Molecular Investigation of the Multi-Phase Photochemistry of Fe(III)-Citrate in Aqueous Solution

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Environmental significance: Photocatalytic reactions of Fe^{III}-carboxylate complexes in nature play an important role in oxidation of dissolved organic constituents and control bioavailability of iron for development of microbial life. This work presents an experimental study on the molecular photochemistry of an Fe-citrate model system, describing in detail the sequence of its photochemical reactions in the aqueous solution. We characterize water soluble organic and Fe-organic components of the reaction system and reveal formation of insoluble colloidal products containing carbon in reduced oxidation state. The analytical and physical chemistry methods presented in this work can be extended to study photochemistry of other Fe-carboxylate systems.

Molecular Investigation of the Multi-Phase Photochemistry of Fe(III)-Citrate in Aqueous Solution

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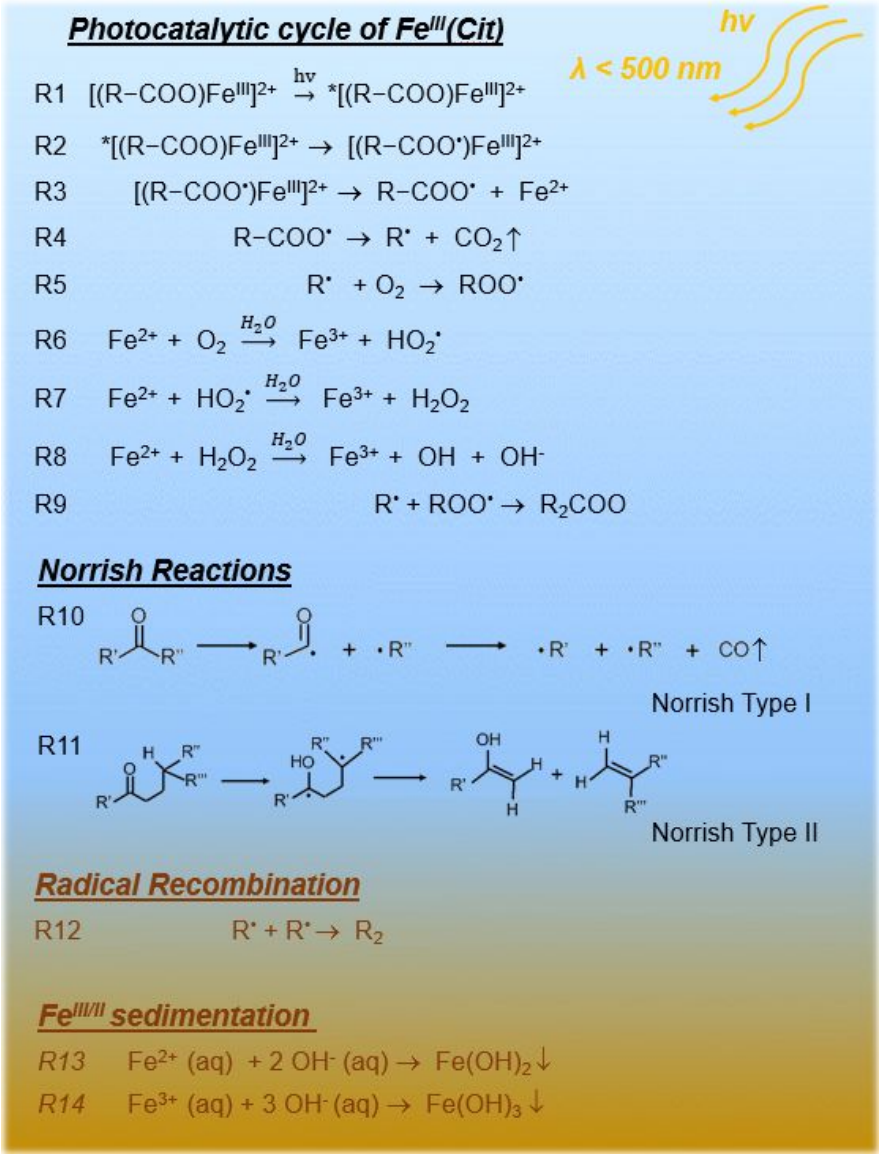
Abstract: Iron (Fe) is ubiquitous in nature and found as Fe^{II} or Fe^{III} in minerals or as dissolved ions Fe^{2+} or Fe^{3+} in aqueous systems. The interactions of soluble Fe have important implications on fresh water and marine biogeochemical cycles, which have impacts on global terrestrial and atmospheric environments. Upon dissolution of Fe^{III} into natural aquatic systems, organic carboxylic acids efficiently chelate Fe^{III} to form $[Fe^{III}\text{-carboxylate}]^{2+}$ complexes that undergo a wide range of photochemistry-induced radical reactions. The chemical composition and photochemical transformations of these mixtures are largely unknown, making it challenging to estimate their environmental impact. To investigate photochemical processing of Fe^{III}-carboxylates at molecular-level, we conduct comprehensive experimental study employing UV-visible spectroscopy, liquid chromatography coupled to photodiode array and high-resolution mass spectrometry, and oil immersion flow microscopy. In this study, aqueous solutions of Fe^{III}-citrate were photolyzed under 365 nm light in an experimental setup with an apparent quantum yield of (Φ) ~ 0.02, followed by chemical analyses of reacted mixtures withdrawn at increment time intervals of the experiment. The apparent photochemical reaction kinetics of Fe^{3+}-citrates (aq) were expressed as two generalized consecutive reactions of *Reactants* (*R*) $\xrightarrow{j_1}$ *Intermediates (I)* $\xrightarrow{j_2}$ *Products (P)* with the experimental rate constants of j_1 ~ 0.12 min^{-1} and j_2 ~ 0.05 min^{-1}, respectively. Molecular characterization results indicate that *R* and *I* consist of both water-soluble organic and Fe-organic species, while *P* compounds are a mixture of water-soluble and colloidal materials. The latter were identified as Fe-carbonaceous colloids formed at long photolysis times. The carbonaceous content of these colloids was identified as unsaturated organic species with low oxygen content and carbon with reduced oxidation state, indicative of their plausible radical recombination mechanism at oxygen-deprived conditions typical for the extensively photolyzed mixtures. Based on the molecular characterization results, we discuss the comprehensive reaction mechanism of Fe^{III}-citrate photochemistry and report on the formation of previously unexplored colloidal reaction products, which may contribute to atmospheric and terrestrial light-absorbing material in aquatic environments.

Keywords: water soluble Fe, Fe-carboxylate complexes, photolysis, reactive oxygen species (ROS), semi-solid colloids, liquid chromatography (LC), UV-visible spectroscopy, high resolution mass spectrometry (HRMS), flow microscopy

INTRODUCTION

Iron (Fe) is the most common element on Earth by mass, and found in atmosphere, biosphere, lithosphere, and hydrosphere.[1,2] A majority of Fe is associated with the solid form of rocks of crustal matter in oxygen-deficient settings,[3] whereas soluble and colloidal Fe-containing species are present in oceanic and terrestrial water environments.[4–6] Atmospheric Fe is also naturally abundant in wind-blown mineral dust and other components of particulate matter (PM).[7–13] The interactions, transport, and environmental fate of elemental Fe are vital in the Fe biogeochemical cycle and necessary to sustain life and facilitate important environmental processes.[14,15] The soluble fractions of Fe from Fe-bearing materials[16–18] are mobilized in aquatic environments as a result of various chemical processes such as photolysis and reactions with inorganic acids. Upon dissolution of Fe into aquatic aerobic systems (pH 4 – 8), available organic carboxylic acid components of dissolved organic matter (DOM) efficiently chelate Fe^{3+} ions to form photocatalytically active [Fe^{III}-carboxylate]$^{2+}$ complexes that promote radical reactions in the aquatic phase. Upon excitation by UV-visible light, the photochemically initiated radical reactions modify the composition of DOM with subsequent effects on optical and physical properties of the environmental aquatic systems.[19]

Molecular-level characterization of reactive components in the Fe-carboxylate photochemical systems is still largely lacking and reported results remain ambiguous. Previous studies utilized optical spectroscopy,[20–24] electrochemistry,[21] and liquid chromatography with optical detection[25] to infer reaction mechanisms and system properties solely from measurements of the bulk solution, but not for the molecular-specific components. However, unravelling the molecular-specific processes leading to the conversion of solid Fe^{III} to soluble Fe^{3+}, Fe^{3+} complexation with carboxylic acids, and the environmental reactions of [Fe^{III}-carboxylate]$^{2+}$ complexes are still needed for quantitative predictions of Fe^{III}-carboxylate photochemistry in aquatic systems.



Scheme 1. Reaction sequence of the photo-catalytic redox cycle of Fe^{III}-citrate complex in aquatic environment. R in reactions R1-R5 and R9 corresponds to $-(CH_2CO_2H)_2COH$, ‘R, “R, and “‘R symbols indicate various parts of organic molecules. Mononuclear monocitrate (or 1:1 complex, $[(R\text{-}COO)Fe^{III}]^{2+}$) is shown here as a representative complex in the reaction scheme. Herein, legends of Fe^{2+} and Fe^{3+} refer to dissolved ions, whereas legends of Fe^{III} and Fe^{II} indicate complexation with ligands.

Photoreactive Fe^{III}-carboxylate complexes absorb light at wavelengths below 500 nm, which catalyzes ligand to metal charge transfer (LMCT) reactions, resulting in the reduction of Fe^{III} to Fe^{II} and oxidation of the carboxylate ligands, a process that represents an important sink of organic acids in marine, terrestrial, and atmospheric water.[22,26–31] Scheme 1 summarizes these and other

relevant aquatic reactions. The LMCT process occurs as a result of an electron transfer from the innermost sp^3 orbital of the carboxylate ligand to the metal center, forming $[Fe^{III}\text{-}COO\text{-}R]^{2+*}$-excited state and the $[Fe^{III}\text{-}COO^{\bullet}\text{-}R]^{2+}$ radical complex, as shown in R1-R2.[32] The equivalent lifetime of the intermediate radical complex, determined in previous studies,[24,33–35] was found to be on the order of a few milliseconds, after which it decomposes into Fe^{2+} and $R\text{-}COO^{\bullet}$ as shown in R3. Further reactions of Fe^{2+} and $R\text{-}COO^{\bullet}$ lead to loss of CO_2 as shown in R4, forming alkyl radicals ($R^{\bullet}$).[36–38] Organic peroxy radicals ($RO_2^{\bullet}$) are later formed in the reaction with oxygen (O_2) as shown in R5.[39] Additional reactions of Fe^{2+} ions with dissolved O_2 lead to the formation of reactive oxygen species (ROS)[40–42] such as $HO_2^{\bullet}$, hydrogen peroxide (H_2O_2), and hydroxyl radicals ($OH^{\bullet}$)[43–45] while cycling Fe^{2+} back to Fe^{3+} through the Fenton reaction,[46] as shown in R6-8. The ROS species react further with a variety of organic and inorganic compounds in aqueous solution.[47–50] Subsequently, organic peroxy radicals ($ROO^{\bullet}$) in solution may decompose into smaller organic acid fragments such as oxygenated volatile organic compounds (OVOC), or undergo radical recombination reactions as shown in R9, and R12 resulting in production of larger oligomeric species.

