

Radiolysis of the Glycolaldehyde-Na⁺Montmorillonite and Glycolaldehyde-Fe³⁺Montmorillonite Systems in Aqueous Suspension under Gamma Radiation Fields: Implications in Chemical Evolution

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Abstract The stability and reactivity of organic molecules with biological and pre-biological significance in primitive conditions are of paramount importance in chemical evolution studies. Sugars are an essential component in biological systems for the different roles that they play in living beings. The objective of the present work is to study the gamma radiolysis of aqueous solutions of glycolaldehyde, the simplest sugar and aqueous suspensions of glycolaldehyde-Na⁺-montmorillonite and glycolaldehyde-Fe³⁺Montmorillonite. Our results indicate that the radiolysis of the aqueous solutions of glycolaldehyde (0.03M), oxygen free, mainly produce the linear dimer known as eritriol (122 g/mol) and a sugar-like compound with six carbon atoms (180 g/mol). The experiments with the clay suspensions show that clays can adsorb glycolaldehyde and protect it from gamma irradiation. Additionally, it was observed that depending on the cation present in the clay, the percentage and the product (monomer or cyclic dimer) adsorption was different. In the case of Fe³⁺ Montmorillonite, this clay catalyzed the decomposition of glycolaldehyde, forming small amounts non-identified products. The analysis of these systems was performed by ATR-FTIR, UV spectroscopy, liquid chromatography (UHPLC-UV), and HPLC coupled to a mass spectrometry.

Keywords: Glycolaldehyde, gamma radiation, chemical evolution, clay

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1. INTRODUCTION

Carbohydrates are compounds with a minimal formula $(\text{CH}_2\text{O})_n$ that play a paramount role in biological systems [2,6] since they participate in several essential functions like (1) the energetic metabolism and (2) as structural molecules in the ribose-phosphate backbone in DNA or RNA. For these roles, sugars are compounds of high interest in the context of the chemical evolution. Their abiotic synthesis, the stability of these in the surrounding environment, and the types of reactions that can participate are important steps in trying to describe how the first self-replicable systems emerged. Glycolaldehyde ($\text{C}_2\text{H}_4\text{O}$) is the simplest sugar that has been detected in the interstellar medium [4, 5]. Also, it is intermediate for the synthesis of more complex sugars in abiotic reactions.

In chemical evolution, the stability of bio-organic compounds, like carbohydrates, in the surrounding geological environment is crucial, especially in the presence of an external energy source (e.g. ionizing radiation, thermal energy, etc.) [1]. Among the proposed mechanism for increasing the stability of organic compounds, in a plausible geological scenario is their adsorptions onto mineral surfaces [7, 8]. Several solid surfaces may have been relevant in this context: sulfides, carbonates, and clays [9].

In this work, we highlight the type of reactions that sugars can have under gamma irradiation, and the possible role of clay minerals as a protecting agent for the bio-organic molecules adsorbed. Clay minerals are relevant due to their adsorption capacity, ancient origin, and their broad geological distribution. This work is focused on the radiolysis of glycolaldehyde adsorbed in two clay minerals: Na^+ -montmorillonite and Fe^{3+} -montmorillonite under a high radiation field. To this end, the radiolysis of both systems was carried out by exposing them to a different irradiation dose. The analysis of these systems was performed by ATR- FTIR, UV spectroscopy, liquid chromatography (UHPLC-UV), and HPLC-coupled to a mass spectrometry.

2. EXPERIMENTAL

2.1 Chemicals and Materials

The chemicals were purchased from Sigma-Aldrich Co. (USA) and were of the highest purity available in the market (glycolaldehyde dimer, ammonium acetate, $\text{FeCl}_3 \cdot 5\text{H}_2\text{O}$). The HPLC-grade solvents (water and methanol) were purchased from Honeywell Burdick & Jackson (NJ, USA). The glassware was treated with a warm mixture of HNO_3 and H_2SO_4 for 20 minutes, followed by a wash with distilled water and heating in an oven at 300°C overnight. All of the chemical and glassware were handled to minimize contamination [11].

