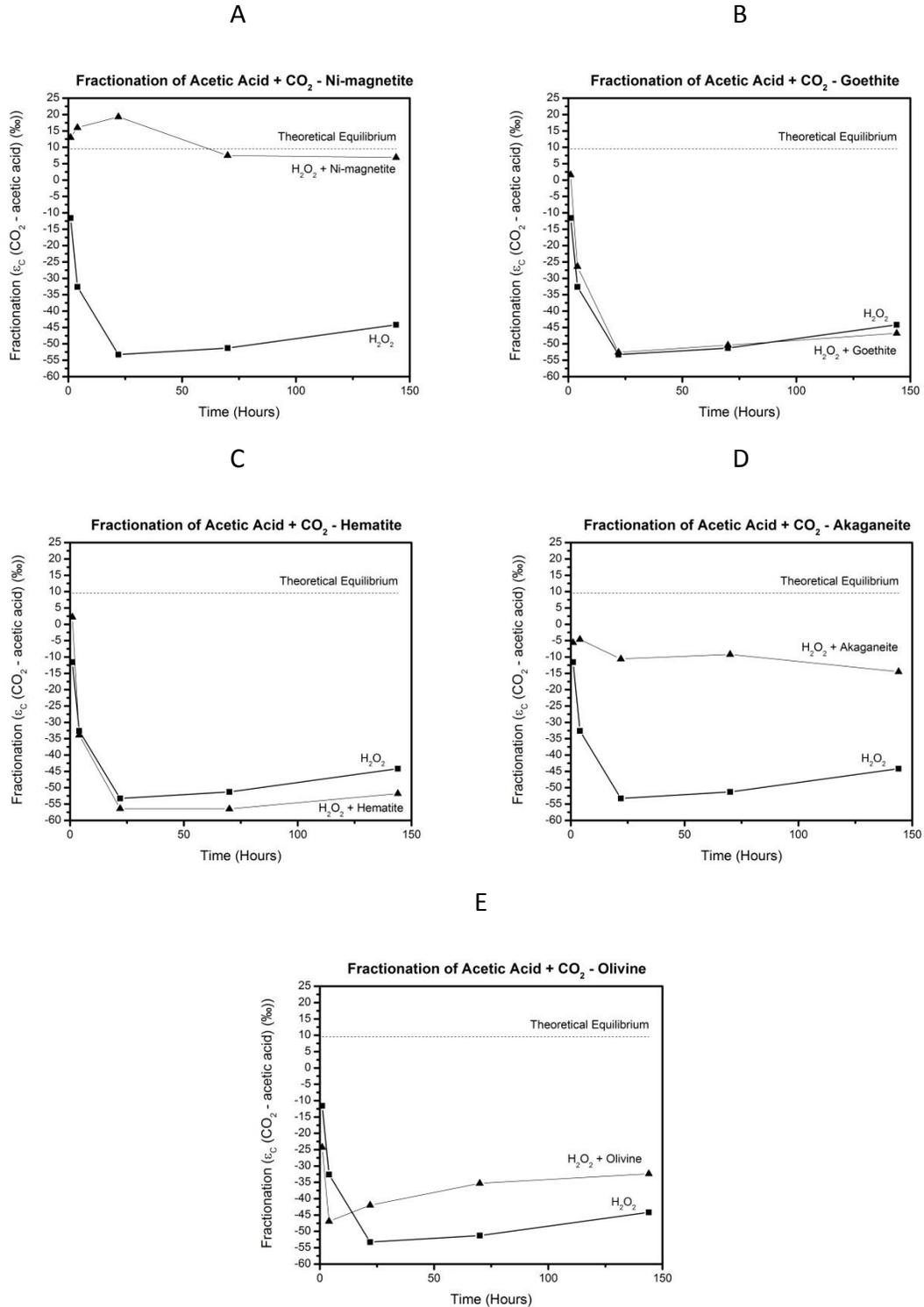


FIGURE 5. Fractionation between acetic acid and measured CO₂ with and without mineral catalysts for the overnight reactions compared to the theoretical equilibrium.

The experiments involving hematite produced a starting isotope ratio of -41.3 ‰ and became more depleted at -73.0 ‰ at 144 h (Figure 6(C)). Reactions with akaganéite yielded a value of -42.0 ‰ at the 1 h then became more depleted with a value of 50.1 ‰ after 144 h as seen in Figure 6(D). The starting isotope ratio of olivine was -52.7 ‰ which became more isotopically light then became increasingly enriched again to a value of -50.4 ‰ at 144 h as seen in Figure 6(E). Comparing the results of both overnight and immediate experiment types for olivine shows a similar trend as seen in Figure 4(E) and 6(E). All numerical data can be found in Table 2.

