

RESEARCH ARTICLE

Radiation-induced reactions in comet analogues

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Abstract

Comets are a source of prebiotic molecules that likely enriched the early Earth during the Late Heavy Bombardment period. Laboratory experiments that replicate cometary conditions may facilitate understanding of the chemical reactions and supplement observational studies of these icy bodies. Prebiotic compounds, such as formic acid and formaldehyde, have been observed in comets. Furthermore, these compounds can easily be formed in experimental models using a variety of gas combinations and energy sources. We conducted experimental cometary simulations using radiation chemistry tools to obtain insight into the possible fate of formic acid and formaldehyde. The main results suggest a redundant system, signifying that the irradiation of formic acid forms formaldehyde molecules and *vice versa*. This phenomenon ensures the permanence of prebiotic molecules in high-radiation environments. Additionally, the potential role of forsterite and graphite was explored in cometary simulations. Our experimental results show the differential formation of aldehydes and other carbonyl-containing compounds dependent on the mineral phase present.

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Introduction

In the 1980s, explorations of the solar system provided new insight into the distribution of organic compounds in extraterrestrial environments. Specifically, organic compounds have been found in meteorites and comets (Kobayashi, 2019). The organic molecules detected in comets are highly diverse. Amino acids, the building blocks of proteins, have been detected in the Murchison meteorite, a CM2 carbonaceous chondrite (Martins *et al.*, 2006). Additionally, HCN-, NH₃ and CN-containing compounds have been detected in comets (Despois and Cottin, 2005; Goesmann *et al.*, 2015), and simple molecules, such as H₂O, H₂CO and HCOOH, are abundant in cometary ices (Delsemme, 1988; Bockelée-Morvan *et al.*, 2004; Llorca, 2005). In this respect, comets are considered a source of prebiotic molecules that may have enriched the early Earth during the Late Heavy Bombardment (Chyba *et al.*, 1990).

Interaction of ionizing radiation with comets

Different types of radiation induce chemical transformations in cometary ices. Irradiation with cosmic rays (an ionizing radiation source) and ultraviolet light can induce the formation of organic compounds via radical reactions. To a lesser extent, embedded radionuclides in the cometary core (⁴⁰K, ²³⁵U, ²³⁸U, ²³²Th, ²⁴⁴Pu, ¹²⁹I, ²⁴⁷Cm, ¹⁰Be and ²³⁷Np) could function as a minor energy source (Draganić and Draganić, 1984), which has been estimated to deposit up to 14 MGy. This corresponds to the expected total dose delivered by the natural decay of the radionuclides in the comet over 4.6×10^9 years (Cataldo *et al.*, 2011; Iglesias-Groth *et al.*, 2011).

Protons from cosmic rays are the most abundant ionizing particles in the solar system: they have an energy of approximately 2 GeV (Draganić and Draganić, 1988) and a linear energy transfer (LET) comparable to gamma rays. As a result, gamma-ray irradiation is an excellent candidate for replicating GeV proton irradiation of cometary nuclei.

Minerals detected in comets

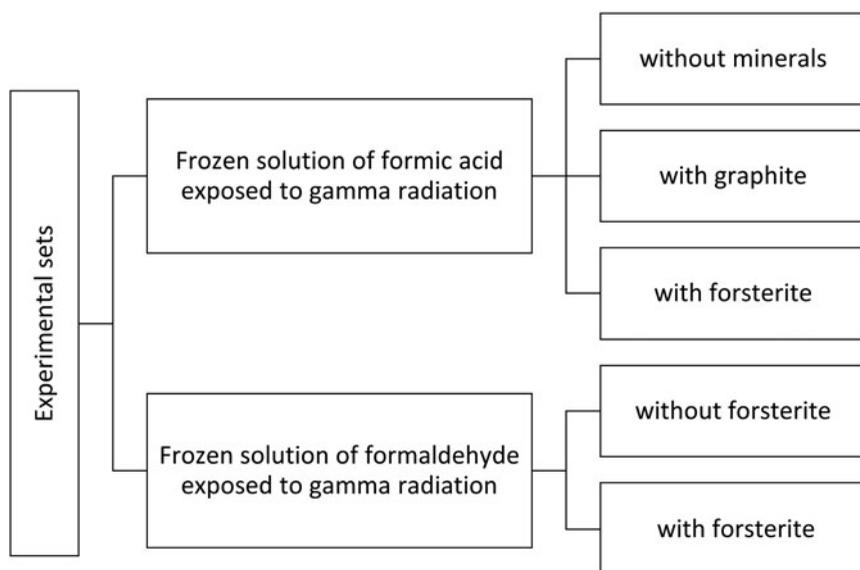
Minerals have also been detected in comets, and they may significantly impact the chemical behaviour of organics. The primary mineral phases in these bodies are olivine and pyroxene. Forsterite (olivine) and enstatite (pyroxene) were detected in cometary dust samples recovered by the Stardust mission from 81P/Wild 2 (Brownlee *et al.*, 2006). Additionally, inorganic carbon has been identified as a component of cometary dust (Kissel *et al.*, 1986a, 1986b). According to studies of particles from 67P/Churyumov–Gerasimenko, comets contain carbon-rich and non-hydrated minerals (Bardyn *et al.*, 2006; Fray *et al.*, 2016). Limited data exist on the role of minerals in prebiotic reactions in comets. This work aimed to evaluate the reactivity of formic acid and formaldehyde in an experimental model of a simple cometary core.

Methodology

The experimental model used in the present work was designed according to the previous one proposed by Draganić *et al.* (1985). The model consisted of a frozen aqueous solution in a glass container. First, the aqueous solution is evacuated to eliminate the atmospheric oxygen and then is frozen with liquid nitrogen. Finally, the glass container with the frozen solution is irradiated with gamma radiation at different doses.