The clay used in the reactions (Na⁺-montmorillonite SWy-1) was obtained from Clay Minerals Repository of the Clay Minerals Society at the University of Missouri. It was treated with hydrogen peroxide to remove organic impurities; the same lot was used in all the experiments. Fe³⁺-montmorillonite was prepared from Na⁺-montmorillonite by an ion exchange reaction [3]. For this, 1N solutions of FeCl₃·5H₂O were prepared to exchange the Na⁺ cations in the clay with the desired Fe³⁺ ions.

2.2 Preparation of samples

Standard stock solutions of glycolaldehyde were prepared using triple distilled water, oxygen-free by bubbling Ar for 20 minutes. Then, 3 mL of the solution (0.03 M) and 100 mg of clay were placed in sealed culture tubes followed by shaking at 250 rpm for 20 minutes. All of the solutions were stored in a refrigerator at 4°C while not in use.

2.3 Irradiation of Samples

All samples were irradiated at room temperature using a high-intensity ⁶⁰Co gamma source (Gammabeam 651 PT) at ICN-UNAM, at two different doses (14 and 29 kGy), and with a dose rate of 240 Gy/min. The dose was evaluated using a ferrous sulfate, copper sulfate dosimeter [10]. The samples were analyzed immediately after irradiation.

2.4 Analysis of samples

2.4.1 HPLC-ESI-MS analysis

The liquid chromatographic analysis was performed on an HPLC system (515-pump from Waters Corp.), coupled with a Single Quadrupole Mass Detection system (SQ-2 manufactured by Waters Corp.), with an electrospray ionization negative mode (ESI-), a positive mode (ESI+) source cone energy of 15V, and a capillary energy of 3kV. The analysis was done in Symmetry C18 column (4.6 x 75mm, 3.5 μm spherical particle size, by Waters Corp.) under an isocratic elution of a mobile phase (0.1M ammonium acetate solution; 80% methanol and 20% water at pH=4), and at a constant flow of 0.4 mL/min. A sample volume (20 μL) was injected using a loop.

2.4.2 UHPLC-UV analysis

The ultra high-pressure liquid chromatography analysis was performed on an UHPLC system Ultimate 3000, manufactured by ThermoFisher Scientific (UltiMate™ ISO-3100SD standard isocratic pump and an UltiMate™ 3000 TCC-3000SD Standard Thermostatted Column Compartment), and coupled

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with Variable Wavelength UV-Vis Detectors, Thermo Scientific™ Dionex™ UltiMate™ 3000 VWD. The analysis was done on a Symmetry C18 column (4.6 x 75 mm, 3.5 μm spherical particle size by Waters Corp), at 50°C under an isocratic elution of mobile phase (0.1 M ammonium acetate solution; 80% methanol, 20% water at pH=4), at a constant flow of 0.4 mL/min, monitored at 260 nm. A sample volume (20 μL) was injected using a loop.

2.4.3 ATR-FTIR

Infrared spectra were obtained by the attenuated total reflection (ATR) sampling technique on Spectrum 100 spectrometer FTIR equipment manufactured by PerkinElmer (USA).

3. RESULTS

Glycolaldehyde in solid state is mainly found as a dimer (Figure 1) with a molecular weight of 120 g/mol and melting point of 85°C. It was identified by its IR spectrum (Figure 2) due to the presence of the characteristic band of alcohols at 3394 cm⁻¹, band of ethers at 1134 cm⁻¹, and by the absence of the carbonyl group tension bands in 1740–1720 cm⁻¹ and in 2800 and 2700 cm⁻¹ (Fermi resonance) characteristic of aldehydes.

The results indicate that the cyclic dimer of glycolaldehyde in aqueous solution is hydrolyzed to form four species that are in chemical equilibrium (Figure 3A) [11], which were identified by their molecular ions in an MS detector by direct infusion with an ESI-source (Figure 3B).

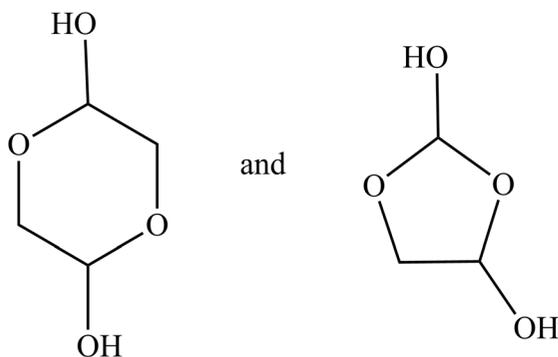


Figure 1: Structure of cyclic dimers of glycolaldehyde in aqueous solution $3 \times 10^{-2}M$.