Overall, the results deviated from the predicted trend in Figure 3 with hematite as an exception. Mostly, the samples did not become isotopically lighter as quickly and show a smaller magnitude of change compared to the predicted trend. In both sets of experiments, the oxidation state of the metal ion (Fe), either Fe²⁺ or Fe³⁺, has a noticeable effect on the $\delta^{13}\text{C}$ values or data trends.

3.4.2 Fractionations for the Immediate Experiments

The experiment without a mineral catalyst preserved its downward trend for the calculated fractionation values. Reactions with Ni-magnetite initially became depleted then appeared to stabilize running parallel to the theoretical equilibrium after 24 h. The fractionation for goethite was similar to the reaction without a mineral catalyst. Its initial value at 1 h was more depleted in comparison. Hematite followed the mineral-catalyst free reaction more closely than any other reaction. Akaganéite and olivine both

initially were more depleted than became more enriched after 4 h of reaction. The fractionations for the experiments in which the acetic acid and hydrogen peroxide were immediately added to the mineral catalyst can be found in Figure 7 and in numerical form in Table 3.

4. Discussion

4.1 Martian Mineralogy

Martian Mineralogy is known to be iron rich and contains many mineral analogs to earth. It has been found that the Martian soil contains mineral catalysts such as hematite (Benner, 2000), Ni-magnetite (Huguenin et al., 1979), olivine (Huguenin et al., 1979), akaganéite (Carter, 2014), and goethite (Benner, 2000). Each of the mineral compositions and their respective metal cations can be found in Table 4. Hematite and goethite are thought to be effective catalysts on the Martian surface (Benner et al., 2000).

Table 4

Mineral catalysts and their associated chemical formulas and metal ion oxidation states.

<i>Mineral Catalyst</i>	<i>Chemical Formula</i>	<i>Metal Ion</i>
Ni-magnetite	NiFe ₂ O ₄	Fe ⁺² , Fe ⁺³
Hematite	Fe ₂ O ₃	Fe ⁺³
Goethite	FeO(OH)	Fe ⁺³
Akaganéite	FeO(OH,Cl)	Fe ⁺³
Olivine	(Mg, Fe) ₂ SiO ₄	Fe ⁺² , Mg ⁺²