In the present study, the experimental model included a frozen aqueous solution of formic acid or formaldehyde and a mineral phase. Next, this simple cometary core was exposed to an ionizing radiation energy source.

The experimental sets are presented in [Scheme 1](#) below: (1) frozen formic acid solutions with and without minerals, and (2) frozen formaldehyde solutions with and without forsterite.



Scheme 1. Experimental sets: (1) frozen (77 K) solutions of formic acid (0.02 M) with and without minerals and (2) frozen (77 K) solutions of formaldehyde (0.3 M) with and without minerals.

Irradiation source

The samples were irradiated in a cobalt-60 source facility (Gammabeam 651 PT) at the Instituto de Ciencias Nucleares, UNAM, Mexico. The dose rates of the gamma source (266 Gy min^{-1} at room temperature and 44 Gy min^{-1} at 77 K, [Gray, $1 \text{ Gy} = \text{J kg}^{-1}$]) were measured using the ferrous sulphate–cupric sulphate dosimeter (O'Donnell and Sangster, 1970; Draganić and Draganić, 1971). In the dosimeter, the transformation of Fe^{2+} to Fe^{3+} induced by radiation was measured via UV spectroscopy at 304 nm. These data can evaluate the energy deposited in the system over time. If the time of exposure is known, the dose can be evaluated.

The samples were placed 10 cm from the source inside a Dewar flask filled with liquid nitrogen. The dosimetry was conducted under the same conditions as the samples to account for the attenuation of the flask and nitrogen. Using these data, the absorbed dose in our model was established as previously described (Cruz-Castañeda *et al.*, 2018; Leal-Acevedo and Gamboa-de Buen, 2020). The irradiation was performed at a fixed position, and the irradiation time was varied.

Preparation and irradiation of a simple cometary core of formic acid

A 95% formic acid solution (Sigma-Aldrich, Saint Louis, Missouri, USA) and triple-distilled water were used to prepare formic acid at 0.02 M. Oxygen-free aliquots (5 ml) of formic acid were frozen in glass tubes using liquid nitrogen and maintained in a Dewar flask (77 K). The samples were exposed to various doses of gamma radiation (0–90 kGy).

Measurement of formic acid decomposition by titration

After exposure to gamma radiation, the decomposition of the formic acid was measured by titration. Sodium hydroxide was used as a titrant solution, 0.5% phenolphthalein (Sigma-Aldrich) was used as an indicator, and formic acid ($1 \times 10^{-3} \text{ M}$) was used as the standard solution.

Aldehyde and ketone detection via derivatization using 2,4-dinitrophenylhydrazine

The detection of aldehydes and ketones in the irradiated formic acid samples (42 kGy) was performed through derivatization using 2,4-dinitrophenylhydrazine (DNPH) (Sigma-Aldrich). The derivatives were recovered by centrifugation (14 000 rpm \times 10 min) and dried at room temperature. Finally, the dried derivatives were dissolved in acetonitrile (Merck, Germany) and analysed using high-performance liquid chromatography (HPLC; Knauer Azura P 4.1S, Germany) coupled with a UV detector. A C-18 ODS 2.7 μm column, (Beckman Coulter, USA), 4.6 mm \times 150 mm was employed. A mixture of acetonitrile and water (70:30) was used as the eluent; the flow rate was 1 ml min⁻¹.

Additionally, DNPH-derivatives (the irradiated samples with minerals) were analysed by HPLC-MS. A 515 HPLC pump was used coupled with a SQ-2 Single Quadrupole Mass Detector system, with electrospray ionization in negative (ESI⁻) mode (Waters®, Massachusetts, USA). The cone energy was 24 V, the capillary energy was 1.46 kV and the desolvation temperature was 350°C. The DNPH-derivatives were separated in a Symmetry C18 3.5 μm column (Waters®), 4.6 mm \times 75 mm. A mixture of acetonitrile and water (70:30) was used as the eluent; the flow rate was 0.8 ml min⁻¹.

Formic acid cometary core with mineral phases

Two sets of experiments were performed for this part of the study: one using graphite and the other using forsterite. Graphite powder (0.1 g) or forsterite grains (1 g) in formic acid solution (5 ml) were placed into glass tubes. The oxygen-free mixtures were frozen using liquid nitrogen (77 K). Later, the glass tubes were placed in a Dewar flask containing liquid nitrogen and irradiated (0–70 kGy). The formic acid decomposition was evaluated by titration, and the radiolytic products (aldehydes) were identified using DNPH derivatization, as described above.

Preparation and irradiation of a simple cometary core of formaldehyde

A 37% formaldehyde solution (Sigma-Aldrich) and triple-distilled water were used to prepare formaldehyde at 0.3 M. Oxygen-free aliquots (5 ml) of formaldehyde were frozen in glass tubes using liquid nitrogen (77 K). The samples were kept in a Dewar flask to maintain the temperature throughout the irradiation. The applied doses ranged from 0 to 600 kGy.

Measurement of formaldehyde decomposition by gas chromatography

The decomposition of the formaldehyde was measured by gas chromatography using a Varian 2400 chromatograph coupled with a flame ionization detector (California, USA) and a Chromosorb 102 column (Sigma-Aldrich), i. d. 1/8-inch \times 4 m. Nitrogen was used as the carrier gas at a flow rate of 30 ml min⁻¹. The temperature ramp started at 60°C and ended at 230°C. The rate of heating was 6°C min⁻¹.

Identification of radiolytic products in the irradiated formaldehyde samples

Titration assays were conducted to quantify the formic acid formation in the irradiated formaldehyde samples. The experimental procedure was performed as previously described in section 'Measurement of formic acid decomposition by titration'.

