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1 **A new source of ammonia and carboxylic acids in cloud**  
2 **water: The first evidence of photochemical process**  
3 **involving an iron-amino acid complex**

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10  
11 **Abstract**

12 In the present study we investigate the photochemical properties and impact on cloud water of  
13 ferric-aspartate complex (Fe(III)–Asp) under irradiation. Fe(III)–Asp complex was  
14 investigated as proxy of ferric-amino acids complexes that could be expected to be present in  
15 cloud water. First, the fate of complex under monochromatic (313 and 365 nm) and  
16 polychromatic ( $\lambda \geq 290$  nm) irradiation is investigated and formation quantum yields of Fe<sup>2+</sup>  
17 are determined. Moreover, hydroxyl radical quantification in the presence of hydrogen  
18 peroxide is investigated at cloud water relevant concentrations and under irradiation. Obtained  
19 results suggest that hydroxyl radical formation rates are expected to be lower than those  
20 obtained considering all iron as aquacomplex or complexed with oxalate. Finally, a  
21 phototransformation mechanism for inorganic and organic products formation such as  
22 ammonia, malonic, oxalic and formic acids is proposed.

23  
24 **Keywords :** Photochemistry, atmospheric water, oxidative capacity, iron complexes

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## 1. Introduction

The atmosphere is a complex medium in which atmospheric particles (liquid and solid) are in continuous interaction with the gas phase. In addition to their direct effect on human health and environmental modifications, atmospheric particles are able to absorb and scatter solar radiation modifying the Earth's radiation budget (Papadimas et al., 2012; Singh et al., 2016; Zhang et al., 2017). Between the compartments of the atmosphere, cloud water droplets have attracted the attention of numerous researchers working in the field of physical-chemistry. In fact, cloud droplets can be considered as a multiphase reactor in which inorganic and organic constituents interact through numerous chemical and photochemical processes (Charbouillot et al., 2012). During the last decade, it has been clearly demonstrated that reactivity of cloud aqueous phase can impact the oxidative budget of the atmosphere. Between the oxidative species present in cloud water, hydroxyl radical ( $\text{HO}^\bullet$ ) is considered as the most important radical due to the ability to oxidize numerous organic constituents (Gligorovski et al., 2015; Herrmann, 2003; Herrmann et al., 2010). In the past few years,  $\text{HO}^\bullet$  quantification became of great interest to estimate the life-time of organic compounds and numerous spectroscopic and chromatographic approaches have been developed. In the gas phase, the photolysis of ozone can produce electronically excited oxygen atom  $\text{O}(^1\text{D})$  which can then react with water to form hydroxyl radicals. Once in the gas phase,  $\text{HO}^\bullet$  can be transferred to aqueous phases (Henry's law constant  $K_{\text{H}} = 3.0 \pm 0.2 \text{ M atm}^{-1}$ ) (Hanson et al., 1992; Mozurkewich, 1995). However, these two possible sources cannot completely explain the concentration of hydroxyl radical in cloud water (also considering the strong reactivity of this radical with organic compounds). In fact, a scarce number of studies measured the production of hydroxyl radicals in cloud water (Arakaki and Faust, 1998; Faust and Allen, 1993) and information on the

50 oxidizing capacity of cloud water in terms of quantification of HO<sup>•</sup> and chemical sources is  
51 still a subject of debate. Between the different cloud water constituents, hydrogen peroxide  
52 (H<sub>2</sub>O<sub>2</sub>), through its photolysis, is considered as one of the most important sources of HO<sup>•</sup>  
53 (Herrmann et al., 2010; Yu and Barker, 2003). Iron reactivity also contributes to the  
54 production of HO<sup>•</sup> in atmospheric aqueous phases upon Fe(III) photolysis and Fenton  
55 reaction (Deguillaume et al., 2005; Faust and Hoigné, 1990; Millero et al., 1991). However,  
56 organic constituents of cloud water such as short-chain carboxylic acids and siderophores are  
57 able to generate stable complexes with iron modifying the photoreactivity and as consequence  
58 the hydroxyl radical formation efficiency (Faust and Zepp, 1993; Long et al., 2013;  
59 Passananti et al., 2016; Weller et al., 2014). In fact, the contribution of iron species (as  
60 aquacomplexes or organic complexes) to the formation of hydroxyl radical is still a subject of  
61 debate (Bianco et al., 2015).