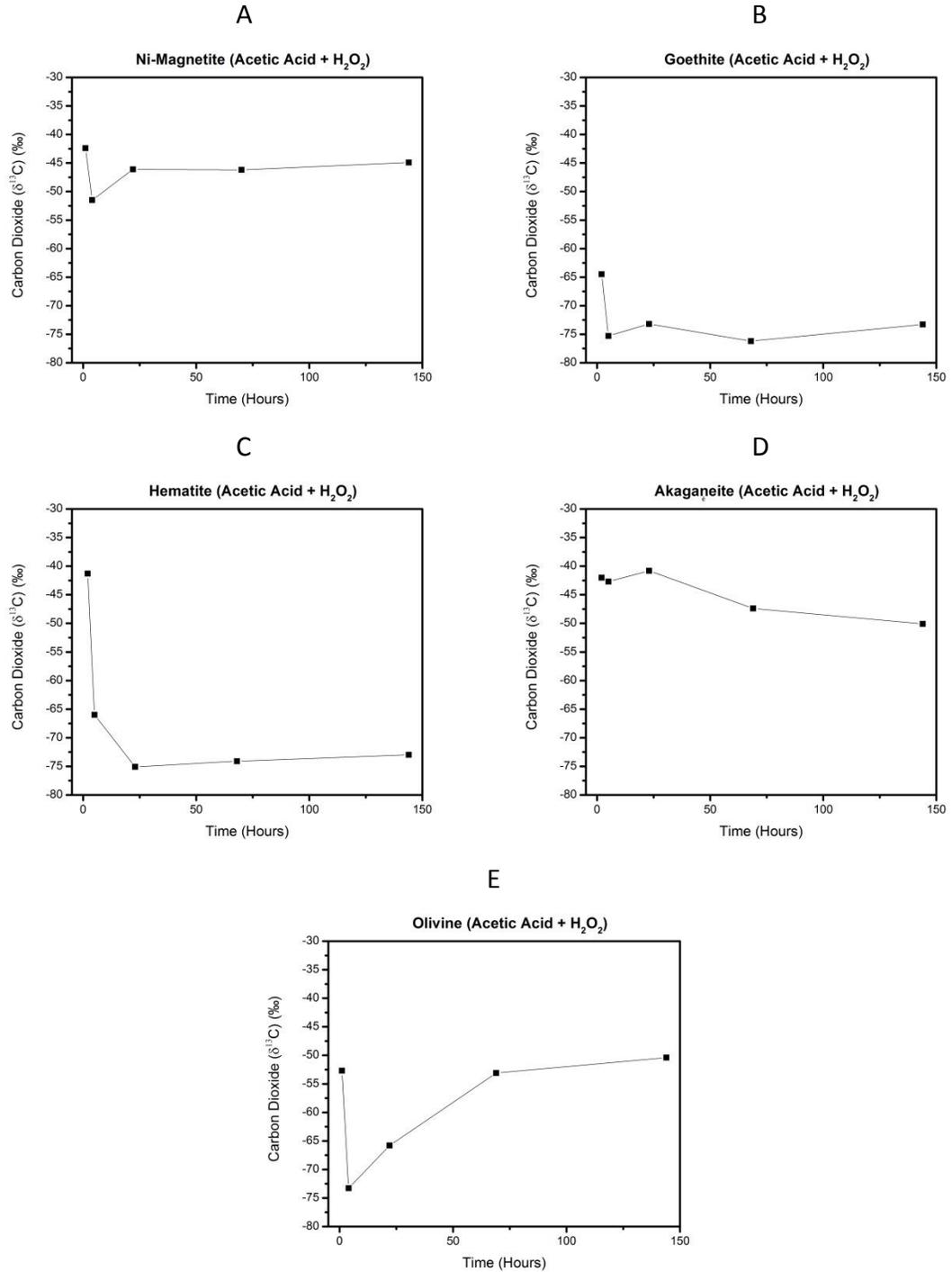


FIGURE 6. Carbon isotope values of carbon dioxide generated from the reaction of acetic acid, hydrogen peroxide, and A) Ni-magnetite (NiFe₂O₄), B) goethite (FeO(OH)), C) hematite (Fe₂O₃), D) akaganéite (Fe³⁺O(OH,Cl)), and E) olivine ((Mg⁺², Fe⁺²)₂SiO₄).