Formaldehyde cometary core with forsterite

Forsterite (1 g) and formaldehyde solutions (5 ml) were placed in glass tubes. The oxygen-free mixtures were frozen using liquid nitrogen. Later, the glass tubes were placed in a Dewar flask containing liquid nitrogen (77 K) and irradiated (0–300 kGy). Gas chromatography was performed to measure the

decomposition of the irradiated formaldehyde under these conditions. Additionally, titration was performed to quantify the radiolytic products.

Results

The analysis of the results presented in this work was based on measuring the decomposition of formic acid and formaldehyde upon exposure to a high radiation environment in the presence of minerals. Additionally, their radiolytic products were identified.

Decomposition of formic acid and the identification of its radiolytic products

Figure 1 shows the percentage of the formic acid samples recovered after irradiation. With gamma radiation exposure from 0 to 90 kGy, there were minimal changes in the decomposition of the formic acid. The recovery rate of this molecule remained greater than 90% after irradiation.

Identification of aldehydes in frozen solutions of formic acid

Frozen solutions of formic acid were exposed to 42 kGy of irradiation. These samples were treated with DNPH and analysed by HPLC. A representative chromatogram of the identified aldehydes is shown in Fig. 2. Formaldehyde was detected in the irradiated samples of formic acid.

Decomposition of formic acid and identification of its radiolytic products in frozen solutions containing minerals

In both mineral systems (forsterite and graphite), the recovery of formic acid remained greater than 80% (Fig. 3). A similar observation was made regarding the frozen solutions that did not contain minerals (dotted line, Fig. 3), in which the recovery was 90%. No significant change in the decomposition of the molecule was observed in the systems, regardless of the presence of minerals. However, the distribution of the radiolytic products changed in the systems studied (Fig. 4).

Figure 4 shows the radiolytic products identified in the frozen solutions of formic acid with and without minerals. The system containing graphite favours the formation of glyoxylic acid, formaldehyde and an unidentified carbonyl-containing molecule (D). In the system containing forsterite,

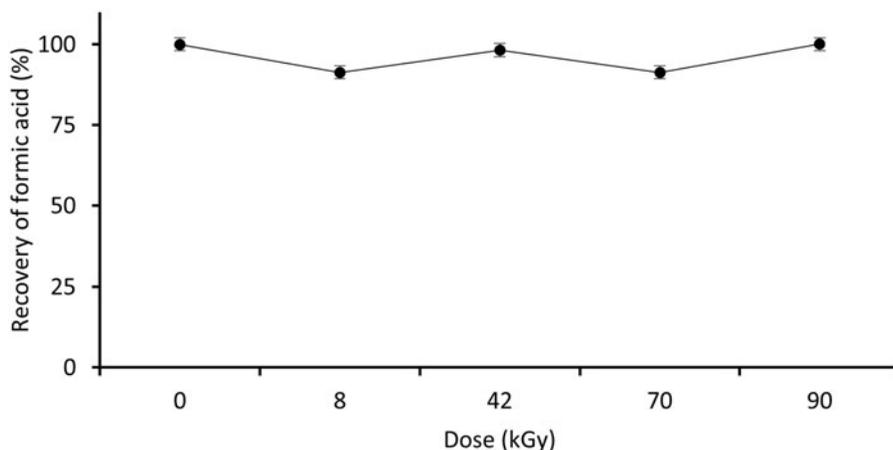


Fig. 1. Recovery of formic acid after irradiation, quantified by titration. Frozen formic acid solutions (0.02 M) were exposed to gamma radiation (0–90 kGy) at a fixed dose rate.

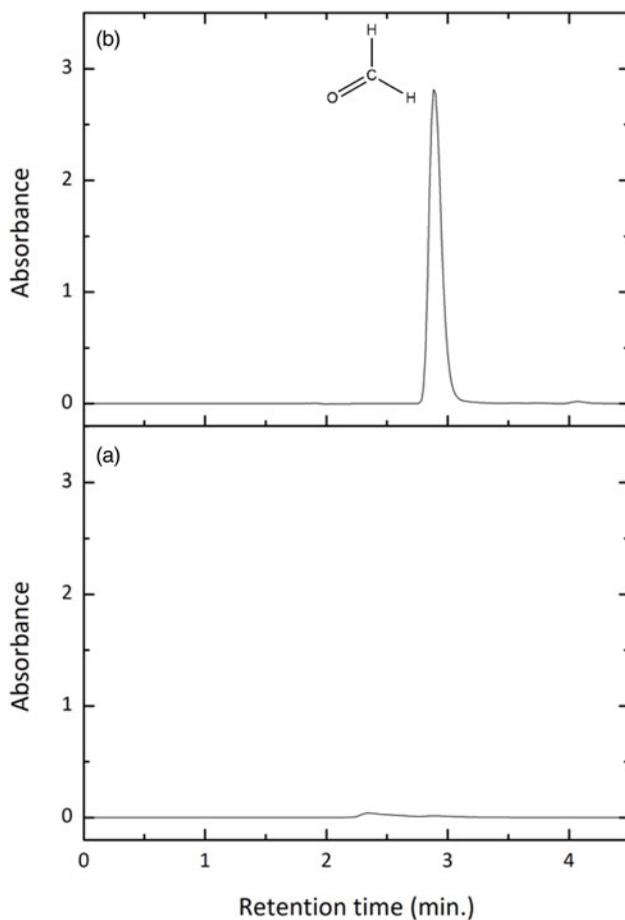


Fig. 2. HPLC chromatograms of (a) unirradiated formic acid treated with DNPH (control) and (b) DNPH-formaldehyde detected in frozen solutions of irradiated formic acid.