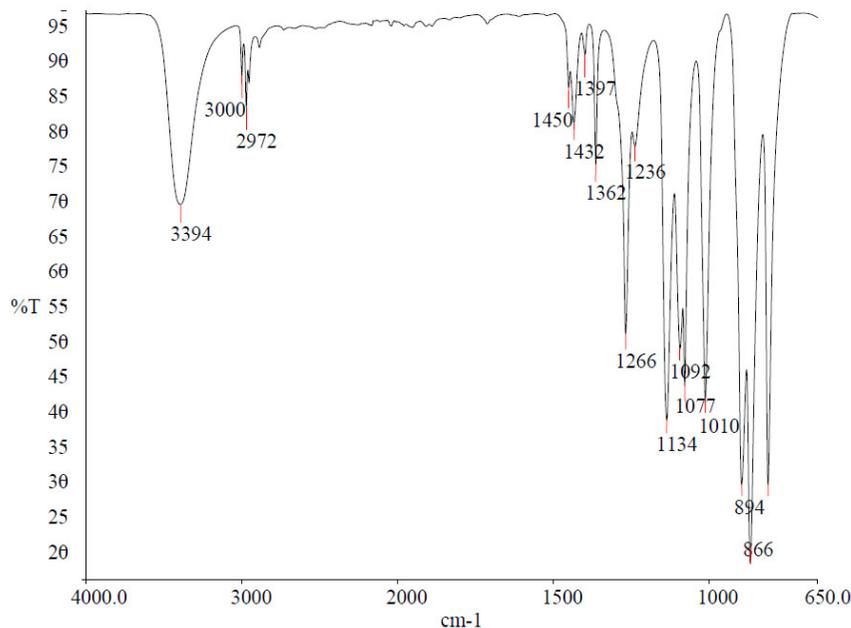


Figure 2: ATR-FTIR spectrum of glycolaldehyde.

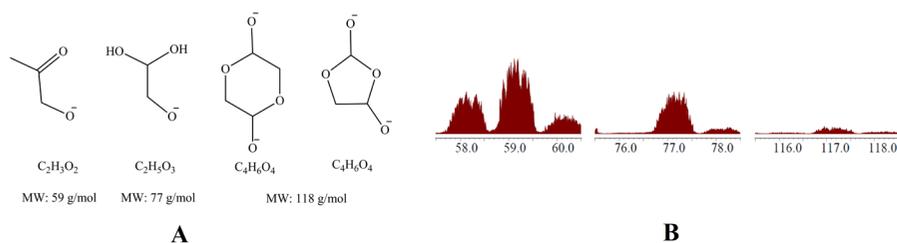


Figure 3: Chemical species of glycolaldehyde in aqueous solution identified by MS detector ESI-source.

The main reaction of glycolaldehyde in aqueous solution under gamma irradiation is the polymerization in which the main products are the linear dimer (Figure 4A) known as eritriol (122 g/mol) and the cyclic dimer (120 g/mol) Figure 4B. Also, a higher molecular weight molecule was detected, and it is a sugar-like compound, with six carbon atoms (180 g/mol) Figure 4C. Identified by their respective fragmentation spectra obtained by the HPLC-ESI-MS analysis.

The polymerization reaction of glycolaldehyde was monitored by UHPLC-UV analysis with the retention times: 1.7 minutes for the dimer and