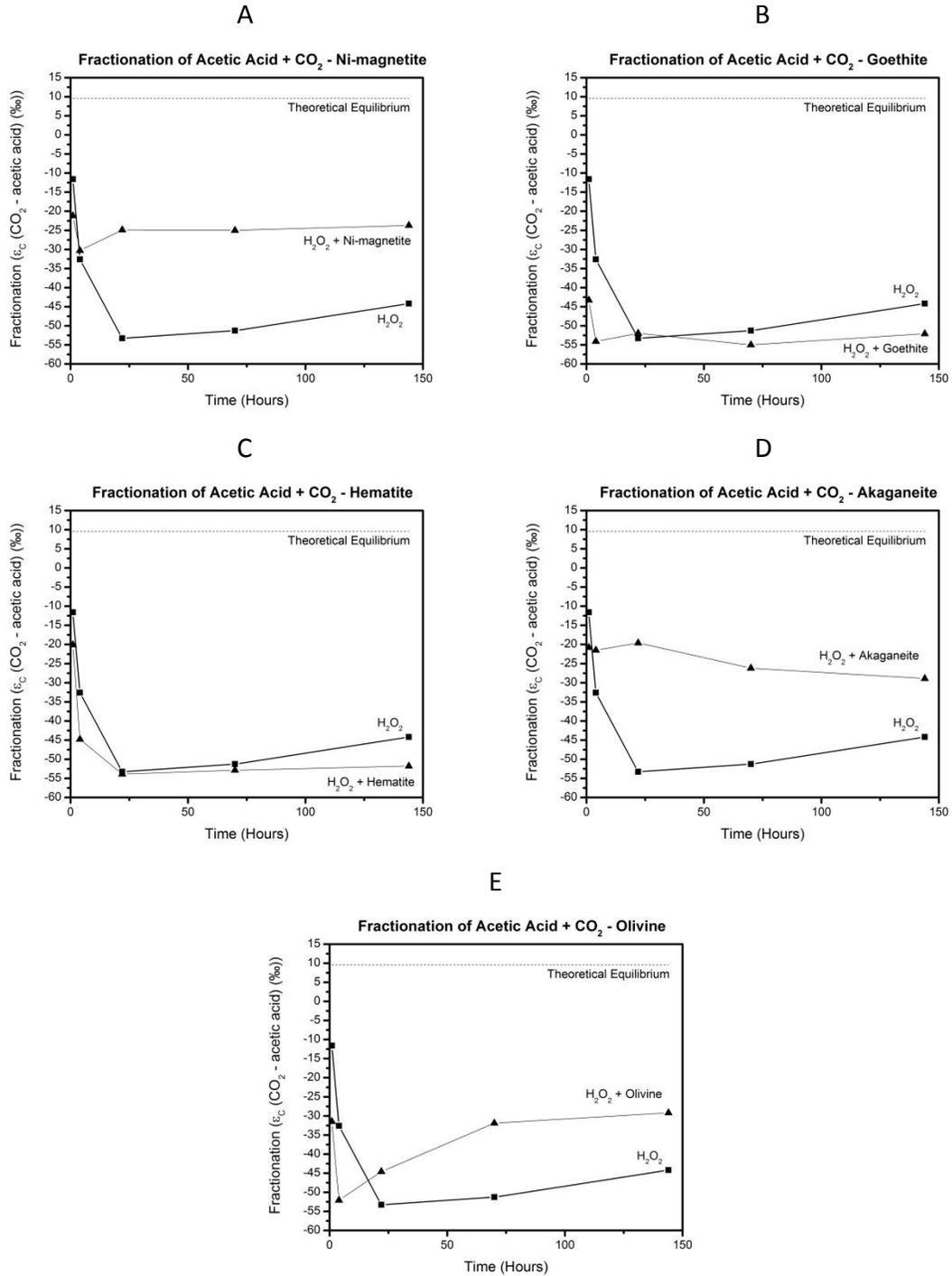


FIGURE 7. Fractionation between acetic acid and measured CO₂ with and without mineral catalysts for experiments with the immediate addition of the oxidizing agent and organic acid. The theoretical equilibrium is displayed for comparison.

4.2 Oxidizing Agents in the Martian Soil

Oxidizing agents have been detected on the surface of Mars. These include hydrogen peroxide, perchlorates, and chlorates. These oxidizers add to the already oxidizing environment supported by incoming UV radiation. These oxidizers, specifically hydrogen peroxide, in the Martian soil produce radicals that can readily react with organic compounds.

4.2.1 Hydrogen Peroxide

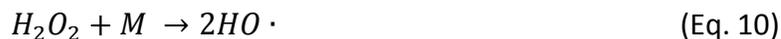
Hydrogen peroxide is an oxidizer known to be present on the Martian surface (Benner et al., 2000). The oxidation of organics could proceed through a number of pathways including the formation of hydroxyl from water or the reaction of oxygen with oxidized organic compounds. Water can cleave to produce hydroxyl radicals by the following reaction (Benner et al., 2000):



In studies of kinetic wet oxidation reactions, clearly defined mechanisms are not well understood (Li et al., 1991). The well-known reactions for the formation of free radicals by the reaction of oxygen with C-H bonds and oxidized organic compound is as follows:



The organic functional group of an organic molecule is represented by R (Li et al., 1991). These mechanisms are associated with wet oxidation reactions. Hydrogen peroxide is a major product of Equation 3 and further decomposes into hydroxyl radicals:



Where M is either a homogenous or heterogeneous compound (Li et al., 1991).

The reaction mechanisms for the oxidation of organic compounds via free radicals is as follows:



The resulting radicals can then react with organic compounds in the Martian soil to produce methane, carbon dioxide, inorganics, and additional hydroxyl radicals.

4.2.2 Perchlorates and Chlorates

Perchlorate (ClO_4^-) has been positively identified by the Phoenix Mars Lander in the northern plains of the Vastitas Borealis (Hecht et al., 2009). The measurements were performed by the Wet Chemistry Laboratory aboard the Phoenix lander. The average concentration of perchlorate was measured to be 2.4 mM from three sample sites (Hecht et al., 2009). By mass, perchlorate was approximately 0.4 to 0.6 % of the sample solutions (Hecht et al., 2009). Chlorates (ClO_3^-) were detected by the Wet Chemistry

Laboratory on the Phoenix Lander (Hanley et al., 2012). This compound is an oxidation intermediate between chloride (Cl^-) and perchlorate (ClO_4^-) (Hanley et al., 2012).