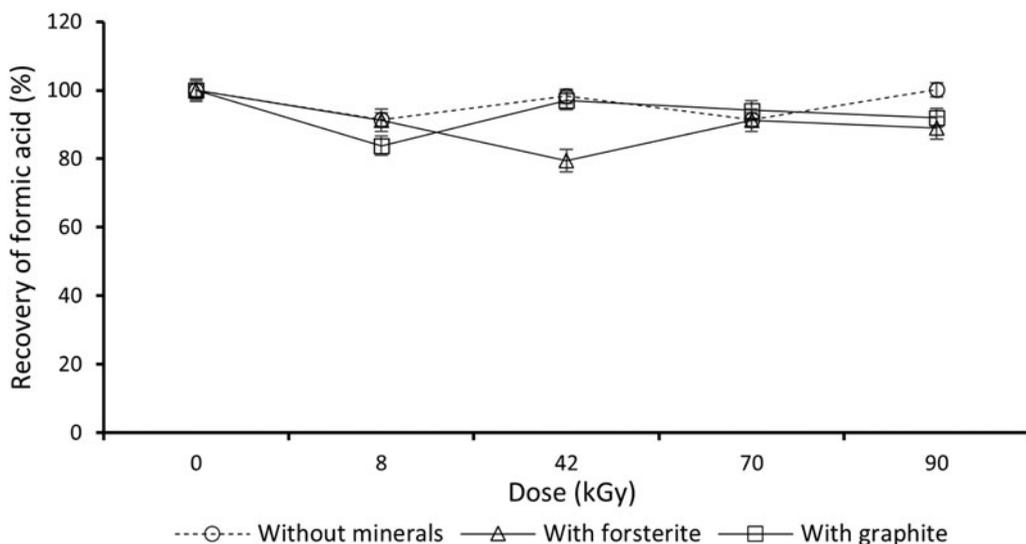


Fig. 3. Recovery of formic acid after irradiation, quantified by titration. Frozen formic acid solutions (0.02 M) with and without minerals were exposed to gamma radiation (0–90 kGy) at a fixed dose rate.

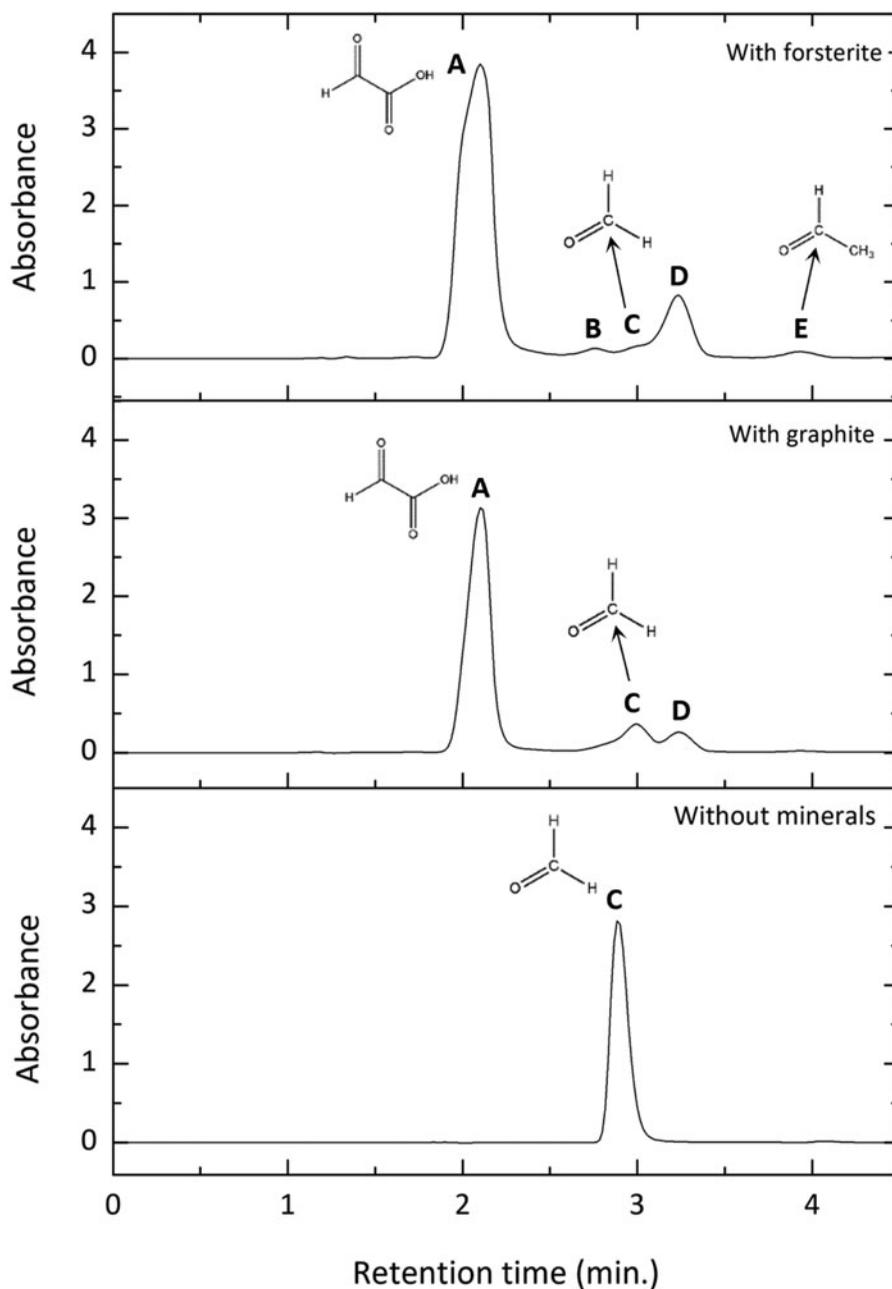


Fig. 4. DNP derivatives detected by HPLC in frozen formic acid solutions without and with minerals. The systems were irradiated at 42 kGy. (a) Glyoxylic acid, (b) unidentified carbonyl-containing molecule, (c) formaldehyde, (d) unidentified carbonyl-containing molecule and (e) acetaldehyde.

glyoxylic acid, formaldehyde, acetaldehyde and two carbonyl-containing molecules (B and D) were identified. In the absence of minerals, only formaldehyde is detected.