Radical species with carbonyl groups formed after decarboxylation, may undergo Norrish type I and II reactions as shown in R10-11,[51–54] triggering radical chain reactions with O_2 and various organic compounds. Norrish reactions produce carbon monoxide (CO) and carbon-centered radicals (CCRs), such as methyl ($^{\bullet}CH_3$), methyl ketones ($O{=}^{\bullet}C\text{-}CH_3$), and triphenylmethyl ($^{\bullet}C(C_6H_5)_3$), among other radicals.[55] As a result, the dissolved oxygen is effectively consumed, while the CO_2 and CO products are degassed, resulting in oxygen-deficient conditions after prolonged photolysis. As shown in R12, radical recombination forms compounds with lower oxygen content and carbon in reduced oxidation state. These products have much lower solubility than oxygenated organic carbon and therefore may contribute to the buildup of insoluble photomineralization products.[56,57] In addition to the reduced carbon colloids, precipitation of insoluble iron hydroxides,[19] $Fe(OH)_2$ and $Fe(OH)_3$, can take place as shown in R12-13,[58,59] which further contributes to the formation and growth of colloid particles. The insoluble colloids of mixed $Fe(OH)_3$/carbonaceous composition exhibit substantially larger light extinction properties than the water-soluble components in the same mixtures.[60]

Multiphase aquatic photochemistry of Fe^{III}-citrate has been studied [20,25,41,55,61,62] as a laboratory proxy for the environmental Fe^{III}-carboxylate systems. To date, the production and detection of gas-phase OVOC upon photolysis of Fe^{III}-secondary organic aerosol proxies containing carboxylic acids in flow reactors[63] have been investigated. Other studies reported changes in the microphysical properties, chemical composition, and ROS capacity of viscous Fe-citrate particles levitated in electrodynamic balance and probed by spectromicroscopy after exposure to UV light.[41,55] These studies[41,55] demonstrated significant photochemical degradation after 24 hours of irradiation, resulting in ~ 80% mass loss of particles due to degassing of CO_2 and OVOC, and slow uptake/molecular diffusion of O_2 in the particle phase, consistent with reactions R1-8 of Scheme 1. The combination of these studies provides surface and physical property characterization results. However, molecular-level composition, optical properties, and extent of the photochemical reactions occurring in the condensed phase are still insufficiently investigated. This knowledge gap precludes quantitative predictions of the photocatalytic processing for Fe-carboxylate systems and their consequences on environmental systems.

In this work, the chemical composition and optical properties of aqueous Fe^{III}-citrate photocatalytic components were investigated using high-performance liquid chromatography coupled to a photodiode array and high-resolution mass spectrometry (HPLC-PDA-HRMS) detectors,[64–71] and were further evaluated with direct infusion (DI) HRMS chemical analysis.[66,70,72] Colloidal products produced during photolysis reactions were imaged with *in situ* oil immersion flow microscopy. Multi-modal datasets from these complementary techniques provide a unique experimental description of various stages of Fe^{III}-citrate photochemistry, elucidate individual components of this reacting system, determine mechanistic insights, and quantify environmental parameters affecting the Fe^{III}-carboxylate photochemistry.

EXPERIMENTAL METHODS

Sample Preparation 10mM stock solutions of ferric citrate ($C_6H_5O_7Fe$, 16.5 – 18.5 % Fe basis, BioReagent, CAS: 3522-50-7; Sigma Aldrich Inc.) and of citric acid ($C_6H_8O_7{\cdot}H_2O$; 99% purity, Mallinckrodt Inc.) analytical blank for HPLC analysis were prepared in 100mL borosilicate volumetric flasks using 18.1 MΩ cm^{-1} Milli-Q ultrapure water. The stock solutions were wrapped

in aluminum foil (Fisher Inc.) and stored in a refrigerator at ~5 °C. The ferric citrate stock solution were further diluted to ~ 9.0 x 10^{-5} M (90 μM) in the ultrapure water and were set to equilibrate for ~ 2-24 h in the dark prior to chemical characterization, as recommended in the literature.[73,74]

Photochemical Experiments and Optical Spectroscopy measurements. A custom-built photolysis reactor setup employing a constant wavelength light emitting diode (LED) that emits blue light at ~ 365 ± 9 nm (Model: M365LP1; Thor Labs Inc.) was placed ~ 20 cm above the sample compartment (qpod2e, Quantum Northwest Inc.). The sample was placed in a 10 mm quartz cuvette (Vernier Inc.). The mounted UV- LED optics and adjusted collimator lens in these experiments resulted in an illuminated cross-sectional area of 0.78 ± 0.05 cm^2. All experiments were conducted at room temperature (~ 24-26 °C), and temperature was monitored throughout the reaction. Additional details of the experimental methods and instrumentation parameters are described in Figure S1 (Appendix A of the SI file). UV-Visible absorption spectra of the photolyzed solutions were acquired using a USB 2000 UV-Vis-NIR (Ocean Optics Inc.) fiber optic spectrophotometer. The samples were analyzed over the 200 – 900 nm wavelength range employing 20 ms integration time, 6 scans to average, and boxcar width of 4.

The spectral flux of the LED radiation (F_{LED}) experienced by the samples was experimentally determined by the chemical actinometry method using a 1 mM solution of potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$; Sigma-Aldrich) in 0.05M sulfuric acid (Honeywell Inc.), described by Lehóczki et al., 2013.[75] The decrease in absorption of ferrioxalate ($\varepsilon_{Fe\text{-}Ox}$ ~ 312 ± 2 L mol^{-1} cm^{-1} at 390 nm)[75] as a function of irradiation time was measured and converted to the F_{LED} ~ 3.85 x 10^{15} photons cm^{-2} s^{-1} at 365 nm, with a quantum yield, Φ ~ 1.26. Description and results of flux calculations is provided in Appendix B and Figure S2 of the SI file.

Quantitation of Dissolved Fe^{2+} Quantification of Fe^{2+} concentrations in irradiated solutions employed colorimetric tests with 1,10-phenanthroline ($C_{12}H_8N_2$; ≥ 99% purity, Sigma-Aldrich Inc.), whereby dissolved Fe^{2+} ions and 1,10-phenanthroline form a red-orange complex that absorbs visible light at ~ 510 nm.[76,77] For analysis, 0.5 mL of analyte sampled at 0, 5, 20, 40, 80, and 120 min irradiation time were mixed with 1.5 mL of 5mM 1,10-phenanthroline and filled to 3mL with 1mL of 18.1 MΩ cm^{-1} Milli-Q ultrapure water. Quantitative [Fe^{2+}] measurements were

performed in triplicate to establish reproducibility. For calibration, chemical standards of Fe^{II} perchlorate hydrate ($Fe(ClO_4)_2 \cdot H_2O$; 98% purity, Sigma Aldrich Inc.), ranging from 1-90 μM concentrations, were mixed with 5 mM 1,10- phenanthroline, and their respective absorbances were measured and recorded via a seven-point calibration curve (Figure S3 in SI file). The limit of detection (LOD) and molar absorptivity (ε_{510nm}) obtained from calibration measurements in this study are ~ 2.3 μM and ~ 7400 L mol^{-1} cm^{-1}, respectively.

Chemical Characterization 300 uL aliquots of the initial (non-photolyzed) and irradiated mixtures were withdrawn from the cuvette containing 3 mL of experimental solutions at 0, 5, 40, 80, and 120 min. Components of the Fe-citrate mixtures were characterized using a Vanquish™ high performance liquid chromatography (HPLC) system equipped with an autosampler, a photodiode array (PDA) detector, and a Q Exactive™ HF-X Orbitrap mass spectrometer interfaced with an IonMAX source which housed a heated electrospray ionization (HESI) probe operated in negative ion mode (all from Thermo Scientific Inc.). Chemical constituents were separated on a zwitterionic hydrophilic interaction liquid chromatography (ZIC-HILIC) column (Synchronis™, 2 mm × 150 mm, 5 μm particles, 100 Å pore size, Thermo Inc.). ZIC-HILIC column can retain ionic and highly polar, hydrophilic compounds, through liquid-liquid partitioning, electrostatic interactions, and hydrogen bonding,[78] which cannot be separated on conventional reversed-phase LC columns.[79] The incorporation of a zwitterionic HILIC stationary phase is particularly applicable for retention of highly polar species such as charged metal-organic complexes (i.e. Fe-citrate, Fe-malate, and Fe-siderophores).[80–85] A multistep gradient elution was performed at a flow rate of 0.2 mL min^{-1} using a binary mobile phase-buffer system: (A) LC/MS-grade water (Optima™, Sigma Aldrich Inc.) with 10 mM ammonium acetate buffer (v/v) and (B) LC/MS-grade methanol (Optima™, Sigma Aldrich Inc.) with 10 mM ammonium acetate buffer (Sigma Aldrich Inc.). The buffer pH for all LC experiments was held within 5.2 - 6.8 to preserve the metal-ligand equilibria.[84] Elution proceeded as follows: 0−3 min held at 95% B, 3−7 min linear gradient to 20% B, 7−15 min held at 20% B, 15-19 min linear gradient to 95% B, and re-equilibration period at 19-57 min held at 95% B to prepare for the next injection in the sequence. The autosampler compartment temperature where sample vials were stored was held at 15°C. The column temperature was held at 35°C and an injection volume of 15 μL (~258 ng of injected organic analyte) was used. No additional sample preparation was performed, and samples were

directly withdrawn and analyzed from the irradiated solutions. The UV−visible absorption spectra of LC-separated components were measured using the PDA detector equipped with a deuterium light-source and 1.0 cm fused-silica LightPipe™ flow cell, with a wavelength range of 200−680 nm (3D Field spectra), a scan rate of 20 Hz, and λ ± 4 nm spectral resolution. The following conditions were used for the HESI source operation in the HPLC experiments: 40 °C probe heater temperature, 100 °C capillary temperature, 30 units of sheath gas flow, 10 units of auxiliary gas flow, 0 units of sweep gas flow, 3.5 kV spray potential, and a funnel RF level of 30. A method blank was used for all LC-PDA-HRMS experiments, corresponding to 90 μM citric acid standard. Analyzed samples were ionized in the negative ionization mode and HPLC-PDA-ESI(−)/HRMS datasets were acquired using Xcalibur software (Thermo Inc.). The HRMS was operated at *m/Δm* 240,000 resolving power at 200 m/z, at a scan rate of 1.5 Hz in the full MS scan mode of 100 – 1300 m/z range. Custom mass calibration was performed using commercial calibration solutions (Thermo Scientific, PI-88324) ionized in the negative ESI mode.

Additionally, two sets of HRMS experiments were performed by (1) directly infusing (DI-HRMS) Fe^{III}-citrate solutions photolyzed at 0, 5, 40, 80, and 120 minutes (Exp. 1) in the negative mode to screen for overall water soluble Fe^{III}-citrate components and their photochemical products, and (Exp. 2) to specifically probe components of the unreacted and 120 min irradiated sample for colloidal/carbonaceous products dissolved in 1 mL of a mixture of organic solvents (2:2:2:1 v/v%, acetonitrile (ACN)/dichloromethane (DCM)/ hexanes/ toluene), the '*org-mix*' hereafter, in the positive ion mode. After this step, colloidal mixture underwent dissolution and intentional disruption assisted by ultrasonication for ~ 40 min, followed by filtering using 0.45 μm PTFE syringe filter cartridges (Thermo Inc.), and solvent evaporation on the TurboVap (Biotage Inc.) at 1.5 L min^{-1} flowrate to ~ 1 mL level of remaining water solvent. 20% methanol was added before DI-HRMS as recommended in the literature.[73,74] DI-HRMS experiments were conducted using similar MS tune conditions described above at 5 μL min^{-1} injection flow rate for the water-soluble fraction and slightly modified tune parameters for analysis of the colloid components dissolved in the *org-mix*. For the analysis of colloid components dissolved in *org-mix*, the sheath, auxiliary gas flow, funnel RF-level, capillary, and source heater temperature were adjusted to 30, 10 arbitrary units, 80, 250 °C and 100 °C, respectively to allow for efficient droplet desolvation, ionization and detection of larger molecular weight species. In Exp. 1 and Exp. 2 mass spectra were acquired in

negative and positive modes, respectively. Targeted MS^2 experiments were performed for structural characterization of selected components of the Fe-citrate mixtures in the negative mode. Additional details of DI-HRMS and targeted MS^2 experiments are described in Appendix C of the SI file.