62 Recently, the presence of amino acids ranging from nM to few μM concentrations has been  
63 reported in cloud water collected at the top of puy de Dôme (France) (Bianco et al., 2016).  
64 Their contribution to the dissolved organic matter has been estimated to be up to ~ 9% and,  
65 considering the high stability constant with ferric ions reported in literature, the presence of  
66 stable iron-complexes could be expected (Perrin, 1959).

67 In the first part of this paper, we investigate the photoreactivity of Fe(III)-aspartic acid  
68 complex as probe for iron-amino acid complexes. Aspartate diaion (Asp) was taken into  
69 account due to the presence in cloud water and the strong stability constant of complex with  
70 ferric ion (log K = 11.4) (Perrin, 1958). The photostability of Fe-Asp complex, considering  
71 stability constants reported in literature, is investigated using UV-vis spectroscopy under  
72 monochromatic and polychromatic irradiation. Quantum yields of ferrous ions and hydroxyl  
73 radical formation rates are determined in the presence or not of hydrogen peroxide to assess  
74 the possible impact of iron-aspartate complex photolysis on the oxidative budget of cloud

75 water. Moreover a phototransformation mechanism leading to the formation of short-chain  
76 carboxylic acid and ammonia under polychromatic irradiation is proposed.

77

## 78 **2. Material and methods**

79

### 80 *2.1 Chemicals*

81 All chemicals were used without additional purification: Fe(III)-perchlorate (99.9 %), aspartic  
82 acid (99.0 %), malonic acid (99 %), ascorbic acid (99.8 %), coumarin (99 %), 7-  
83 hydroxycoumarin (99 %), sodium hydroxide (99.9 %), perchloric acid (70 %), and hydrogen  
84 peroxide were purchased from Sigma Aldrich. Ferrous perchlorate (99 %), ferrozine (97 %),  
85 sodium formate (99 %) were purchased from Fluka. Ammonium oxalate (99 %) was  
86 purchased from Prolabo. All solutions were prepared in water purified by a Millipore milli-Q  
87 device (Millipore  $\alpha$ Q, resistivity 18 M $\Omega$  cm, DOC < 0.1 mg L<sup>-1</sup>).

88

### 89 *2.2 Complex preparation and spectroscopic characterisation*

90 Fresh solutions of Fe-Asp complex are prepared before each experiment by mixing  
91 appropriate volumes of Fe(ClO<sub>4</sub>)<sub>3</sub> and aspartate stock solutions (each 10 mM). The natural pH  
92 of mixture was 3.7 and was adjusted using sodium hydroxide if necessary.

93 In Figure 1 UV-vis spectrum of Fe<sup>3+</sup>, Asp and Fe-Asp (100  $\mu$ M + 200  $\mu$ M) solutions in milli-  
94 Q water at pH 3.7 are presented showing the overlap with lamp emission spectra (see  
95 irradiation experiments description). Complex speciation is predicted using Hyperquad  
96 Simulation and Speciation (HYSS2009) software (Alderighi et al., 1999). Hydrogen peroxide  
97 was added to the solution just before each experiment in order to avoid a dark reactivity in the  
98 presence of iron (*i.e.* Fenton reaction).