Although B and D molecules have not been fully characterized, these compounds contain a carbonyl group in their structure because DNP reacts specifically with the carbonyl groups of aldehydes or ketones (Shriner *et al.*, 2004). Additionally, the irradiated samples with minerals were analysed by

HPLC-MS. DNPH-derivatives with molecular masses of 363 and 325 g mol^{-1} were detected (data not shown), that could correspond to the unidentified molecules (B and D). The differences observed in the distribution of the radiolytic products are discussed in the subsequent sections.

Decomposition of formaldehyde in the control and frozen solutions

The recovery of formaldehyde after irradiation was quantified by gas chromatography. The measurements are presented in Fig. 5. In an interval of exposure of 0–300 kGy, a recovery of greater than 90% was observed, whereas between 400 and 600 kGy, the recovery remained above 80%.

Formic acid, a radiolytic product identified in the irradiated formaldehyde samples

In previous studies conducted by our research group (López-Islas *et al.*, 2018), formic acid in irradiated formaldehyde samples was detected by mass spectrometry. In the present study, formic acid in the formaldehyde samples that were exposed to gamma radiation was measured by titration. Molarity calculations show low concentrations (0.007–0.002 M) of formic acid (Fig. 6). These data are consistent with the recovery of formaldehyde. The data presented in Fig. 5 show that the formaldehyde molecules remained stable at high doses of gamma radiation; therefore, the formation of radiolytic products was low.

Decomposition of formaldehyde in systems containing forsterite and the quantification of its radiolytic product: formic acid

According to the findings of the present study, the recovery of formaldehyde after irradiation was similar in the systems with and without forsterite. More than 90% of the formaldehyde was preserved in the samples exposed to 300 kGy of irradiation. Under these conditions, the mineral phase did not influence the formaldehyde decomposition, and these results agreed with the quantification of the formic acid (radiolytic product of formaldehyde irradiation). The highest concentration of formic acid observed in the formaldehyde–forsterite system was 0.002 M (Figs. 7 and 8).

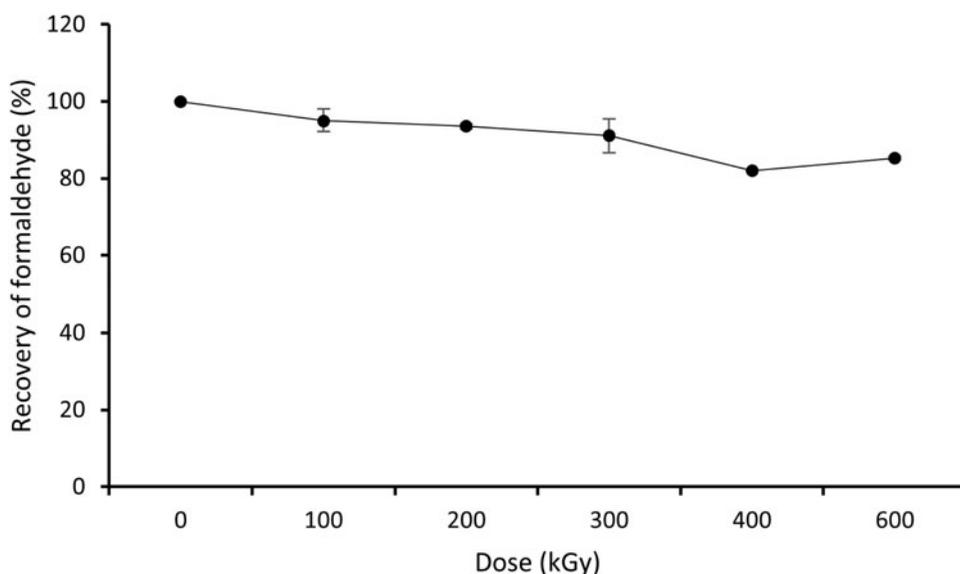


Fig. 5. Recovery of formaldehyde from frozen solutions after irradiation (0–600 kGy). Gas chromatography was performed to quantify the amount of formaldehyde recovered.

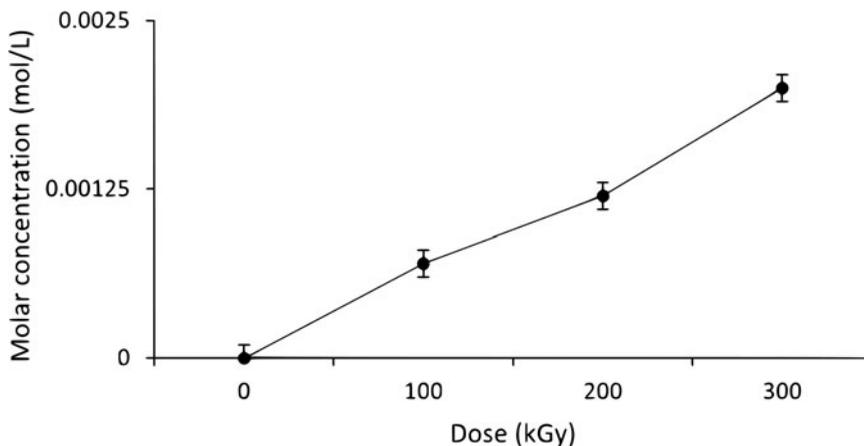


Fig. 6. Quantification of formic acid in the irradiated formaldehyde samples by titration. The frozen solutions of formaldehyde were irradiated from 0 to 300 kGy.