Data Processing & Analysis. Raw Xcalibur data files were background-subtracted prior to data processing and analysis to remove any signal attributed to the method blank. The HPLC-ESI/HRMS datasets were batch-processed with customized java script in the open-source software, MZmine 2 (v. 2.51, http://mzmine.github.io/), to perform data preprocessing, chromatogram construction, peak deconvolution, peak smoothing, peak alignment, peak annotation, and analyte identification with the CAMERA R-package (Bioconductor R-repository).[86,87] The ADAP chromatogram builder[88] was used to reconstruct extracted ion chromatograms (EIC) and obtain the output chromatographic feature list, using a minimum peak height of 10^3, LC peak duration of 0.6 min, and mass tolerance of 0.001 m/z. The combined software algorithm identifies the analyte species, assuming the annotated ions in the range 100 – 1300 m/z were formed by the loss of a proton in the ESI(–) mode. The detected peaks identified by MZmine 2 were cross evaluated using the Xcalibur software (Thermo Scientific Inc.), thus eliminating erroneous formula assignments occasionally made by the algorithm. In addition, the overall screenings of the Fe-containing peaks detected in the bulk samples were performed in DI-ESI(–/+)/HRMS experiments. Obtained data sets were extracted with the DeconTools AutoProcessor software developed at the Pacific Northwest National Laboratory (v. 1.0; http://omics.pnl.gov/software/)[89] and processed using custom Excel macros (Microsoft Inc.) developed for mass alignment, background subtraction, and ^{13}C isotope filtering. Formula assignments were assisted with grouping of the homologous species assigned based on first-order (CH_2) and second-order (CH_2, H_2) Kendrick mass defects, followed by the group-representative formula assignments[90] using the MIDAS molecular formula calculator (v 1.1; http://nationalmaglab.org/user-facilities/icr/icr-software). Isotope distributions of Fe-containing peaks were compared with results obtained from mass spectral isotope distribution simulator software, IsoPro (v. 3.0; https://sites.google.com/site/isoproms/), as well as isotope peak scanner function in MZmine 2 to search for m/z and intensity distribution of a calculated isotope pattern within the feature list. The following constraints were applied for all formula assignments: $C_{1\text{-}60}$,

H_{1-100}, O_{0-22}, Fe_{0-5}, charge ≤ 2, and mass tolerance of ± 3 ppm. MS peaks with a signal to noise (S/N) ratio ≥ 5 were only considered for this analysis. Double-bond equivalent (DBE) values of the neutral assigned species were calculated using the following equation[91]:

$$\mathrm{DBE} = C - H/2 + N/2 + 1. \qquad (1)$$

Throughout the manuscript, all molecular formulas discussed in the text below correspond to neutral molecules in case of $C_xH_yO_z$ composition and to ions in case Fe-containing organic compounds, superscripted by their corresponding charges.

Calculation of Mass Absorption Coefficient ($MAC_{\lambda,OM}$)

Optical Measurements of Bulk Solutions. The absorption spectra presented in this work are in the units of wavelength-dependent mass absorption coefficient ($MAC(\lambda)_{bulk}$ eq. 2),[92] which is calculated from log base-10 absorbance ($A_{10}^{solution}$) of the aqueous solution with organic mass (OM) concentration (C_{mass}, g m^{-3}), and optical path length (b = 0.01 m).

$$MAC(\lambda)_{bulk}(\mathrm{m^2\ g^{-1}}) = \frac{A_{10}^{solution}(\lambda) \times ln\,(10)}{b \times C_{mass}} \qquad (2)$$

Whereas C_{mass} is calculated as mass concentration of the organic component (i.e., citrate, $C_6H_5O_7^{3-}$). Therefore, C_{mass} in the case of 90 μM Fe-citrate ($C_6H_5FeO_7$) is ~ 17.02 g m^{-3}. The calculation assumes that total OM value does not change in the reacted Fe-citrate mixtures. This assumption, however, underestimates $MAC(\lambda)_{bulk}$ values as decarboxylation reactions produce CO_2 and small oxygenated VOC products, which can volatilize from the solution, therefore reducing OM concentration in the reacted solutions. The open headspace in the experimental setup leads to evaporation and degassing of VOC products from photoreacted solutions. Thus, the computed $MAC(\lambda)_{bulk}$ values reported here should be viewed as the lower estimates. The wavelength dependence of $MAC(\lambda)_{bulk}$ expressed through absorption Ångström exponent (AAE) was assumed using the following formula:

$$MAC(\lambda)_{bulk} = k \times \lambda^{-AAE} \quad (3)$$

AAE values were derived by computing the slope of the linear dependence of $MAC(\lambda)_{bulk}$ versus wavelength plotted on a ln-ln scale, while *k* is the imaginary part of the refractive index.[93] For the analytes of this study, we calculate *AAE* over 250-450 nm spectral range.

Photodiode Array (PDA) Optical Measurements of Solution Components. The $MAC(\lambda)^{PDA}$ values derived from integrated UV-vis records obtained in LC-PDA measurements and corresponding to the total light absorption in each of the aliquot samples were computed using eq. 4.[94,95]

$$MAC(\lambda)_{\Sigma}^{PDA}(\mathrm{m^2\,g^{-1}}) = \frac{A(\lambda)_{\Sigma}^{PDA}(\mu AU) \times \Delta t \times F \times ln\,(10)}{b\,(cm) \times m_{inj} \times 10} \quad (4)$$

In this analytical expression, $A(\lambda)_{\Sigma}^{PDA}$ is the optical absorbance from PDA detector recorded at wavelength λ over the period of LC separation (Σ = 0 – 12 min), including the unretained fraction eluting at 0 – 3 min. Δt is the elution time range (12 min); *F* is the LC flow rate (0.2 mL min^{-1}); *b* is the optical pathlength of the PDA flow cell (1 cm), and m_{inj} is the injected mass (258 ng) of OM analyte. The coefficient 10 accounts for the combined conversion of µAU into AU, cm^3 into m^3, cm into m, and ng into g.[94,95]

The relative fractional contributions of $MAC(\lambda)_{\mathrm{i}}^{PDA}$ attributable to each of the individual LC-separated features (*i*) in the analyzed samples were computed using equation 5.

$$MAC(\lambda)_{i}^{PDA} = MAC(\lambda)_{\Sigma}^{PDA} \times \left(\frac{A(\lambda)_{i}^{PDA} \times \Delta t_i}{A(\lambda)_{\Sigma}^{PDA} \times \Delta t_{\Sigma}}\right) \quad (5)$$

where $A(\lambda)_{i}^{PDA}$ (µAU) is the averaged UV-visible absorbance of the individual feature *i* and Δt_i (min) is its time duration. All UV-visible absorption data presented here were processed and exported using custom MATLAB (R2018a, MathWorks Inc., USA) scripts developed in our group. In our study, we report on the molecular composition of the Fe-Citrate reacting mixture and specify the individual $MAC(\lambda)_{i}^{PDA}$ contributions as a function of reaction time. From there, we

incorporate a 'bottom up' approach to interpret optical transformations of the bulk Fe-citrate material in terms of a practical concept of simplified sequential reactions where first-order reaction kinetics are quantified based on computed $MAC(\lambda)_{bulk}$ values.

***In Situ* Flow Microscopy Detection of Colloids.** 300 µL of the unreacted, 5 min, 40 min, 80 min, and 120 min irradiated solutions sampled from same cuvette were analyzed *in situ* using a FlowCam® Nano instrument (Yokogawa Fluid Imaging Technologies Inc.) operated with the VisualSpreadsheet 5.6.26 software (Fluid Imaging Technologies). The FlowCam® Nano instrument uses oil immersion flow microscopy[96,97] to focus and image particles as they pass through a flow cell. Prior to imaging experiments, the instrument was autofocused with NIST Traceable Polymer Microspheres standard (Lot No: 247697) with known diameter (*Dp*) of 0.702 $\pm$ 0.006 µm. The background intensity in all experiments were measured within the 173-178 A.U. range. The instrument parameters are as follows: x40 objective lens, 0.1 µm distance to nearest neighbor, threshold dark/light 18/18, 1 close hole (iterations), 60 µm flow cell depth, 500 µm flow cell width, 0.3 mL sample volume, 0.025 mL min^{-1} sampling flow rate, auto image rate of 137 frames s^{-1}, sample run time 12.00 min, particle size range 0.3 – 60 µm when operated in relative count mode. Particle number concentrations were determined using count calibrated mode with the instrument default settings of 0.1 µm distance to nearest neighbor, threshold dark/light 20/20, 1 close hole (iterations), 60 µm flow cell depth, 500 µm flow cell width, 0.3 mL sample volume, 0.025 mL min^{-1} sampling flow rate, auto image rate of 137 frames s^{-1}, sample run time 12.00 min, and a particle size range 0.3 – 60 µm. After each measurement, the microfluidic system was rinsed with 0.20 µm filtered Windex® or 0.1% Liquinox surfactant soap in water (Optima™, Sigma Aldrich Inc.) followed with a rinse of pure water. Diameters reported from this measurement are equivalent size diameter.

RESULTS AND DISCUSSION

Photolysis of the Fe^{III}-Citrate aqueous system. Figure 1a shows the $MAC(\lambda)_{bulk}$ absorption spectra of the Fe^{III} citrate system measured at selected time intervals during the photolysis experiment. Figure 1b further illustrates evolution of the same $MAC(\lambda)_{bulk}$ spectra but shown as a continuing progression recorded at 5 s intervals using transient optical spectroscopy. The plots show very rapid decrease of the *MAC* values over the first ~ 5 min of the irradiation, followed by

gradual increase over next ~100 min of the experiment. From the beginning of the reaction and during the initial decrease, $MAC(\lambda)_{bulk}$ spectra show a significant drop in their *AAE* values (from 6.86 to 4.21) but remain featureless. In contrast, over the follow-up increase period, $MAC(\lambda)_{bulk}$ spectra consistently show buildup of an absorption feature at 256 nm and *AAE* values of the spectra show only moderate change (from 4.21 to 3.62). Figure 1c shows a time-resolved record of MAC_{256nm} values over the entire irradiation time, indicating a reaction trend consistent with the formal kinetics of two first-order consecutive reactions of *Reactants (R)* $\xrightarrow{j_1}$ *Intermediates (I)* $\xrightarrow{j_2}$ *Products (P)*. Figure 1c shows kinetic modeling results using this apparent first-order kinetic scheme, featuring relative concentration profiles of *R, I,* and *P* components. Details of the kinetic model are described in Appendix D of the SI file. The pH of the initial ferric citrate solution was measured to be 6.7 and changes slightly to 6.52 in the 120 min photoreacted sample. Therefore all photolysis reactions were reproduced within the narrow pH range of this study.

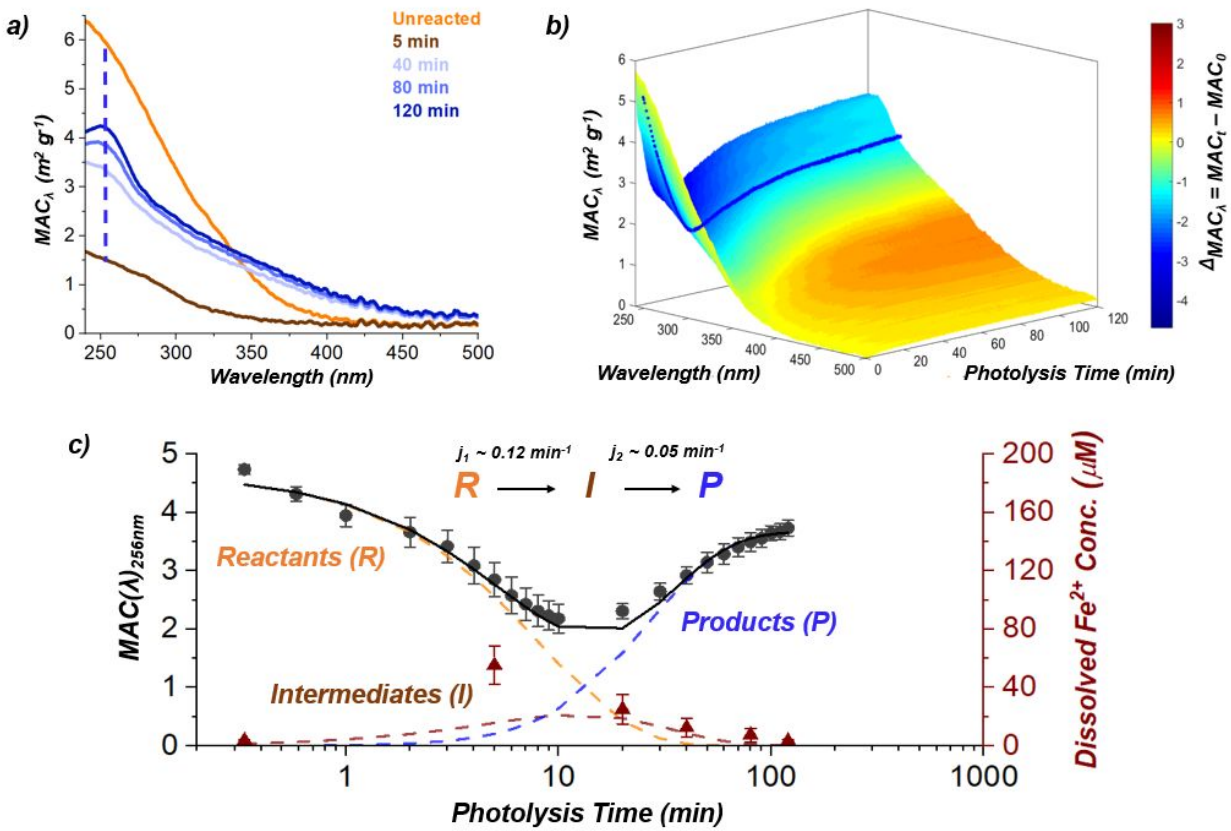


Figure 1. a) *MAC(λ)* spectra of 90 μM Fe^{III}-citrate (1:1 M:L) solution undergoing photochemical transformations recorded at t = 0, 5, 40, 80, 120 min of irradiation time. Dashed line indicates absorption at 256 nm b) 3D *MAC(λ)* plot illustrating the same transformations recorded at high time resolution (5s) in