4.3 Martian Carbon Cycle

Carbon in the form of methane (CH_4) and carbon dioxide (CO_2) are present in multiple reservoirs on Mars (Chassefière et al., 2010). Both methane and carbon dioxide are important to understanding the role of organic molecules on Mars. Methane and carbon dioxide are known products of acetic acid oxidation (Ogata et al., 1980). Organic oxidation on Mars then becomes significant and has implications on the atmospheric chemistry and geochemistry of the planet.

It has been suggested that atmospheric methane is of hydrothermal origin (Chassefière et al., 2010). Hydrothermal vents are known sites of increased chemical and possibly biogenic activity on earth. It may be plausible that organic reactions may have then contributed to the production of methane at hydrothermal sites in past Martian geologic history. It is thought that there is presently widespread sequestration of carbon in subsurface carbonates that contain CO_2 initially present in the Martian atmosphere (Chassefière et al., 2010).

4.4 Organic Molecules and the Martian Surface

The organic material available for reactions on Mars is conjectured to be carboxylic acid derivatives from organic materials from meteorites (Benner, 2000). It has been

estimated that there is 2 kg of benzenecarboxylic acids per m² of the Martian surface from the influx of meteorites alone (Benner, 2000). However, the oxidation of benzenecarboxylic acids yields carboxylic acid derivatives that are not detectable by Gas Chromatography - Mass Spectrometry (GC-MS) due to oxidation processes via a variety of reaction mechanisms (Benner, 2000).

4.5 Previous Research

The oxidation reaction of 1 mL of C₁ – C₄ carboxylic acids have been conducted with hydrogen peroxide (H₂O₂, 50 wt %, 0.1 ml) acting as an oxidizing agent (Fu et al., 2012). Time series carbon isotope measurements were taken at 1 h and 48 h intervals. The reaction was repeated with the addition of a mineral catalyst, Ni-magnetite (1 mg) (NiFe₂O₄). After a reaction time of 1 h, carbon isotope measurements were taken. The results showed that CO₂ evolved from these experiments without Ni-magnetite became isotopically lighter after 1 h of reaction compared to its initial $\delta^{13}\text{C}$ value (Fu et al., 2012). With exception of the results for C₁, the samples became increasingly lighter after 48 h. In experiments with Ni-magnetite, however, the $\delta^{13}\text{C}$ value of CO₂ was heavier than the corresponding acid after 1 h of reaction time.

The most recent study follows the same experimental protocol with the exceptions of times of isotope measurement, oxidizing chemicals, and carboxylic acid samples. Carbon isotope measurements were taken at 2 h, 4 h, 24 hours, 48 h, 72 h and 120 h. Hydrogen peroxide (0.1 ml, 50 wt %) and magnesium perchlorate (0.1 ml, 1 M) were used as

oxidizers (Mujib et al., 2015). The organic molecule of interest was acetic acid. Results showed that Ni-magnetite caused an increase in abundance of CO₂ evolved from experiments. Magnesium perchlorate did not produce adequate CO₂ for carbon isotope measurement after 120 h. In experiments without the Ni-magnetite catalyst, the δ¹³C value of acetic acid decreases initially. The value remains constant and then increases from 75 h to 120 h. In the presence of Ni-magnetite, carbon isotope values of acetic acid decrease up to 75 h, and then increase slightly until 120 h. The higher δ¹³C values of CO₂ in the Ni-magnetite experiments may be attributed to the different reaction pathway in the Fenton reaction.

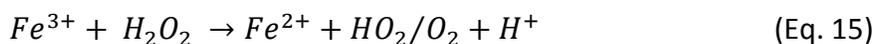
4.6 The Fenton Reaction

The Fenton reaction is the primary chemical reaction of focus. Each of the proposed mineral catalysts contains an iron oxide (II, III) and was subjected to hydrogen peroxide. It has also been shown that hydroxyl radicals ([•]OH) can be produced by the Fenton reaction with iron (II) oxide (Fe²⁺) (Costa et al., 2006):



With [•]OH as the oxidant, the reaction pathway and organic intermediate(s) may be different than in the experiments with H₂O₂ only, resulting in different isotope partitioning.

For mineral catalysts with a ferric ion (Fe³⁺), the reaction pathway proceeds through a Fe(III)-initiated Fenton-like reaction (Kwan et al., 2002):



The Fenton reaction outlines two distinct pathways as depicted in Figure 1. The value of carbon isotope ratios determines which is the favored reaction pathway for that experiment. The reported value for the methyl group of the acetic acid is -29.0 ‰ and the value for the carboxyl group is -13.4 ‰ (Fu et al., 2012).