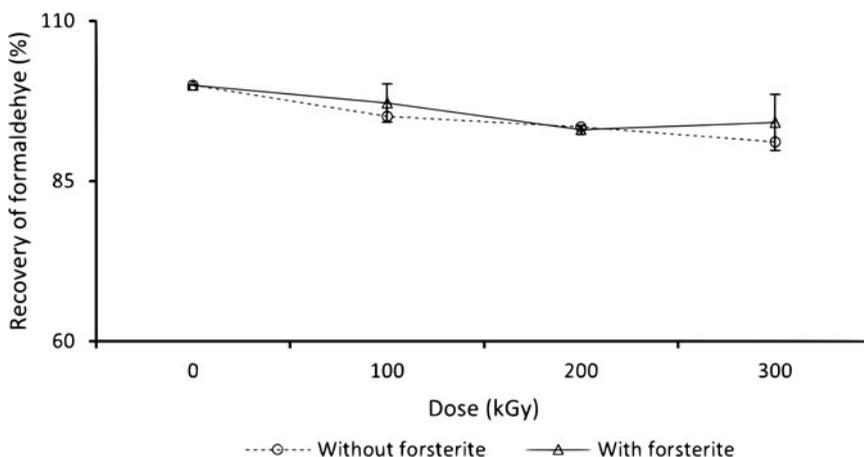


Fig. 7. The recovery of formaldehyde in the frozen systems with and without forsterite after irradiation (0–300 kGy) quantified by gas chromatography.

Discussion

It has been proposed that comets delivered organic compounds to the early Earth (Chyba *et al.*, 1990). The organic content of comets is crucially important in prebiotic chemistry and the origin of life. The presence of important molecules, such as H_2O , C_2H_6 , C_2H_4 , HCN , CO , CH_3OH , H_2CO , C_2H_2 and CH_4 , was confirmed on Comet 9P/Tempel 1 by the Deep Impact mission (Mumma *et al.*, 2005). When the Giotto, Vega 1 and Vega 2 missions flew by the comae of the comets Halley, Hyakutake and Hale-Bopp in 1986 (Henbest, 1986; Hornung *et al.*, 1986; Fray *et al.*, 2016), they confirmed 30 organic and inorganic compounds, including formic acid and formaldehyde. As comets are maintained in the outer solar system, they have conserved the solar nebula composition. However, researchers have proposed that comets have been exposed to radiation for over 4.6 billion years from an internal source due to radionuclides embedded in the comet and from external sources of cosmic radiation (Donn, 1977; Whipple, 1977; Draganić and Draganić, 1984).

Comet irradiation

Significant radiation processing of comets is expected when they enter the solar system. Therefore, the molecules observed during the passage of comets near the Sun result from the irradiation of icy

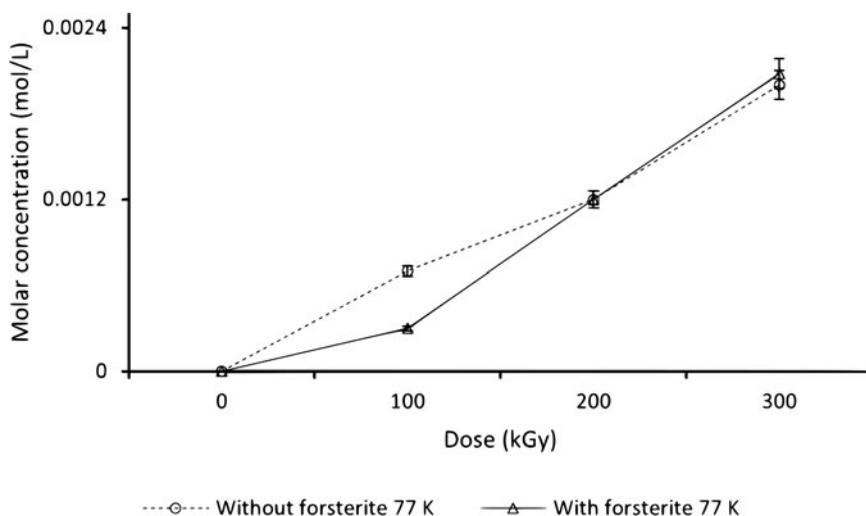


Fig. 8. Formic acid quantification by titration of the frozen solutions of formaldehyde with and without forsterite.

materials at low temperatures (Hudson and Moore, 1999), among other factors. Many of the products observed in the comae of comets are evidence of continuous transformation rather than direct sublimation of ice in the nuclei.

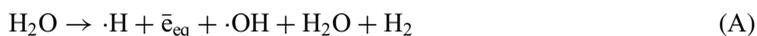
Considering their exposure to high-energy radiation, a radiation chemistry approach can be advantageous to study the behaviour of the molecules detected in comets. Cobalt-60 generates two high-energy emission lines (1.17 and 1.33 MeV) that are extremely penetrating. Numerous experiments have shown that radiation using the same or similar LET causes the same or similar radiation-induced chemical changes in a particular chemical system (Draganić and Draganić, 1971). The cobalt-60 photons, which have a low LET of $0.2 \text{ keV } \mu\text{m}^{-1}$, are a suitable tool for examining potential alterations brought on by high-energy cosmic ray protons, which have LET values comparable to the gammas of radioactive cobalt-60 at energies between 1 and 5 GeV. Thus, the average energy deposits along the radiation paths are comparable. The interaction with charged particles at GeV relativistic energies is undoubtedly far more complex than the interaction with gamma rays from cobalt-60, yet the average energy deposition per unit path length is comparable in both cases (Draganić and Draganić, 1984).