a separate experiment. The x, y, and z-axis represent the absorbing wavelength (nm), MAC_{λ}, and photolysis time (min), respectively. Colormap is scaled by the difference in *MAC* units ($^{\Delta}MAC = MAC_t - MAC_0$). 2D contour line indicating transient absorption at 256 nm. c) Single-wavelength MAC_{256nm} experimental data of the Fe^{III}-citrate photolytic time-resolved transformations (black circles, error bars represent standard deviation of 3 replicated measurements). The reaction extent is modeled (dashed lines) using Apparent First Order Kinetics for a formal mechanism of two consecutive irreversible reactions: *Reactants* (*R*) → *Intermediates* (*I*) → *Products* (*P*). Right Y axis of figure 1c shows the overall concentrations of Fe^{2+} ions (brown triangles) measured in the solutions at 0, 5, 20, 40, 80, 120 min of irradiation time.

The $MAC(\lambda)_{bulk}$ spectrum of the original Fe^{III}-citrate solution (Fig 1a, orange trace) exhibits characteristic tailing that extends to the visible region of the spectrum. These absorption characteristics are very consistent with previous literature reports,[21,22,61,98,99] and are similar to optical characteristics exhibited by other Fe^{III} – carboxylate complexes.[34,100–102] Spectral characteristics of Fe^{II}-ligand species presented here and in the later text may be attributed to the λ_{max} at ~ 256 nm. Previous study[103] report the UV-vis spectra of Fe^{II}- tannic acid complexes at acidic pH absorbing closer to 260 nm, while Fe^{II}-cationic complexes in aprotic solutions exhibit a unique and narrow λ_{max} at 262 nm.[104] The photochemical mechanism of the Fe^{III}-citrate system (scheme I) explains the evolution of the $MAC(\lambda)_{bulk}$ spectra observed in our experiment. Specifically, the initial photolysis of Fe^{III}-citrate (*R* → *I* reactions) proceeds through rapid ligand to metal charge transfer (LMCT) excitation,[105] reducing Fe^{3+} to Fe^{2+} and dissociating and oxidizing the citrate-radical pair.[31] Reduced Fe^{2+} products exist as intermediate species; they are oxidized back to Fe^{3+} (*I* → *P* reactions) at the longer photolysis times in the presence of ROS species and dissolved oxygen. The formal kinetics and modeled curves describing relative fractions of *R, I,* and *P* components in the photoreacting system shown in Figure 1c indicate a net apparent effect of reactions similar to R1-9 (Scheme 1). To validate our assumption that *I* products are indeed associated with Fe^{II} intermediates, we measured dissolved [Fe^{2+}] concentrations at selected irradiation times. The Fe^{2+} concentration is low in the unreacted sample (3.8 μM), which is close to the limit of detection (~2.3 μM). As the photolysis progresses to 5 min, the averaged concentration of dissolved Fe^{2+} increases to 55.3 μM, then gradually decreases to 25-12 μM at 20-40 min and to 7-3 μM at 80-120 min, respectively. Figure 1c shows that overall concentrations of Fe^{2+} ions in the solutions (brown triangles) agree well with the modeled time-resolved profile of the intermediate products *I* (brown dashed lines). The processes influencing [Fe^{2+}] production are

related to (1) dissociation of citrate ligand from Fe^{III} center and reduction following LMCT as previously mentioned.[31,105] (2) The reactions and rate of reactions of available ROS (i.e. H_2O_2, O_2, and HO_2) in the solution with dissolved Fe^{2+} and (3) speciation of Fe(II) in the aqueous solution at the higher pH (~6.5 - 6.7) ranges where peroxides react with photoreduced Fe^{2+} and re-oxidize back to Fe^{3+}, significantly faster than at the lower pH conditions in separate studies.[43,62,106]

The apparent quantum yield, Φ of the generalized photochemical decomposition of R (Fe^{III}-citrate reactant) was calculated based on the observed number of reacted Fe^{III}-citrate molecules divided by the number of photons to which the experimental solutions were exposed. The latter was calculated based on the photon flux measured in the actinometry experiments (Appendix B in SI file). The calculated apparent Φ is ~ 0.02, which is only ~10% of the intrinsic Φ values reported in the range of ~ 0.16 – 0.30 for Fe^{III}-carboxylates.[25,61] Lower values of the apparent Φ are a combined result of additional absorbance and scattering by other components in the reaction mixture, which evolve over the reaction time. Therefore, apparent first-order reaction rates of j_1= 0.12 min^{-1} and j_2= 0.05 min^{-1} obtained from the formal kinetic modeling need to be considered as specific to our experimental conditions. Details of the kinetic model are described in Appendix E of the SI file. For the extrapolations of kinetic data to experiments external to our study, the apparent rates and the apparent Φ need to be considered together, scalable to the relevant Φ values determined in the corresponding experiments.

Molecular Characterization of the Irradiated Samples. Figure 2a illustrates HPLC-PDA experimental results showing separated components of Fe^{III}-citrate solutions irradiated for 0, 5, 40, 80, and 120 min. For our analysis, the major separated absorbing components eluted between 0 – 3 min RT unretained period and 3 – 12 min RT for weakly to strongly retained species. Therefore, we discuss those identified within these two LC ranges. The individual features are labeled accordingly in each of the respective panels as reactants (R_i), intermediates (I_i), and products (P_i), with their respective coloring schemes from Figure 1c describing the $R \rightarrow I \rightarrow P$ progression. In total, 31 individual HPLC-PDA features (~ 95% of all features) are detected and identified in 5 irradiated samples based on the correlative assessment of HPLC-PDA and HPLC-ESI(–)/HRMS records. Table 1 includes a list of separated features and proposed structures commonly grouped with R_x, I_y, and P_z components, whereas the full list of separated features with corresponding retention times, UV-vis spectra, and HRMS information are reported in Table S1 of the SI file.

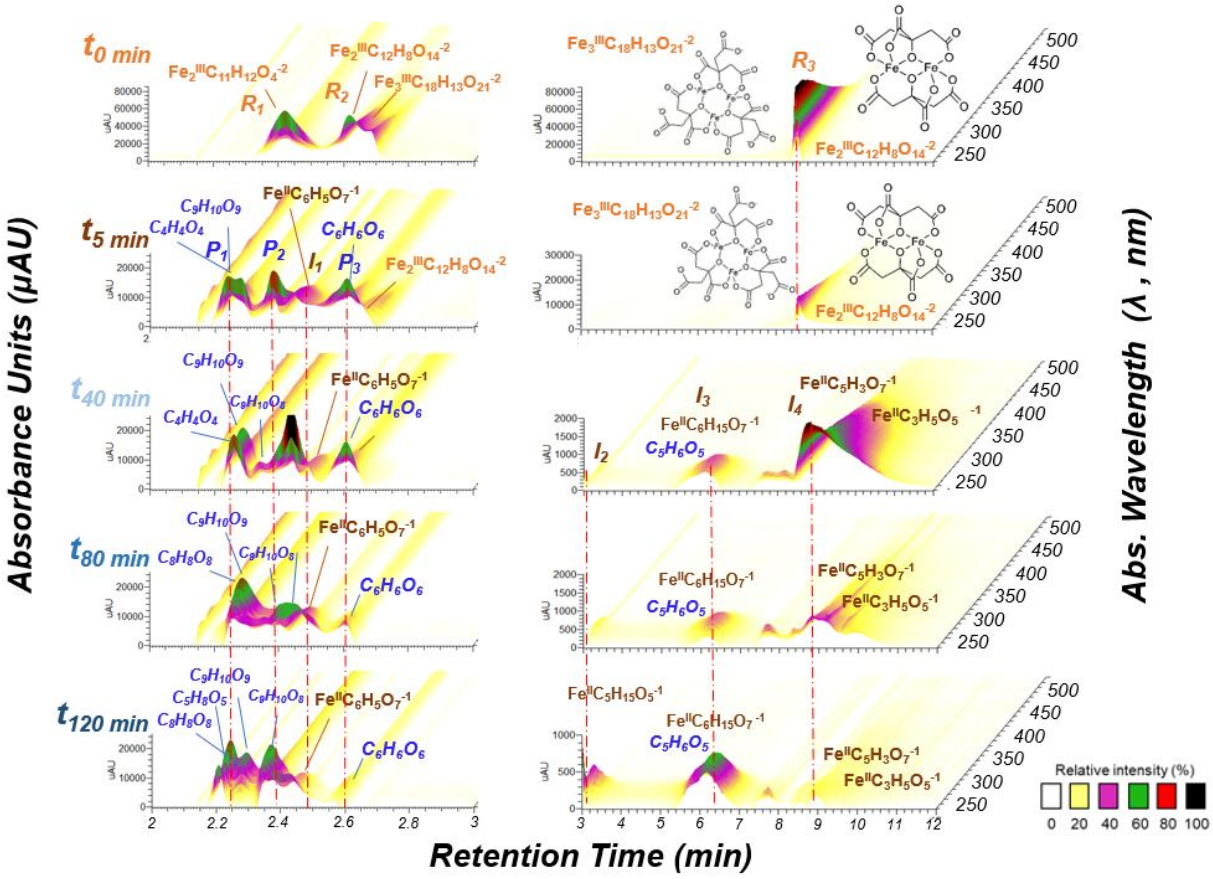
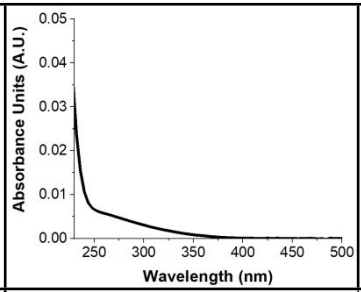
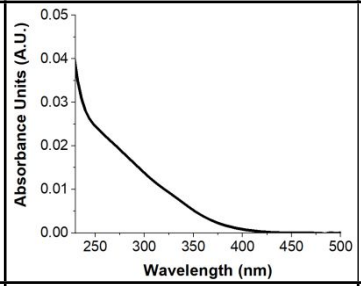
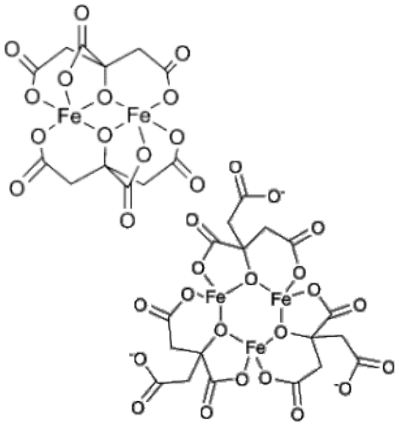
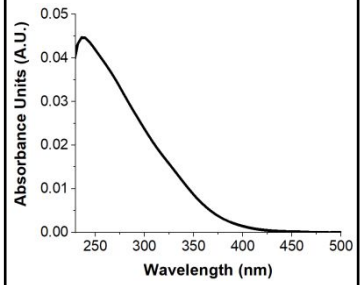