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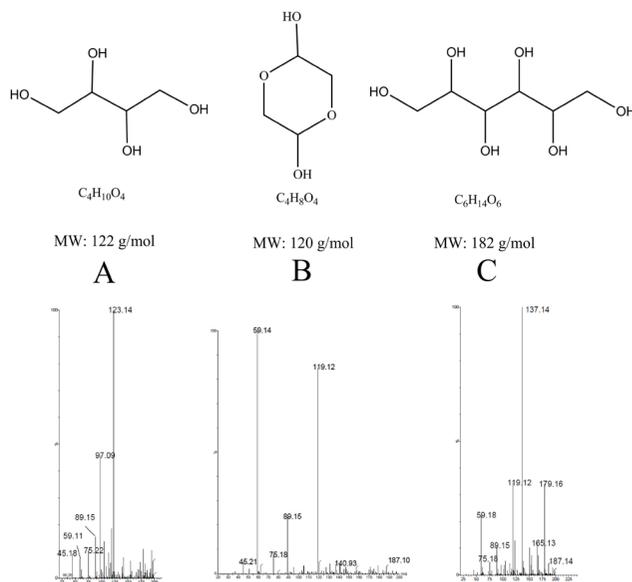


Figure 4: MS fragmentation spectra products of radiolysis.

1.8 minutes for the monomer (Figure 5); the formation of the dimers and other polymers is dependent on the irradiation dose; if it is high, the irradiation dose also increases (Figure 6).

The possible reaction mechanism for the radiolysis is shown in Fig. 7. The results of UHPLC-UV analysis show that Fe^{3+} -montmorillonite preferentially adsorbed the glycolaldehyde monomer by 97% (retention time: 1.7 minutes) to the cyclic dimer (retention time: 1.8 minutes). However, Na^+ montmorillonite

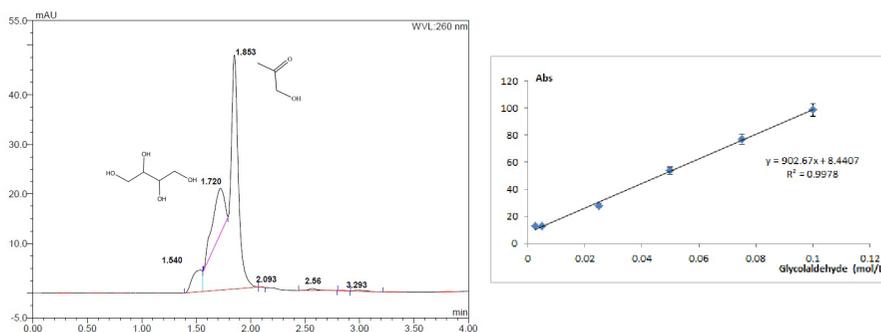


Figure 5: HPLC-UV analysis of glycolaldehyde at 260nm.