Experimental simulations aid in studying the chemistry of the formation and destruction of molecules in a comet and predict the formation of more complex molecules based on those already detected. Due to the high penetration of gamma rays, the irradiation reaches the bulk of the solution (in the experimental model). Our focus was to study the behaviour of formic acid and formaldehyde under high-energy irradiation and in the presence of an inorganic compound (graphite or forsterite).

Water ice is the most abundant icy component in astrophysical environments and comets (Ehrenfreund *et al.*, 2002; Zheng *et al.*, 2006). Energy deposition from the radiation occurs primarily in water ice, forming radicals that react with one or more compounds present in low concentrations ($\sim 0.1 \text{ M}$). In comet simulation experiments, ionizing radiation is an efficient promoter of chemical processes, potential synthesis and the subsequent chemical evolution of important prebiotic molecules (Spinks and Woods, 1990).

Frozen systems

As previously mentioned, ionizing radiation induces the radical formation, for example in the water molecule, as it is summarized in equation (A) (O'Donnell and Sangster, 1970; Spinks and Woods, 1990).



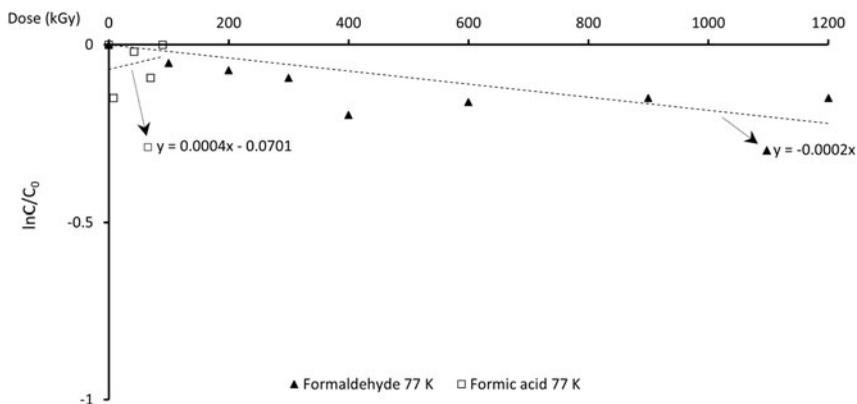


Fig. 9. Reactivity of formic acid and formaldehyde in frozen solutions (77 K).

The radicals formed react with themselves and with a solute present in the medium. However, at low temperatures the radical production and diffusion rate is lower than in liquid systems (Sanner, 1965; Burton and Magee, 1969; Spinks and Woods, 1990), this will yield less decomposition in a frozen system than in a liquid phase. To compare the rate of decomposition of formic acid and formaldehyde under irradiation in frozen solutions, the kinetic model proposed by Mincher and Curry (2000), Criquet and Leitner (2011, 2012) and Criquet *et al.* (2010) was applied (Fig. 9).

Although the model is purely descriptive and does not attempt to explain the entire physical and chemical processes of radiolysis, it can provide an understanding of the reactivity of the target compounds towards irradiation (Mincher and Curry, 2000; Criquet and Leitner, 2012). A pseudo-first-order approximation is made at a constant dose rate:

$$\ln C/C_0 = -k_0 D,$$

where k_0 is the dose constant; C_0 is the initial concentration; and C is the concentration at the absorbed dose, D (kGy). When the trend is linear, the slope is the dose constant. For the systems examined in the present study (Fig. 9), the evaluated dose constants were 0.0002 kGy^{-1} for formaldehyde and 0.0004 kGy^{-1} for formic acid (at 77 K).

These data show that formic acid is more sensitive to irradiation (Fig. 1) than formaldehyde (Fig. 5) because of the different rate constants (Fig. 9). At 77 K, the dose constant for formaldehyde is ten times lower than at 298 K (0.0038 kGy^{-1}), and the probability of survival in those conditions increases.

The role of minerals in frozen solutions

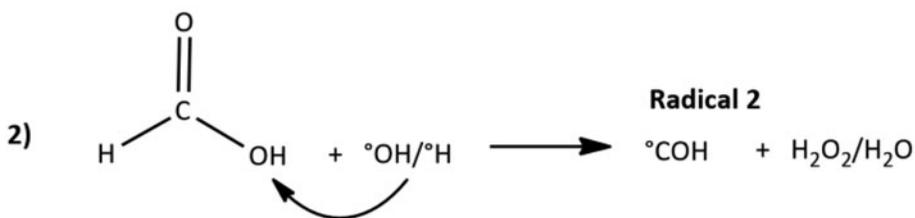
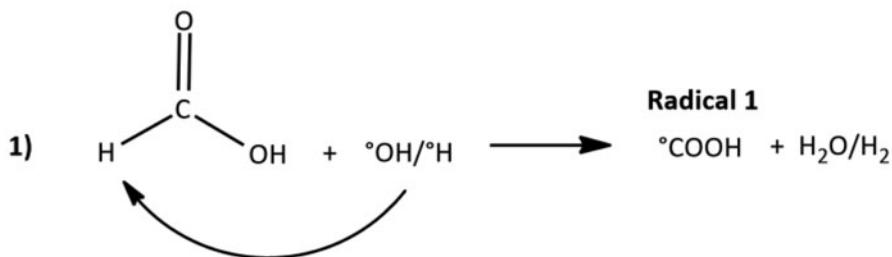
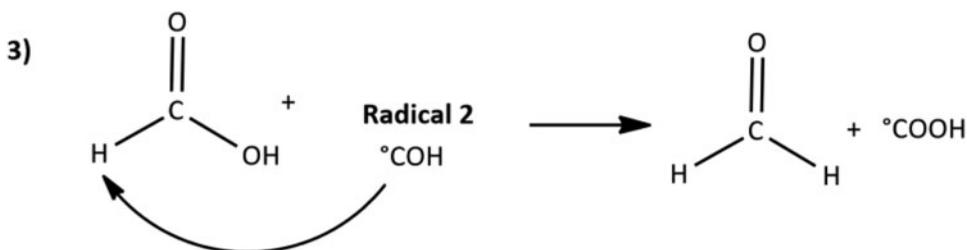
Mineral phases, such as olivine (forsterite) and solid carbon (as non-crystalline amorphous matter), are important components of comets (Messenger *et al.*, 2005). The catalysis capacity of some minerals and their role in forming organic compounds have been explored in meteorites (Anders *et al.*, 1973). However, limited data exist for comets. In the present study, two mineral phases, forsterite and graphite, were used to simulate the olivine and amorphous carbon detected on comets.