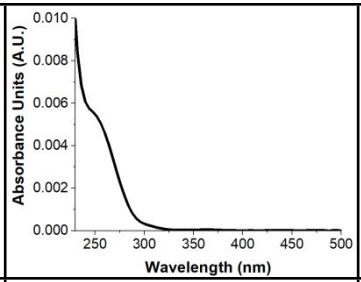
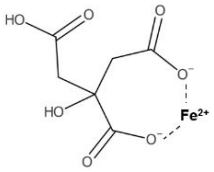
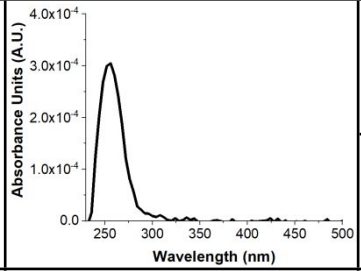
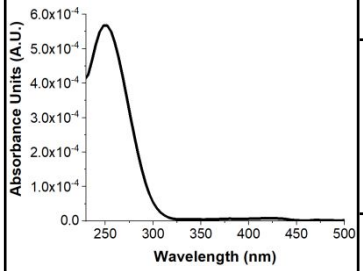
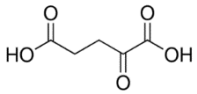
Figure 2. HPLC-PDA chromatograms of individually separated components formed in irradiated Fe^{III}-citrate solutions at 0, 5, 40, 80, and 120 min. The x-axis is retention time, y-axis is UV–vis absorbance and z axis is wavelength. Color indicates relative absorbance as depicted by the color map at the bottom. Assigned formulas corresponding to organic compounds (CHO-) recorded here as neutral molecules, whereas Fe-organic compounds denoted as corresponding ions.

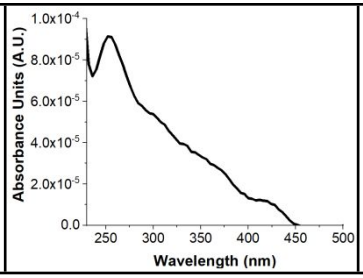
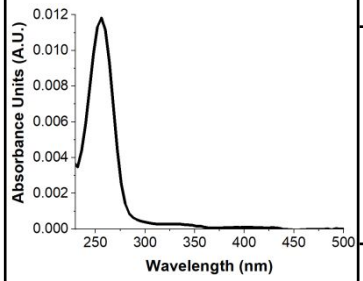
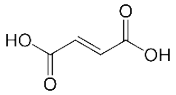
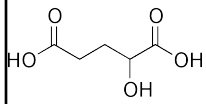
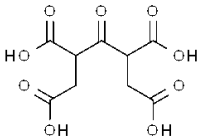
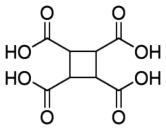
The molecular components of the unreacted solution show three HPLC-PDA features at 2.4, 2.7and 8.7 min RT, marked as R_1, R_2 and R_3, respectively. Analysis of the corresponding HRMS datasets revealed deprotonated ions $[M\text{-}H]^-$ of $^{56}Fe_2^{III}C_{12}H_8O_{14}^{-2}$, $^{56}Fe_3^{III}C_{18}H_{13}O_{21}^{-2}$, $^{56}Fe_3^{III}C_{18}H_{15}O_{22}^{-2}$, and $^{56}Fe_3^{III}C_{12}H_{10}O_{14}^{-2}$ eluted at the corresponding time of R_2 and R_3, which collectively represent the dinuclear dicitrate (Fe_2Cit_2), trinuclear tricitrate (Fe_3Cit_3 & Fe_3Cit_3O), and trinuclear dicitrate (Fe_3Cit_2) complexes, respectively.[73,74,84] The R_1 feature corresponds to $[M\text{-}H]^-$ of $^{56}Fe_2^{III}C_{11}H_{12}O_4^{-2}$. Detection of this Fe-containing peak did not correspond to any of the Fe_xCit_y complexes observed here, nor in previous studies. It is assumed that this is likely a chemical impurity of the Fe^{III}-citrate chemical used in the study. Detection of their characteristic ^{54}Fe

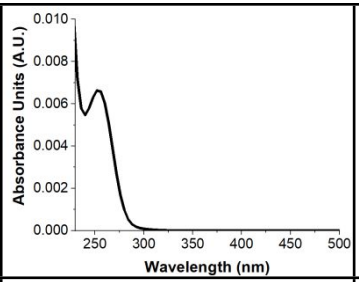
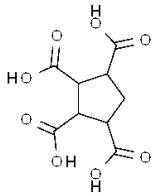
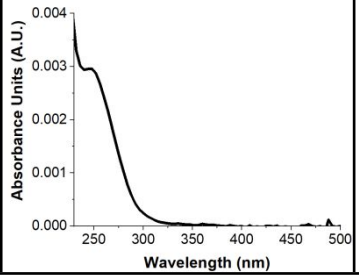
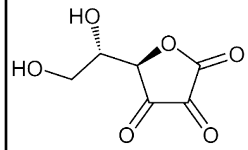
isotopes in the integrated MS spectra explicitly confirmed molecular assignments of the Fe-containing ions. Extracted ion chromatograms of the Fe^{III}-citrate complexes overlaid with the LC-PDA chromatographic peaks are illustrated in Figure S4 of the SI file. Details of DI-ESI(-)/HRMS and ESI-MS^2 characterization of all Fe-containing peaks in the unreacted sample are described in Figures S5, S6 and Table S2 of the SI file. After 5 min of photolysis, all *R* features decrease substantially, indicating their lower concentrations. We estimate the summed concentration of Fe^{III}-citrate complexes (R_2 and R_3) from the HPLC-PDA measurement based on the literature reported molar extinction coefficient at λ = 365 nm (ε = 900 L mol^{-1} cm^{-1})[107] to be ~ 78.4 and 1.4 μM for 0 and 5 min samples, respectively. Considering that this concentration of the Fe^{III}-citrate complexes in the unreacted mixture is lower than concentration of the dissolved Fe^{III}-citrate salt (~ 90μM), the remaining 11.6 μM likely corresponds to un-complexed/un-dissolved $[Fe]^{3+}$, $[citrate]^{3-}$ ions, and surface-bound Fe^{III}-citrate complexes on the high surface area iron oxide (i.e. FeOOH) colloids in the solution.[108] At the relevant Fe concentrations used in this study, formation of insoluble iron oxide colloids precipitated in the aqueous solution at the higher pH setting form.[109] For mechanistic interpretation of Fe(III)-citrate photochemical degradation discussed here, special consideration of multi-phase photoreductive dissolution processes of colloidal surface-bound Fe^{III}-citrate and other Fe-organic complexes in the aqueous solution should be accounted for.[108,110–112] The photodegradation of oxide bound Fe^{III}-citrate complexes lead to dissolution of Fe^{III}-citrate, followed by Fe(III) reduction and immediate release of soluble Fe^{2+} and citrate from colloid to the aqueous solution.[108] Overall, photodegradation of the soluble and surface bound Fe^{III}-citrate complexes initiated through LMCT reactions[31] R1-R4 (Scheme 1) is very fast, resulting in rapid reduction of Fe^{III} to Fe^{II} over the first 5 min of photolysis. *R* components were not detected in the samples collected at longer irradiation times.

Table 1: Summary table of identified components in LC-PDA-HRMS datasets.

ID	*RT (min)*	*UV-Vis Spectrum*	*Exp. m/z* (-)ESI	*Chemical Formula*	*Mass Error (ppm)*	*Proposed Structure & Description*
Reactants (R_i)						
R_1	2.3		159.972	$Fe_2^{III}C_{11}H_{12}O_4^{-2}$	1.875	
R_2	2.6		366.401 375.406 243.931 488.870 271.899	$Fe_3^{III}C_{18}H_{13}O_{21}^{-2}$ $Fe_3^{III}C_{18}H_{15}O_{22}^{-2}$ $Fe_2^{III}C_{12}H_8O_{14}^{-2}$ $Fe_2^{III}C_{12}H_9O_{14}^{-1}$ $Fe_3^{III}C_{12}H_{10}O_{14}^{-2}$	0.689 0.533 0.152 0.466 0.345	 *Iron(III)-citrate (Fe:Cit) complexes based on previous literature, Fe isotope distribution, and optical signals/UV-vis spectra.*[74,113]
R_3	8.4		366.400 375.406 243.931 488.870 271.898	$Fe_3^{III}C_{18}H_{13}O_{21}^{-2}$ $Fe_3^{III}C_{18}H_{15}O_{22}^{-2}$ $Fe_2^{III}C_{12}H_8O_{14}^{-2}$ $Fe_2^{III}C_{12}H_9O_{14}^{-1}$ $Fe_3^{III}C_{12}H_{10}O_{14}^{-2}$	0.307 0.134 0.152 0.998 1.530	
Intermediates (I_i)						

***I*$_1$**	2.4		244.939	$Fe^{II}C_6H_5O_7^{-1}$	1.48	 *Iron(II)Citrate based on spectral database match and isotope distribution.*[114]
***I*$_2$**	3.1		211.028	$Fe^{II}C_5H_{15}O_5^{-1}$	3.2	
			197.012	$Fe^{II}C_4H_{13}O_5^{-1}$	3.2	
***I*$_3$**	6.2		255.018	$Fe^{II}C_6H_{15}O_7^{-1}$	2.01	
			211.028	$Fe^{II}C_5H_{15}O_5^{-1}$	3.2	
			145.014	$C_5H_6O_5$	0.37	 *Alpha-ketoglutaric acid*
***I*$_4$**	8.8		230.923	$Fe^{II}C_5H_3O_7^{-1}$	0.23	
			190.965	$Fe^{II}C_4H_7O_5^{-1}$	0.58	

			176.949	$Fe^{II}C_3H_5O_5^{-1}$	0.79	
Products (P_i)						
P_1	2.2		115.004	$C_4H_4O_4$	0.853	 *Fumaric acid*
			147.029	$C_5H_8O_5$	0.200	 *2-hydroxyglutaric acid*
			261.025	$C_9H_{10}O_9$	0.594	 *3-oxo-1,2,4,5-pentanetetracarboxylic acid*
P_2	2.3		231.015	$C_8H_8O_8$	0.431	 *cyclobutanetetracarboxylic acid*

			245.030	$C_9H_{10}O_8$	0.451	 *cyclopentanecarboxylic acid*
***P*$_3$**	2.6		173.009	$C_6H_6O_6$	0.122	 *Dehydroascorbic acid*

The identified HPLC-PDA features eluting at RTs of 2.4, 3.1, 6.2, and 8.8 min in the samples from 5 and 40 min irradiation times correspond to Fe^{II}-organic intermediates I_1, I_2, I_3, and I_4, respectively. I_1 is plausibly identified as the reduced mono-charged Fe^{II}-citrate complex, corresponding to $^{56}Fe^{II}C_6H_5O_7^{1-}$, which is chemically different than the Fe^{III}-citrate complex(es) observed as *R* species. Fe^{II}-citrate was detected in all of the photoreacted samples. Extracted ion chromatograms for both $^{56}Fe^{II}Cit$ and $^{56}Fe_2^{III}Cit_2$ complexes eluting at different retention times along with corresponding UV-visible spectra recorded by PDA detector are described in Figure S7 of the SI file. The complexation of Fe^{2+} to citric acid occurs at neutral and alkaline pH conditions (within LC buffer ranges), as the hydroxyl groups in citrate molecule become ionized in solution forming the monomeric Fe^{II}-citrate complex.[115] Our results show that Fe^{II}-citrate and Fe^{III}-citrate are uniquely identifiable and distinguishable in these LC experiments. However, those species are considered unstable and relatively weak complexes in the aqueous solution[116]; therefore it is difficult to quantify Fe^{II}-citrate (aq) in these experiments. Nevertheless, to the best of our knowledge, separated and distinguished Fe^{III}- and Fe^{II}-citrate complexes are shown here for the first time. Detection of these Fe^{II}-citrate intermediates implies that a fraction of these species did not degrade immediately following LMCT conversion of both soluble and oxide bound[108] Fe^{III}-citrate complexes to Fe^{2+} and citrate ions. I_2 corresponds to two coeluting monocharged Fe-organic complexes of $^{56}Fe^{II}C_5H_{15}O_5^{1-}$ and $^{56}Fe^{II}C_4H_{15}O_5^{1-}$ while I_3 corresponds to a mixture of two ions: $^{56}Fe^{II}C_6H_{15}O_7^{1-}$ monocharged complex and α-ketoglutaric di-carboxylic acid ($C_5H_6O_5$), which was reported in a previous study[25] as an abundant organic intermediate in the photodecomposition of Fe^{III}-citrate. Finally, strongly absorbing I_4 feature corresponds to several co-eluting mono-charged ions: $^{56}Fe^{II}C_3H_5O_5^{1-}$, $^{56}Fe^{II}C_4H_7O_5^{1-}$, and $^{56}Fe^{II}C_5H_3O_7^{1-}$, which exhibit maximum absorbance at ~ 250 – 256 nm and tailing in the 350 – 400 nm ranges (see Table 1 and Table S1 of SI file). Consistently with the observed $R \rightarrow I \rightarrow P$ formal kinetics, all *I* features identified here degrade substantially at longer irradiation times and are therefore poorly seen in the 80 and 120 min samples. The degradation of Fe(II) intermediate species here is likely due to the oxidation of Fe^{2+} back to Fe^{3+} in the presence of citrate and available oxygen at the relevant pH conditions similar to previous work.[117] The rate of Fe(II)-citrate oxidation is enhanced in the presence of high concentrations of citrate in the solution,[118] therefore we should expect the rate of Fe(II) oxidation to be proportional to the concentration of citrate ions in the solution.