99

### 100 *2.3 Irradiation Experiments*

101 Photochemical experiments are performed under monochromatic and polychromatic  
102 irradiation to investigate the Fe-complex disappearance and formation of ferrous ions,  
103 hydroxyl radicals and transformation products. For monochromatic irradiation, the procedure  
104 is the following: 3 mL of solution are irradiated in a quartz cuvette (Hellma QS) under  
105 monochromatic light (313 and 365 nm) using a Hg 200W lamp (Oriel) equipped with a  
106 monochromator. At fixed interval time the cuvette is transferred into a Varian Carry 300 UV-  
107 vis spectrophotometer to follow the time evolution of UV-vis spectra. The radiation fluxes  
108 reaching the solution at 313 and 365 nm are respectively 516 and 1230  $\mu\text{W cm}^{-2}$ . Sun-  
109 simulated irradiations are performed in homemade photochemical reactor equipped with four  
110 fluorescent lamps (Sylvania Blacklight F15W/350BL) with emission from 290 to 450 nm  
111 (centered at 350 nm).

112 To investigate the photochemical behavior under polychromatic radiation, 250 mL of solution  
113 are irradiated in a jacketed cylindrical reactor (length = 10 cm, volume = 30 mL) thermostated  
114 at  $283 \pm 2$  K using a circulation cooling system under aerated conditions. The total irradiance  
115 reaching the solution in the UV region (290-400 nm) is equal to 1.27  $\text{mW cm}^{-2}$  that is closed  
116 to the value measured in a sunny day in Clermont-Ferrand (France) (1.23  $\text{mW cm}^{-2}$ ) (see  
117 Figure 1)

118 The emission spectra of the irradiation systems (monochromatic and polychromatic) reaching  
119 the solution surface are recorded using an optical fiber with a charge coupled device (CCD)  
120 spectrophotometer (Ocean Optics USD 2000 + UV-vis) which is calibrated using a DH-2000-  
121 CAL Deuterium Tungsten Halogen reference lamp.

122

#### 123 *2.4 Ferrous ions, hydroxyl radical formation yields and transformation products identification*

124 Ferrous ions ( $\text{Fe}^{2+}$ ) formation is determined using ferrozine complexing agent and detection  
125 of complex is performed at 562 nm ( $\epsilon_{562\text{nm}} = 27900 \text{ M}^{-1} \text{ cm}^{-1}$ ) (Stookey, 1970) using a Cary

126 300 UV-vis spectrophotometer.

127 Hydroxyl radical formation is determined using coumarin as trapping molecules that leads to  
128 the formation of stable 7-hydroxycoumarin (7OHC) as high fluorescence product ( $\lambda_{\text{ex}}= 325$   
129 nm,  $\lambda_{\text{em}} = 456$  nm).

130 Coumarin is added to the solution just before each experiment (a concentration of 500  $\mu\text{M}$   
131 was used to trap all generated hydroxyl radical) and formation of 7OHC is monitored by  
132 transferring an aliquot of solution to the spectrofluorometer at fixed interval times. For dark  
133 reactivity, coumarin is spiked in a quartz cell previously filled with  $\text{Fe(III)-Asp}^+ + \text{H}_2\text{O}_2$   
134 solution. 7OHC formation at different times is directly monitored by putting the cell inside the  
135 spectrofluorimeter.

136 7OHC formation yield ( $Y_{7\text{OHC}}$ ) is determined following by HPLC coumarin disappearance  
137 and formation of 7OHC using Fenton-like reaction ( $\text{Fe(III)} + \text{H}_2\text{O}_2$ ) as source of hydroxyl  
138 radical. The experiment, presented in Figure SM3, is repeated 4 times at pH 3.7 and 283K.  
139 7OHC formation yield is then estimated as the ratio between formation rate of 7OHC and  
140 degradation rate of coumarin for each experiment and an average yield of  $Y_{7\text{OHC}}$  is determined  
141 to be  $4.6 \pm 0.5$  %. Considering the reactivity constant of hydroxyl radical with coumarin and  
142 aspartate ( $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  and  $7.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  respectively) (Buxton et al., 1988; Gopakumar et  
143 al., 1977) we can estimate that under experimental conditions (highest aspartate  
144 concentration of 200  $\mu\text{M}$  and 0.5 mM of coumarin) about 98.5% of photogenerated hydroxyl  
145 radicals react with our probe.