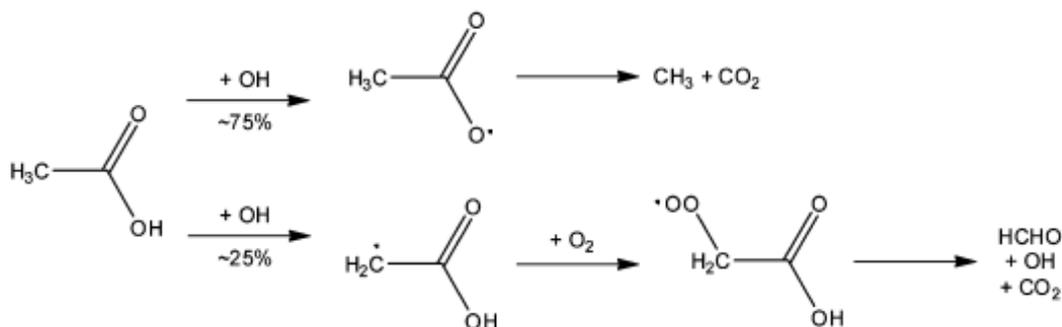


FIGURE 8. The reaction pathways of the Fenton reaction with acetic acid and their associated products (de Silva, 2010).

4.7 Reactants

Mineral catalysts that had significant effects on the oxidation of acetic acid were Ni-magnetite, goethite, akaganéite, and olivine for the $\delta^{13}C$ values and Ni-magnetite, akaganéite and olivine for the fractionations for the experiments with the immediate addition of acetic acid and hydrogen peroxide. For the overnight reactions, Ni-magnetite, akaganéite, and olivine had the most effect on the $\delta^{13}C$ values and fractionations.

The mineral catalysts that had little effect on the results of the oxidation of acetic acid by hydrogen peroxide were hematite and goethite for the overnight reactions and fractionations. Hematite had small effects on the $\delta^{13}\text{C}$ values for the experiments with the immediate addition of acetic acid and hydrogen peroxide.

Ni-magnetite caused the sample to become isotopically lighter by approximately -9 ‰ from 1 h to 4 h of reaction and increases slightly between 4 h and 24 h of reaction as seen in Figure 7. The reaction stabilized after 24 h until 144 h. Overall, the isotope values were more depleted than the heavier isotope values in the overnight reaction with Ni-magnetite as seen in Figure 4. In the overnight experiments, the CO_2 samples produced increasingly heavy isotopes then decreased and stabilized after 72 h. Because these reactions produced relatively heavy isotope values than the other reactions, Ni-magnetite causes heavy carbon isotopes to react and catalyze to CO_2 . Kinetically, this means that Ni-magnetite slows the reaction process knowing that lighter elements are typically the first to react. This has implications for the Martian carbon cycle. Since Ni-magnetite catalyzes the oxidation reaction in such a way that heavy isotopes are released as carbon dioxide gas, the remaining isotope ratios would be depleted. This would mean that soils containing Ni-magnetite are expected to yield depleted values. Also, because the CO_2 produced has a relatively heavier signature, unaltered sub-surface carbonates would match the same signature due to early carbon sequestration in Martian history (Chassefière et al., 2010). Fractionations for both types of experiments with Ni-magnetite, overnight and immediate, reinforce the production of heavy CO_2 . In

Figure 5, it can be shown that the fractionation between acetic acid and carbon dioxide almost reaches equilibrium. The fractionation for the immediate reactions ran parallel with the theoretical equilibrium but was much more isotopically light than the equilibrium. It can be concluded that different reaction times with an oxidizing agent, either overnight or immediate, produced different isotope values and therefore proceeded through an alternate reaction pathway. Because hydrogen peroxide had a longer reaction time with the mineral catalyst, there may be an increase in hydroxyl radical concentration leading to increased reactions with heavier isotopes of carbon. In comparison, the short reaction with hydrogen peroxide would produce much less radicals for reaction and may favor a selective reaction in which lighter isotopes of carbon are preferred. Based on the data, Ni-magnetite may possibly reach equilibrium between acetic acid and carbon dioxide when subjected to longer periods of oxidation prior to the addition of the organic compound.