Features *P_1, P_2,* and *P_3,* eluting at 2.2, 2.3, and 2.6 min RT were detected in each of the irradiated mixtures. However, they become most abundant in the 80 and 120 min samples. The plausible identification of *P_1* is a mixture of co-eluting organic compounds such as fumaric acid ($C_4H_4O_4$), 2-hydroxyglutaric acid ($C_5H_8O_5$), and 3-oxo-1,2,4,5-pentanetetracarboxylic acid ($C_9H_{10}O_9$), while *P_2* feature is associated with cyclobutanetetracarboxylic ($C_8H_8O_8$) and cyclopentane carboxylic ($C_9H_{10}O_8$) acids. Detection of small organic acid byproducts such as fumaric (C_4) and hydroxy glutaric acid (C_5) in the irradiated mixtures results from decarboxylation of citrate radical in the presence of oxygen (R4 in Scheme 1). In addition, plausible Norrish I and II photodegradation pathways (R10-11 in Scheme 1) are the source of small organic acids with C=C double bonds and other radical recombinant species (R-R). Photolysis of citric acid by $OH^{\bullet}$ mediated heterogenous oxidation in a separate study[119] results in extensive fragmentation of C-C bonds through acid-base, free-radical chemical reactions, as well as decarboxylation and formation of carboxyl and carbonyl-groups. Therefore, fumaric acid, 2-hydroxy glutaric acid and other small molecules are expected byproducts of the decarboxylation and they are also common enzymatic metabolites in the citric acid 'Krebs' cycle.[120] Alternatively, detection of highly oxygenated multi-carboxylic acid and hydroxy dimers in this photolyzed system, such as $C_7H_8O_8$, $C_8H_{10}O_9$, and $C_{10}H_{12}O_{10}$, are consistent with a previous study investigating the heterogenous photooxidation of dicarboxylic acids catalyzed on the surface of TiO_2/Fe_2O_3 dust particles.[121] Carboxylic dimer products can arise from radical-radical recombination reactions (R9-10 in Scheme 1) of two carboxylic monomer radicals in the irradiated solution. Lastly, HPLC feature *P_3* eluting at 2.6 min RT corresponds plausibly to dehydroascorbic acid ($C_6H_6O_6$), a cyclic molecule with multiple carbonyl (C=O) groups and two hydroxyl groups. The characteristic absorption profile of this molecule is similar to that reported in previous study[122] investigating similar species and ascorbic acid via HPLC-PDA. However, this molecule may also undergo consequent Norrish photochemistry or reactions[123] with H_2O_2 to yield other oxidized, ring-opening products such as $C_6H_8O_8$ detected in the irradiated samples. Full list of identified CHO-containing species is included in Table S3 of the SI file. Overall, cyclic Fe redox reactions in the solution catalyzes the oxidation of citrate to several of the intermediate and product species representing structurally similar species.

Optical Properties of the Irradiated Samples Figure 3 illustrates contributions of individual *R, I* and *P* components to $MAC(\lambda)_{\Sigma}^{PDA}$ spectra recorded by HPLC-PDA for each of the five analyzed samples. Overall, the systematic and quantitative changes in the absolute values of $MAC(\lambda)_{\Sigma}^{PDA}$ and the relative fractions of *R, I* and *P* contributions can be observed as the photolysis reactions progress. Components *R* dominate absorbance in the unreacted sample. Their contribution is halved in the sample irradiated for 5 min, where contributions by the *R* and *I* components become nearly equal, and influence of the *P* components also becomes detectable. At the later irradiation times (40 – 120 min), contributions from *P* continue to grow, while contributions from *I* decline and contributions from *R* are undetectable. Notably, absolute values of $MAC(\lambda)_{\Sigma}^{PDA}$ decline steadily as the photolysis reactions proceed and the spectral shape changes from featureless to more defined with a well-distinguished peak at 256 nm. At 80 – 120 min irradiation time, the $MAC(\lambda)_{\Sigma}^{PDA}$ values decrease by a factor of ~5 compared to those measured for the unreacted sample. These observations are in striking contrast to the $MAC(\lambda)_{bulk}$ measurements using a UV-vis spectrophotometer shown in Figures 1a and 1b. While both measurements show the same trend of the *MAC* declining during the photolysis, absorption detected by the UV-vis spectroscopy of bulk samples is much higher than that inferred from the HPLC-PDA measurements of the same samples. The plausible reason for this discrepancy is a difference in the analyte material probed in two measurements. Specifically, the $MAC(\lambda)_{bulk}$ spectra reflect absorption by total organic carbon (TOC) which includes dissolved water-soluble organic carbon (WSOC) and colloids, while the $MAC(\lambda)_{\Sigma}^{PDA}$ spectra correspond to the light absorption by WSOC only. Therefore $MAC(\lambda)_{\Sigma}^{PDA} \stackrel{\text{def}}{=} MAC(\lambda)_{\Sigma}^{WSOC}$.

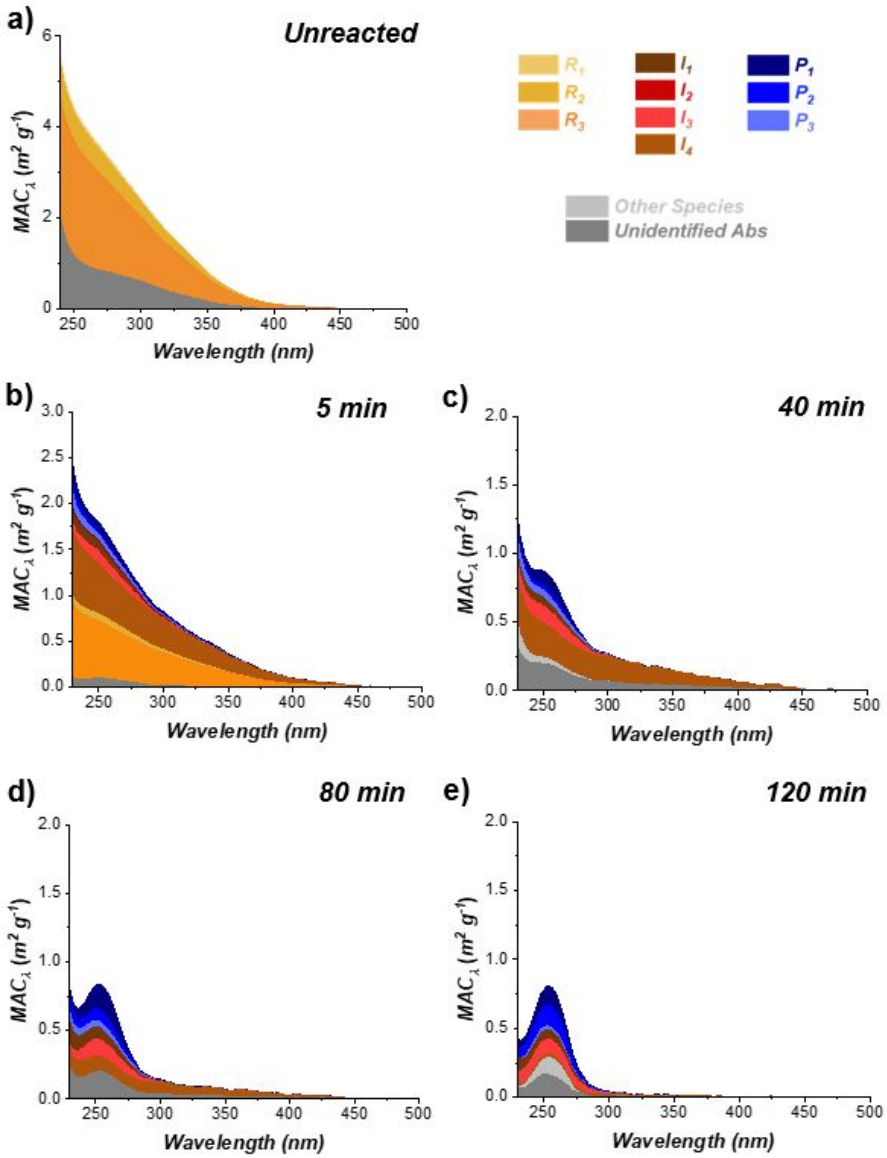


Figure 3: Fractions of $MAC(\lambda)_{\Sigma}^{PDA}$ attributed to water-soluble individual components of the Fe^{III}-citrate irradiated mixtures. Orange, brown, and blue colors indicate contributions from reactants (*R*), intermediates (*I*), and products (*P*) defined in Figure 2.

Figure 4 further illustrates the relationship between $MAC(\lambda)_{bulk}$ and $MAC(\lambda)_{\Sigma}^{WSOC}$ values determined for all 5 samples studied here. Individual panels illustrate relative fractions of $MAC(\lambda)_{\Sigma}^{WSOC}$ and $MAC(\lambda)_{colloids}$ out of $MAC(\lambda)_{bulk}$ spectra measured for the unreacted and irradiated samples. The $MAC(\lambda)_{\Sigma}^{WSOC}$ is the major fraction of $MAC(\lambda)_{bulk}$ for the unreacted and 5 min irradiated mixtures, suggesting only minor effects of colloids (likely $Fe(OH)_3$) at the beginning of reaction. At later irradiation times (40-120 min), the buildup of colloidal products is

evident from increased values of $MAC(\lambda)_{colloids} = MAC(\lambda)_{bulk} - MAC(\lambda)_{\Sigma}^{WSOC}$ illustrated in the plots. The $MAC(\lambda)_{colloids}$ absorbing fraction in these mixtures is presumably related to formation of insoluble $Fe(OH)_3$ and poorly soluble reduced carbon products of reactions R12 (Scheme 1) that contribute to formation and growth of colloids. To test this assumption, we conducted a focused study to provide insights on the sizes, concentration, and chemical composition of these colloidal products.