Frozen solutions of formic acid: Figures 2 and 4 show the chromatograms of the aldehydes and carbonyl-containing compounds detected in the irradiated frozen formic acid solutions under various experimental conditions. Our results suggest a differential distribution of aldehydes and carbonyl-containing compounds (Fig. 4, Table 1) that depends on the mineral phase used in the experiments.

The irradiated formic acid samples that did not contain minerals yielded an extremely limited number of compounds, and formaldehyde was the only aldehyde detected (Fig. 2). In equation (3) of Scheme 2, a potential mechanism for the formation of formaldehyde through abstraction reactions by radical $\cdot\text{COH}$ (Scheme 2) is proposed.

Table 1. Carbonyl-containing molecules identified in frozen solutions of formic acid with and without minerals

System	DNP derivatives identified
Frozen solution of formic acid	Formaldehyde
Frozen solution of formic acid containing graphite	Glyoxylic acid, formaldehyde and D compound
Frozen solution of formic acid containing forsterite	Glyoxylic acid, formaldehyde, acetaldehyde, B and D compounds

Reducing and oxidizing species of water radiolysis**Radical reactions****Scheme 2.** Proposed mechanisms for forming formaldehyde in frozen solutions of formic acid.

In contrast, the variety and number of radiolytic products increased in the presence of minerals. Graphite and forsterite promoted the synthesis of carbonyl-containing compounds in the formic acid solutions irradiated at low temperatures (77 K). In particular, the major number of carbonyl-containing compounds was detected in the systems that contained forsterite (Fig. 4, Table 1).

Although further studies are required to establish a mechanism for synthesizing these molecules, Li *et al.* (2018) have proposed adsorption processes as a first step in the catalysis reactions of organic compounds. The authors used forsterite and methanol in their experiments as starting materials to synthesize PAHs. They observed the oxygen atom of methanol binds to the silicon atom of forsterite, which leads to the elongation of the O-H bond of methanol and its subsequent rupture, resulting in the formation of radicals (Li *et al.*, 2018).

Although limited data exist regarding the role of carbonaceous material in the synthesis of prebiotic compounds, several aspects of its reactivity and structure are known. The properties of amorphous carbon suggest that the randomness of its structure and its lack of long-range order results in a higher proportion of chemically active sites (Duley and Williams, 1981). Therefore, amorphous carbon is reactive concerning the sorption of atoms and molecules at these sites. This high reactivity promotes interaction with a wide variety of chemical species and potential catalytic reactions.

Frozen solutions of formaldehyde: As illustrated in Figs. 7 and 8, in the formaldehyde systems containing forsterite that were irradiated, no significant changes were observed in the decomposition of formaldehyde or the formation of its radiolytic product (formic acid). This was most likely driven by the low reactivity of formaldehyde at 77 K (Fig. 9) and not by the catalytic activity of forsterite.

Relevance of the radiolytic products of formic acid and formaldehyde in prebiotic chemistry

Aldehydes are of prebiotic interest because they are precursors to pre-biological molecules such as sugars and amino acids (Cleaves, 2008). In the present study, formaldehyde, acetaldehyde and glyoxylic acid were detected in the formic acid samples after irradiation. These compounds are useful precursors to more complex molecules.

Under basic conditions, formaldehyde is the raw material for synthesizing sugars through the formose reaction (Cleaves, 2008). Conversely, acetaldehyde has been reported as a precursor of acrolein, which is involved in synthesizing amino acids and alternative genetic materials (Cleaves, 2002, 2003). Similarly, glyoxylic acid participates in the synthesis of nucleobases (Menor-Salván and Marin-Yaseli, 2013).

Conclusion

Comets are the prime candidates to link cosmic phenomena to the origin of life. They are a source of raw materials and water to initiate chemical evolution on early Earth. However, comets are surrounded by a radiative environment that may affect prebiotic molecule stability. The ionizing radiation is primarily generated by highly penetrating energetic particles, and the energy delivery is mainly produced on the surfaces of icy bodies up to several metres deep. Embedded radionuclides are the other source of ionizing radiation. Our investigation suggests that prebiotic molecules, such as formaldehyde, in comet simulations can withstand high radiation via two mechanisms: (a) a frozen system is a protective mechanism in degradative environments. Solid material, such as water ice, tends to modulate the energy of radiation. Thus, the radical production and diffusion rate decreases, as well as the decomposition of formaldehyde. (b) The separate irradiation of frozen solutions of formic acid and formaldehyde constitutes a redundant system, i.e. the irradiation of formic acid forms formaldehyde and *vice versa*. This system is capable of regenerating prebiotic molecules through interconversion.

Finally, the response of the minerals will depend on the type of organic molecule with which they interact. In the frozen solutions of formic acid that contained forsterite, aldehydes and other carbonyl-containing compounds were detected. In contrast, in the frozen solutions of formaldehyde, the presence of forsterite did not contribute to the formation of products.

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Conflict of interest. None.

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