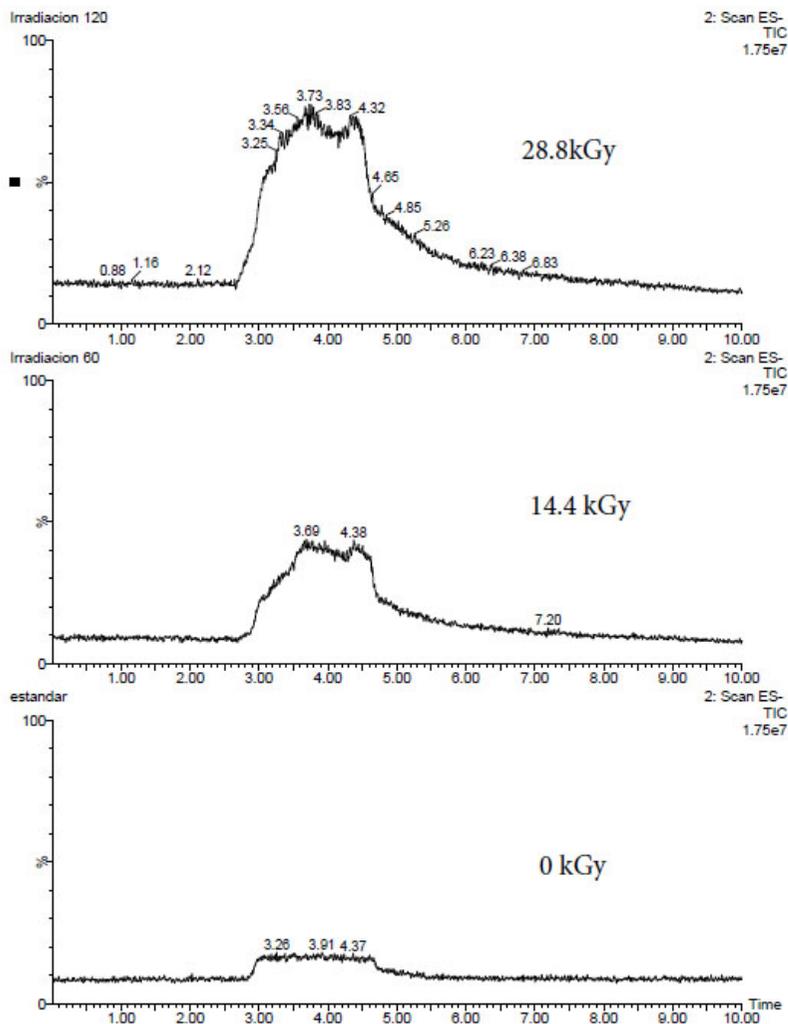


Figure 6: TIC HPLC-MS analysis of glycolaldehyde.

adsorbs the cyclic dimer preferentially (75%, retention time 1.8 minutes), as it is showed in Figure 8. Both clays were able to protect the glycolaldehyde adsorbed onto them when the clay-organic systems were exposed to gamma radiation, since the recovery of glycolaldehyde after the irradiation and desorption processes was higher, and the polymers were formed in smaller quantities than those in the experiments without clay.

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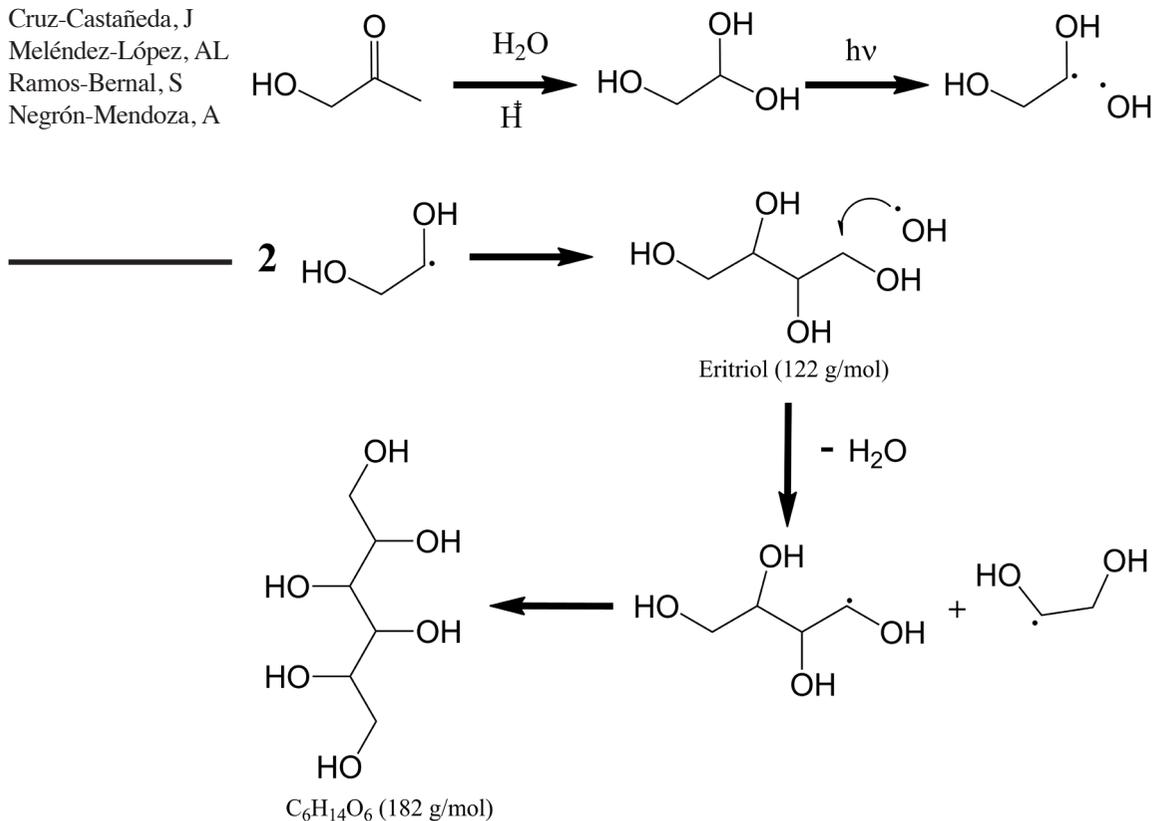


Figure 7: The suggested mechanism for the formation of polymers from the glycolaldehyde radiolysis Radiolysis of glycolaldehyde-clay suspensions.