Goethite had similar $\delta^{13}\text{C}$ and followed more or less the same trend for both the overnight and immediate reaction with an exception. The values of both experiments were startlingly different. Having a longer oxidation period caused the starting value at 1 h to be -19.6 ‰ while the starting value for the immediate reaction was -64.5 ‰. This is consistent with the idea that increased hydroxyl concentration from the reaction of the mineral catalyst with hydrogen peroxide produces heavier $\delta^{13}\text{C}$ values. It is important to note that goethite, regardless of initial conditions, bottoms out around -75 ‰ and continues to increase after 72 h for both reactions. Compared to Ni-magnetite which

has a metal cation of Fe^{+2} , it can be determined that the Fe^{+3} with a higher oxidation state within goethite causes slower rates of production of hydroxyl radicals. Possibly, the ferric ion may proceed through Eq. 15 before proceeding through Eq. 14. This means that Eq. 15 may be a controlling factor in the production of hydroxyl radicals and therefore causes lighter $\delta^{13}\text{C}$ values. The fractionations between acetic acid and carbon dioxide for goethite closely follow the same trend as fractionations without the presence of a mineral catalyst. Within the first 24 h, the samples become drastically depleted then started to increase in heavy isotopes after 24 h. Though the samples did not reach theoretical equilibrium, it may be possible that the samples do reach equilibrium after an increased residence time.

Reactions with hematite as the mineral catalyst yielded interesting results. Both the overnight and immediate experiments yielded nearly identical trends in terms of $\delta^{13}\text{C}$ values. However, the results for the overnight experiments were shifted by approximately -45 ‰ to the less negative values. This means hematite, when subjected to longer periods of oxidation, produces heavier stable carbon isotope values. This is consistent with the results from the reactions containing Ni-magnetite and goethite. Like goethite, hematite also has the ferric ion, Fe^{+3} . It follows that the hydroxyl radical production was therefore slowed and the resulting isotope values were much lighter than Ni-magnetite (Fe^{+2}). Fractionation values for hematite in both types of experiments show that equilibrium was not reached within 144 h. Both fractionation trends are aligned with the trend for the reaction without a mineral catalyst. The difference

between the two fractionations is the starting fractionation at 1 h of reaction. The fractionation for the overnight reaction has a positive $\delta^{13}\text{C}$ while the immediate reaction has a negative $\delta^{13}\text{C}$. It is possible that in both reactions, carbon dioxide does eventually reach equilibrium with acetic acid. The upward trend starting at 24 h and continuing until 144 h indicates that after time equilibrium may be reached.

Akaganéite, like goethite and hematite, had nearly the same trend of $\delta^{13}\text{C}$ values for the overnight and immediate experiments. Again, the difference in the results are the shifted $\delta^{13}\text{C}$ values. In the overnight experiments, the samples did not produce values that became severely depleted within the first 24 h like the other experiments with goethite and hematite. The values changed less than -2 ‰ within the first 4 h of reaction. After 72 h of reaction, the $\delta^{13}\text{C}$ values became increasingly depleted. As with the previously discussed reactions, the overnight experiments produced heavier isotopes than the immediate experiments. Akaganéite contains the ferric ion, Fe^{3+} , which results in $\delta^{13}\text{C}$ values within the same range as goethite and hematite but more depleted than $\delta^{13}\text{C}$ values associated with Ni-magnetite. Fractionations for akaganéite did not follow the trend for experiments without a mineral catalyst. They were significantly enriched in comparison. Due to the downward trend starting at 72 h of reaction it does not seem likely that the reactions in both experiments reach the theoretical equilibrium. Akaganéite, therefore, is the only mineral catalyst that prevents the possible equilibration of carbon dioxide with acetic acid.

Experiments with olivine as the mineral catalyst yield much the same results as all of the previous catalysts except for Ni-magnetite. The $\delta^{13}\text{C}$ graphical trends for the overnight and immediate experiments were nearly identical in shape. Olivine contains the ferrous ion, Fe^{+2} , but did not display the relatively enriched values like Ni-magnetite. The isotope values were within the range of goethite, hematite, and akaganéite. This may be due to the presence of a second metallic ion, Mg^{+2} . The lower concentration of iron in the San Carlos olivine used in this experiment in conjunction with another reactive ion in higher concentrations may have limited the production of the hydroxyl radical and thus resulting in more depleted samples. Fractionation results yield nearly identical fractionation curves. Both experiments yielded initial fractionation values that were close. The fractionation curves show an upward trend after 4 h of reaction indicating that attaining theoretical equilibrium may be possible after additional reaction time. The destruction of acetic acid or other low molecular weight carboxylic acids is a rate-limiting step in the oxidation of the acid (Larachi et al., 1998). It was found that Fe^{+2} exchanged in NaY zeolites was a proficient homogenous catalyst in reactions with acetic acid and hydrogen peroxide (Larachi et al., 1998). In reactions with stearic acid and clay minerals, acid-base reactions with Mg displayed increased decarboxylation compared to clays containing Fe (Heller-Kallai et. al, 1984). These results agree with the olivine experiments in that the faster decarboxylation by Mg than Fe produced relatively lighter isotope ratios for measured CO_2 .