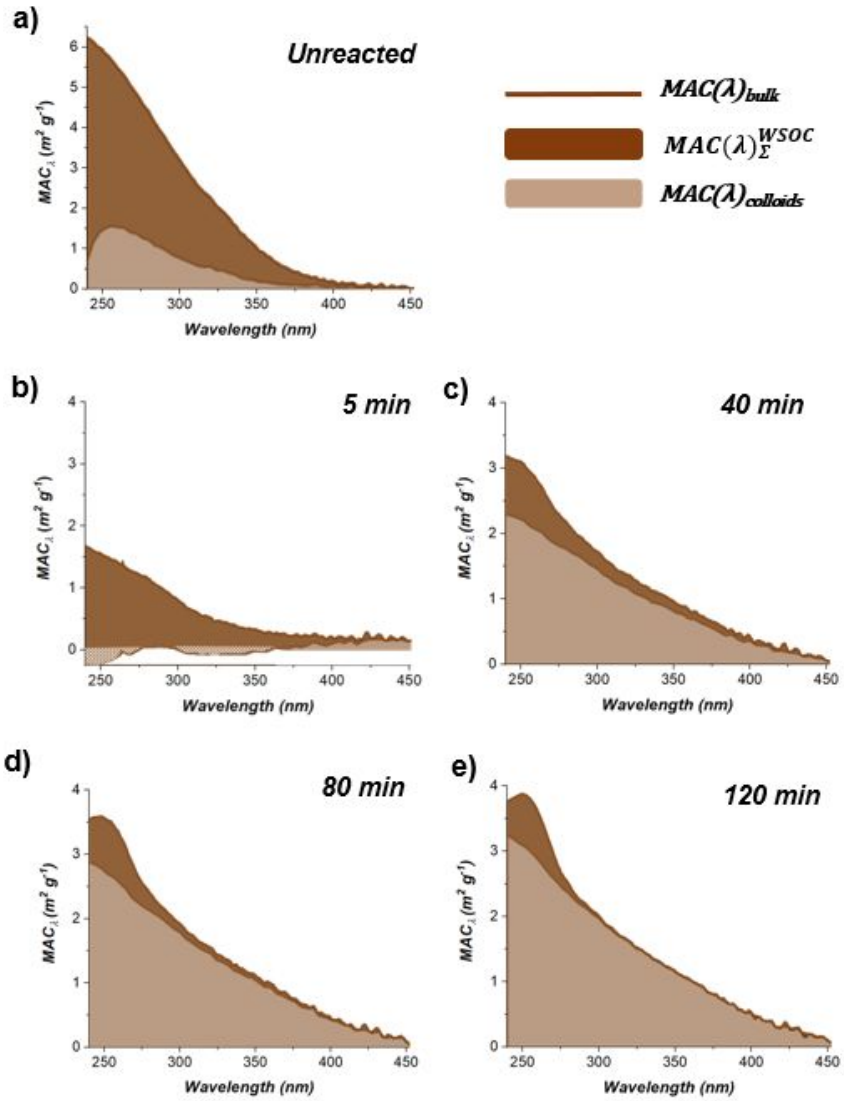


Figure 4. The relative fractions of $MAC(\lambda)_{\Sigma}^{WSOC}$ and $MAC(\lambda)_{colloids}$ out of $MAC(\lambda)_{bulk}$ spectra measured for the samples analyzed in this study.

***In Situ* Flow Microscopy Detection of Colloids** Colloidal components of the unreacted and irradiated samples at 5, 40, 80, and 120 min were measured using the FlowCam® Nano oil immersion flow microscope that is capable to image and count individual colloidal particles larger than 0.3 μm. Figures 5a-5e shows the 8-bin per decade number size distributions ($\Delta N/\Delta \log D_p$; particles cm^{-3}) for the unreacted, 5 min, 40, 80 min, and 120 min photoreacted samples. In the unreacted sample, the particle number concentration is low. The representative particle images (included in Figure S8 of the SI file) reveal relatively smaller and round colloidal particles in the unreacted system, which are likely commonly occurring $Fe(OH)_3$ colloids and the presumed oxide bound Fe^{III}-citrate particles. As the photolysis progresses from 5 – 120 min, the number concentrations and size distributions of the particles detected grow in the reacted solutions, which reveal significantly larger and more fractional colloids, as shown in Figure S8 of the SI file. The estimated mass loadings shown in Figure 5f indicate progressive increase from <50 μg/L in the unreacted sample to >1000 μg/L in the irradiated samples. Ranges of lower and upper mass limits are shown to reduce bias of larger particles (> 3 μm) that are sparsely present. Details of the data analysis are described in Appendix F of the SI file. With respect to the unreacted sample, the mass-size distributions are shifted to larger particle sizes, suggesting that reduced carbon components formed after prolonged photolysis contribute to the buildup of colloids in the irradiated samples (see Figure S9 of the SI file). The mass loading of colloids in the 80 and 120 min irradiated sample corresponds to ~ 8% and 5% of the original Fe(III)-Cit reactant mass. However, particles within the 0.3 – 0.5 μm size ranges contribute most to the observed scattering of UV-visible light in the near visible regions of the absorption spectrum shown in Figure 1a. Nevertheless, these results show the formation of new colloids that effectively increase in concentration under prolonged irradiation to UV-Vis light, representing an important pathway to nanoparticle products formation in photochemical Fe^{III}-carboxylate systems.

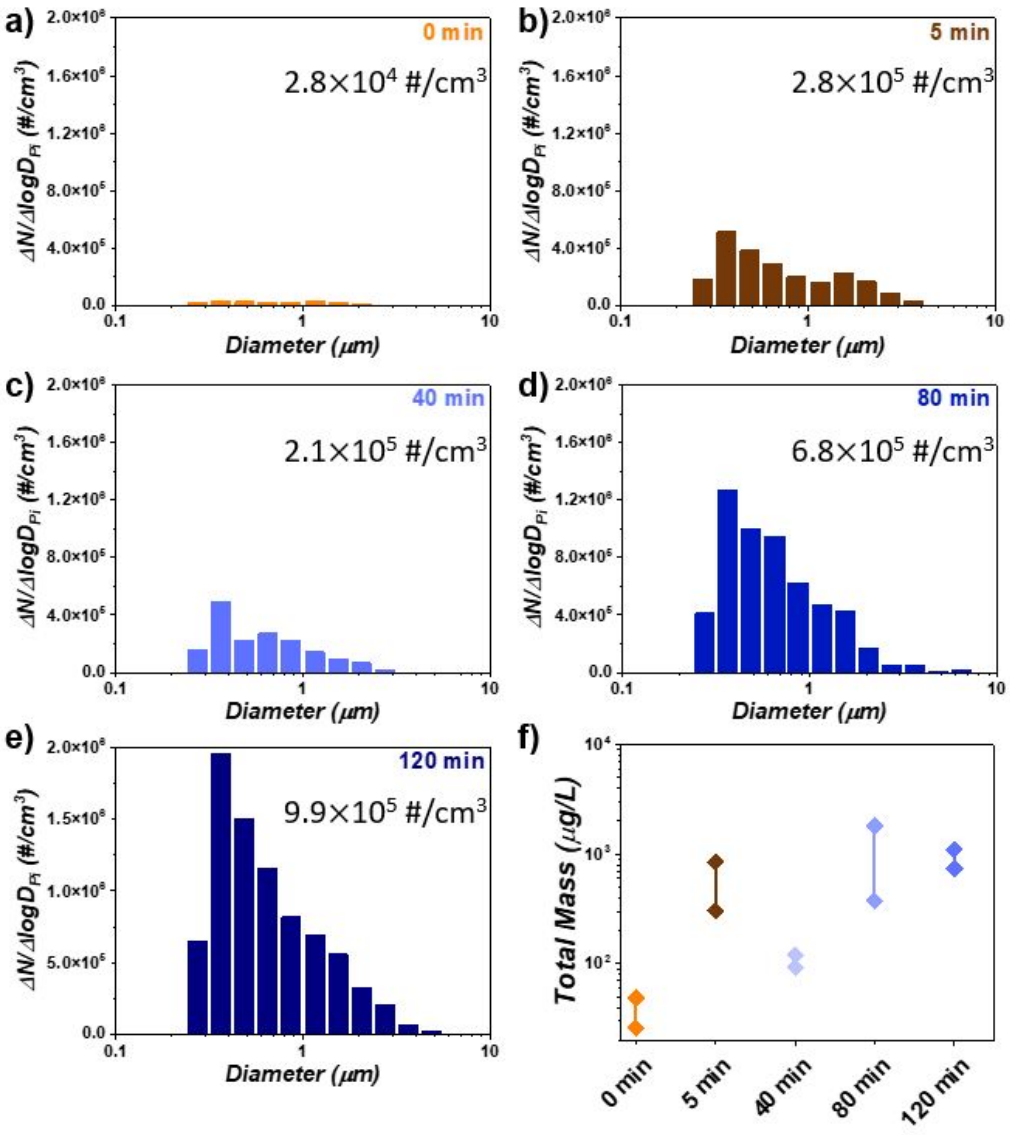


Figure 5. Particle number size distribution of colloids detected in the unreacted (orange) and photoreacted samples at 5 (brown), 40, 80, and 120 min (light blue - dark blue). Diameter reported by the flow microscope is the equivalent size diameter (ESD) in µm. Calculated mass loadings for each of the cases are reported as upper and lower limit values in panel f (see Fig S9 for additional details).

Chemical Characterization of Colloidal Material Colloidal material found in the 120 min irradiated sample was used for chemical characterization. Extracted colloidal material was dissolved in the '*org-mix*' solvent and the obtained solutions were analyzed in DI-ESI(+)-HRMS

experiments for detection of high molecular weight components formed from radical recombination (R12 of Scheme 1). Figure 6a illustrates results of the ESI(+)-HRMS analysis, indicating MS features identified and assigned in the 500-1100 Da mass range. The representative inset plot in Figure 6a illustrates selected CHO peaks and their formula assignments in the 650-730 m/z range. Figure 6b and 6c show the hydrogen-to-carbon (H/C) elemental ratios and DBE of species found in colloidal components, plotted as a function of number of carbon atoms (C) and color-coded by their oxygen-to-carbon (O/C) ratio (Figure 6b). Reference lines in Figure 6c correspond to cata-PAH′s (DBE = 0.75 × C − 0.5)[124] and linear conjugated polyenes C_xH_x+2 (DBE = 0.5 × C).[125] The molecular species representative of dissolved colloids in this HRMS dataset span 30 – 60 carbon atoms with varying degree of oxygenation and unsaturation due to double bonds in the organic structures. The adsorbed components of the colloidal material is composed of moderately saturated aliphatic and unsaturated hydrocarbon species with variable DBE and low oxygen content. Majority of the assigned features with higher HRMS signal intensity fall below the linear conjugated polyene boundary line, while some of the lower intensity features fall closer to the condensed aromatic reference line. Few selected species such as: $C_{34}H_{64}O_{11}$ (DBE = 3; O/C = 0.32), $C_{37}H_{56}O_{12}$ (DBE = 10; O/C = 0.32), $C_{40}H_{62}O_8$ (DBE = 10; O/C = 0.2), $C_{47}H_{58}O_5$ (DBE = 19; O/C = 0.11), and $C_{49}H_{54}O_5$ (DBE = 23; O/C = 0.1) represent less oxygenated/ more reduced carbon fragments that were adsorbed on colloid surfaces.