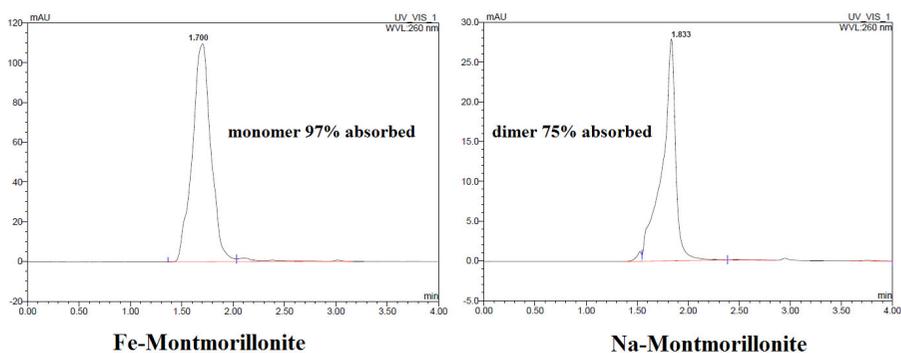


Figure 8: Adsorption experiments analyzed by UHPLC-UV in the aqueous phase.

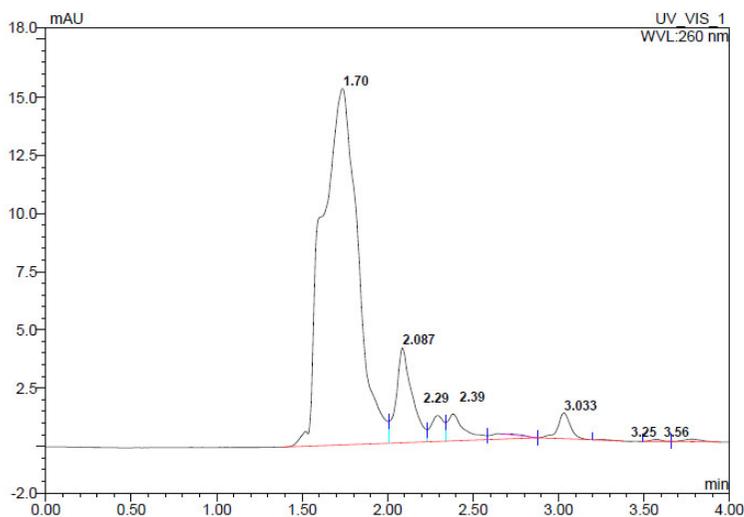


Figure 9: Adsorption experiments analyzed by UHPLC-UV.

Additionally, it was found that Fe³⁺ montmorillonite promotes chemical reactions in the aqueous suspension with glycolaldehyde without gamma radiation, since, after the adsorption and desorption experiments, low-yield reaction products were detected by UHPLC-UV. These products are not yet identified, and they presented retention times of 2.087, 2.29, 2.39, and 3.033 minutes (Figure 9).

REMARKS

The sugars are bio-compounds of paramount importance in biological systems. For this reason, it is relevant to find the possible physicochemical and geological conditions of its possible abiotic synthesis and the mechanisms of its polymerization in chemical evolution studies. Sugar-like compounds may have been important intermediates in the reaction mechanisms for the synthesis and polymerization of sugars used by early biological systems. The results obtained indicate that the glycolaldehyde in aqueous solution in the presence of a high energy source is polymerized forming sugar-like compounds.

Glycolaldehyde adsorbed onto clays minerals and exposed to gamma irradiation presented a higher yield of recovery in comparison with the samples without clay. Also, it was found a preferential adsorption of the monomer and cyclic dimer of glycolaldehyde by the different clays used in these experiments. Energy sources, as well as the presence of solid surfaces, played diverse roles

Cruz-Castañeda, J in the chemical evolution, such as catalysts, reaction directing agents, and
Meléndez-López, AL especially as protective agents for compounds of biological significance.
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