4.8 Intermediates

The Fenton reaction with acetic acid and hydrogen peroxide produces known intermediates. Through the pathway that produces methane and carbon dioxide, the known intermediate is $\text{CH}_3\text{COO}^\cdot$ and seen in Figure 8. The pathway that produces oxygen, carbon dioxide, hydroxyl radicals, and inorganic material has two intermediates, the less common (25 %) reaction pathway is $^\cdot\text{CH}_2\text{COOH}$ and the second is $^\cdot\text{OOCH}_2\text{COOH}$ (see Figure 8).

In the presence of mineral catalysts, intermediates may be different than reactions without mineral catalysts. The iron oxides could possibly react with the acetic acid radical intermediates.

In the oxidation of acetic acid with hematite and magnesium sulfate (C_2), methane production was substantially lower than without hematite (Pan et al., 2006). Because of the increase after 72 h with magnesium sulfate alone, methane was determined as one of the final products of the acetic acid oxidation (Pan et al., 2006). It has been confirmed that methane and carbon dioxide are produced by the photolysis of acetic acid (Ogata et al., 1980).

The measurement of the produced carbon dioxide yields stable isotope values. Depending on the isotope value, $\delta^{13}\text{C}$, the reaction pathway may be determined. For carbon dioxide from the methyl group, the $\delta^{13}\text{C}$ value is -43.4 ‰. The $\delta^{13}\text{C}$ value for carbon dioxide is -1.0 ‰ for the carboxyl group. Based on the data from all reactions, it appears that only the overnight reaction with Ni-magnetite produces CO_2 from the

carboxyl group. This particular reaction gave stable isotope values of carbon that were closer to -1.0 ‰. All other reactions yielded results that were closer to the $\delta^{13}\text{C}$ of -43.4 ‰. This means that all but one reaction probably proceeded through the pathway yielding methane and carbon dioxide.

4.9 Predictions for Future Experiments

If these experiments were to be conducted with higher order carboxylic acids ($\text{C}_1\text{-C}_5$), the rate of oxidation may increase with increasing number of carbon atoms (Pan et al., 2006). The $\delta^{13}\text{C}$ values of higher order hydrocarbons in these theoretical experiments may become more enriched and have increased fractionations with increasing carbon number and oxidation rate (Pan et al., 2006).

It is worth noting that in some reactions, higher order complexing was observed after 24 hours of reaction. The complexes were most likely carbon and oxygen containing polycyclic and long chain molecules. Further investigation and characterization is necessary to positively identify these by products.

5. Conclusions

The resulting $\delta^{13}\text{C}$ values of the all of the experiments are significantly isotopically lighter than previously thought (Fu et al., 2012). In the all experiments, goethite, hematite, akaganéite, and olivine showed similar trends and isotope values. Ni-magnetite and akaganéite as mineral catalysts produced $\delta^{13}\text{C}$ values that deviated from

the expected trend from reactions without a mineral catalyst. While the akaganéite experimental values indicate the same reaction pathway as goethite, hematite, and olivine, the Ni-magnetite experimental values do not. It is possible that the Ni-magnetite catalyst produces CO₂ generated from the carboxyl group of the acetic acid while all of the other experiments produce methyl group CO₂.

As the $\delta^{13}\text{C}$ values of these experiments are significantly lighter than the predicted $\delta^{13}\text{C}$ value of the carboxyl pathway of the Fenton reaction, it is probable that all iterations of this experiment followed the pathway that produces CO₂ generated from the methyl group of the acetic acid except for the overnight reactions with Ni-magnetite.

The overnight reaction with Ni-magnetite was the only experiment that approached equilibrium. All other reactions, excluding akaganéite, may eventually reach equilibrium but beyond the time constraints of this experiment.

The oxidation state of the iron oxide in the mineral catalysts altered the reaction pathway by effecting the production of hydroxyl radicals and therefore controlling their rate of production.

It can be confirmed that organic intermediates and reaction pathways are different with different oxidizing agents, which control the isotope values of CO₂ and other organic compounds. Considering the high oxidation state in Martian atmosphere and upper subsurface, information on the controlling factors associated with organic oxidation may be instrumental in understanding the history of carbon-bearing compounds on Mars.

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