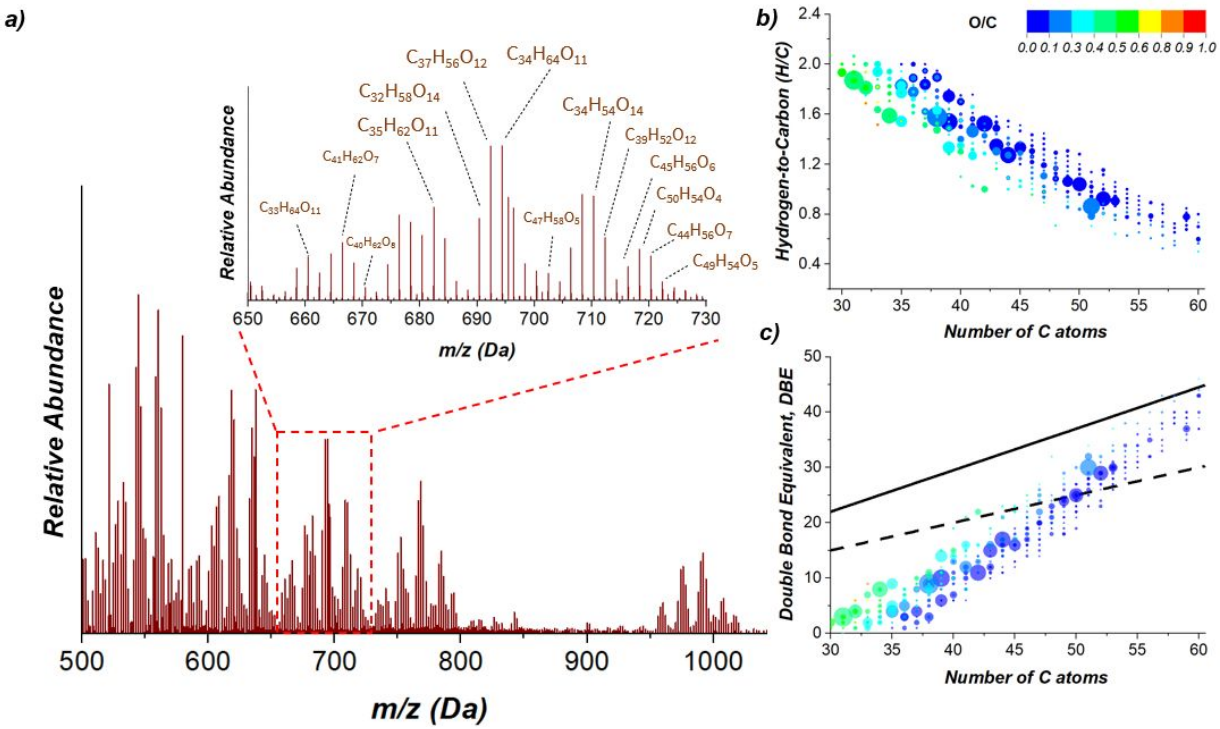


Figure 6. a) (+)ESI-HRMS spectrum representative of the '*org-mix'* digested colloidal components identified in the Fe^{III}-citrate mixture irradiated for 120 min. Inset plot shows zoomed in HRMS spectrum in the range 650-730 Da, b) H/C ratio vs number of carbon atoms (C) plot and c) DBE vs C plot scaled to O/C ratio. Reference lines represent DBE values of linear polyenes (dotted line; 0.5×C)[125] and condensed aromatics (dashed line; 0.75×C-0.5).[124] The size of all individual symbols is scaled to the square root of the MS peak intensity.

Overall, we observe unique low and high molecular weight features in the mixture compromising dissolved colloid fragments composed of *C*, *H* and *O* immediately following dissolution in *'org-mix'* followed by ultrasonication. Of note, those features were only observed in the HRMS spectra of sonicated samples, confirming their apportionment to the degraded colloids (see Figure S9 of SI file for more details). Furthermore, those features were also absent in MS spectra acquired from the unreacted sample prepared following the same dissolution procedures (see Figure S10 of the SI file). Therefore, adsorbed colloidal analytes probed at the longer photolysis time are composed of less oxygenated (more reduced) carbon material, resulting from the radical recombination reactions in R12 of Scheme 1.

CONCLUSIONS

This study investigated multi-phase photochemistry of Fe-citrate and reported on the formation of unexplored colloidal products under prolonged light exposure. Apparent reaction rates of the $R \xrightarrow{j_1} I \xrightarrow{j_2} P$ formal kinetics derived from our experiments are $j_1 \sim 0.12$ min^{-1} and $j_2 \sim 0.05$ min^{-1}, which correspond to the laboratory half-lifetimes of $\tau_{lab} \sim 8.3$ and 20 min, respectively (Appendix D). Scaling these half -lifetimes with respect to intensity of the solar radiation at summer solstice in Southern California and Mediterranean region suggests environmental half-lifetimes of ~ 32 min and ~1.3 hr, respectively. (Appendixes G and H). Therefore, we conclude that photochemical formation of colloidal products with carbon in a relatively reduced oxidation state may take place at the time scale relevant to the real-world environment of the Fe-carboxylate systems.

The light-absorbing properties of the photochemically reacting Fe-citrate mixtures are very much dynamic and overall comparable to those reported for atmospheric brown carbon (BrC). Figure 7 illustrates the $MAC(\lambda)_{bulk}$ values for the Fe-citrate samples of our study shown with respect to the optical-based AAE versus $MAC_{405\text{nm}}$ classification framework.[70,95,126,127] The light-absorbing properties of the unreacted and photoreacted Fe-citrate mixtures are skewed between weak (W) and moderate (M) light-absorbing classes, and they are less-absorbing than BrC from biomass burning [93,128] Over the course photochemical aging, BrC characteristics of the Fe-citrate mixture follows the $W \rightarrow M$ transition, resulting in stronger absorption by the photoreacted mixtures. This darkening is largely attributed to the carbonaceous colloidal material formed after prolonged photolysis under oxygen-deprived conditions. To date, no study has observed these systematic changes of Fe^{III}-carboxylates leading to production of insoluble carbonaceous colloids in aqueous photochemical reactions. To that extent, we therefore presume that formation of condensed reduced carbon species in this system is most likely similar to other extensively photolyzed brown carbon proxies,[129] and other Fe^{III}-carboxylate systems.[20,24,34]

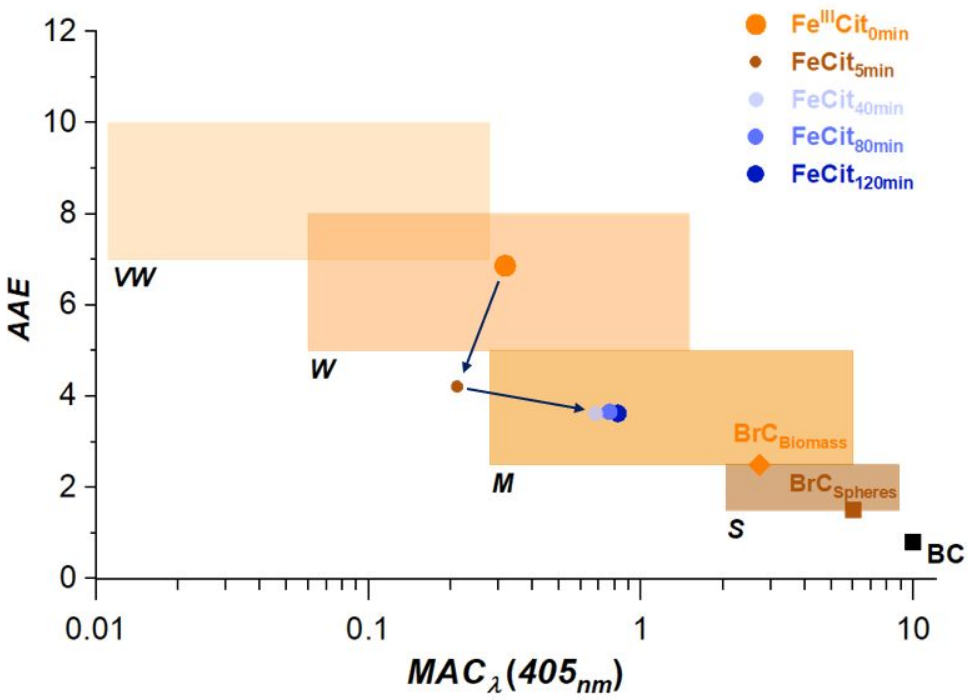


Figure 7. Optical properties of Fe-citrate photolysis samples mapped in the *AAE-MAC*$_{405\ nm}$ space introduced by *Saleh*.[126] The shaded regions represent "optical bins" for "very weak (VW)", "weak (W)", "moderate (M)", and "strong (S)" absorbing BrC classes. Literature-reported *MAC* values at 405 nm for BrC related to biomass burning,[93] spherical tar-balls,[128] and black carbon (BC)[130] are shown.

Overall, the results of this work demonstrate a multi-phase mechanism of the Fe^{III}-citrate photochemistry in aquatic systems of environmental relevance. The photochemical products identified in this representative Fe^{III}-carboxylate system are water-soluble components (*R*, *I*, and *P* components) and carbonaceous colloids formed under oxygen-deprived conditions in the extensively photolyzed mixtures. The detection of colloidal products in this system may contribute to yet unrecognized atmospheric and terrestrial light-absorbing material in aquatic environments with direct effects on the radiative forcing of climate. Further investigation of additional photoreactive Fe^{III}-carboxylate systems need to consider and account for formation of colloidal products that remain poorly characterized, overlooked in previous studies, and received little attention in the literature.[62,131] In particular, ferric oxalate in natural aquatic environments may also behave similarly in the context of our work. Aqueous photolysis of ferric oxalate complex as shown in Figure S11 of the SI file follows similar trend, where degradation of Fe(III)-oxalate complex occurs, followed by formation of short-lived Fe(II)-intermediate species, and build-up of

water-soluble and insoluble colloidal reaction products where the light extinction extends beyond 500nm. Additionally, the aqueous photolysis of Fe-carboxylate complexes in natural waters are important for $Fe^{III/II}$ catalytic cycling, controlling the bioavailability of Fe(II) to microorganisms,[132] photo-mineralization of DOM, and oxidation of organic carbon in irradiated environmental waters and in atmospheric aerosol particles.[62,133–135]

Photoreactive Fe-carboxylates may also play an important role in initiating photocatalytic reactions in snowpack. In particular, snow covered areas of inland central Asia[127,136–138] located near Fe^{III} dust sources may serve as an important medium for photocatalytic cycling of Fe^{III}-carboxylates and the subsequent photooxidation of other water-soluble species (i.e. brown carbon, carboxylic acids, ketones), halogenated species, and other inorganics in the snowpack. The interactions of externally mixed Fe-mineral dust[137] and subsequent photochemical transformations due to Fe^{III}-carboxylates can significantly enhance light absorption and modify the resulting snow and surface albedo, with implications to indirect radiative forcing changes on the snow/surface energy budgets. Specifically, carbonaceous colloid products resulted from Fe-carboxylate photochemistry may accelerate melting of the snowpack, similar to BC and BrC deposits,[136] leading to reduction of the snow albedo.

SUPPORTING INFORMATION

Appendix A and Figure S1 describe transient optical and photochemical experimental setup of this study; Appendix B and Figure S2 describes chemical actinometry experiments and relevant calculations; Appendix C describes detailed direct infusion-HRMS parameters; Appendix D, E, F, G, and H describes the formal kinetic modelling, quantum yields, particle size distributions, atmospheric scaling, and TUV model calculations and selected parameters, respectively. Figure S3 illustrates experimental quantitation of dissolved Fe^{2+} and calibration curve of Fe^{II}-phenanthroline complexes; Figure S4 illustrate selected ion chromatograms (SIC`s) of $Fe^{III}$-citrate complex ions; Figure S5 and S6 describe DI-HRMS screening and $MS^2$ experiments of $Fe^{III}$-citrate complexes for identification and structural characterization. Figure S7 illustrates SIC`s for $Fe^{III/II}$-citrate complexes detected in HPLC-HRMS. Figure S8 show *in situ* FlowCam Nano images of colloidal particles. Figure S9 shows mass size distributions of colloids detected by FlowCam Nano.

Figure S10, S11 illustrate DI-HRMS results of dissolved colloidal products under specified conditions. Figure S12 UV-visible spectrum of ferric oxalate photolysis. List of all molecular assignments in HPLC-PDA-HRMS and DI-HRMS are reported in Table S1, S2, and S3.

Data Availability The dataset used for this work is available for download as a .zip file from https://doi.org/10.4231/xxx-yyyy (West et al., 2022).

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Author Contributions. C.P.W and A.L designed the overall project framework and experiments. C.P.W, J.R, M.M, and B.N.L performed the photolysis and chemical actinometry experiments. C.P.W, M.M, A.P.S.H, and P.L performed the LC separations and method development protocols. C.P.W performed the molecular characterization experiments and processed, analyzed, and interpreted the hyphenated LC-PDA-HRMS and direct infusion HRMS data with the assistance of J.R, A.D., and B.N.L. F.R and J.M.T performed microscopy imaging. C.P.W and A.C.M performed FlowCam measurements and data analysis. A.C.M designed custom MATLAB scripts used for processing and analysis of all UV-visible spectroscopy data in this work. C.P.W and A.L wrote the manuscript with contributions with all co-authors.

Competing Interests. The authors declare that they have no conflict of interest.

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