146 The quantum yield of ferrous ions formation is defined as the ratio between the number  
147 of ferrous ions formed and the number of absorbed photons during the same period of time.  
148 This value gives an estimation of the photochemical process efficiency. In our experiments  
149 iron-aspartate complex is the only absorbing specie present in water and the polychromatic

150 quantum yield formation of Fe(II) ( $\phi_{Fe(II)}$ ) can be estimated in the overlap range 290-400 ( $\lambda_1$   
151 and  $\lambda_2$ ) by (eq 1).

$$152 \quad \phi_{Fe(II)} = \frac{R_{Fe(II)}^f}{I_a} \quad \text{eq 1}$$

153 where  $R_{Fe(II)}^f$  is the Fe(II) formation rate ( $M s^{-1}$ ) and  $I_a$  is the absorbed photon flux per unit of  
154 surface and unit of time in the wavelength range by iron-complex. The latter was calculated  
155 from eq 2:

$$156 \quad I_a = \int_{\lambda_1}^{\lambda_2} I_0(\lambda) (1 - 10^{-\varepsilon(\lambda)[Fe(III)-Asp]}) d\lambda \quad \text{eq 2}$$

157 Where  $I_0$  is the incident photon flux,  $\varepsilon$  the molar absorption coefficient of iron-aspartate,  $l$  the  
158 optical path length inside the cell or the reactor and  $[Fe(III)-Asp]$  the initial complex  
159 concentration.

160 Ion chromatography (IC) analysis is performed using a Dionex DX-320 apparatus with a  
161 KOH gradient elution and equipped with an IonPac AG11 (guard column  $4 \times 50$  mm) and an  
162 IonPac AS11 (analytical column  $5 \times 250$  mm) for anions and Dionex ICS-1500 equipped with  
163 an IonPac CG16 (guard-column  $4 \times 50$  mm) and an Ion-Pac CS16 (analytical column  $5 \times 250$   
164 mm) and a metasulfonic acid (MSA) solution as eluent with an isocratic elution for cations.

165

### 166 *2.5 Laser flash photolysis*

167 The laser flash photolysis system has been previously described (Brigante et al., 2010) and the  
168 only difference is that the current experiments used the fourth harmonic ( $\lambda_{exc} = 266$  nm) for  
169 the excitation (the energy is set to 50 mJ/pulse). An appropriate volume of chemical stock  
170 solutions ( $Fe^{3+}$  and aspartate) is mixed just before each experiment to obtain the desired  
171 mixtures and concentrations. All experiments are performed at ambient temperature ( $293 \pm 2$   
172 K) and in aerated solutions at pH  $3.7 \pm 0.2$ .



173  
174 *2.6 Phototransformation experiments*  
175  
176 To assess the impact of hydrogen peroxide on the Fe(III)-Asp complex phototransformation,  
177 different irradiation experiments are performed in the presence or not of H<sub>2</sub>O<sub>2</sub>.  
178 5 μM of ferric ions are mixed to 200 μM of aspartate before irradiation. The amount of  
179 aspartate needed was determined using Hyperquad Simulation and Speciation (HYSS2009)  
180 software in order to obtain more than 90% of Fe(III)-Asp<sup>+</sup> complex in solution. Three  
181 experiments are performed: with the presence of Fe(III)-Asp complex in the absence or  
182 presence of H<sub>2</sub>O<sub>2</sub>. Moreover, to identify the mechanism in the presence of H<sub>2</sub>O<sub>2</sub>, additions of  
183 ferric ions or H<sub>2</sub>O<sub>2</sub> are performed after 240 min of irradiation.  
184 The disappearance of Fe(III)-Asp complex is followed by measuring the absorption at 289 nm  
185 while concentration of ferrous ions is determined using the ferrozine method previously  
186 described while ammonium ions are quantified with ionic chromatography.

187

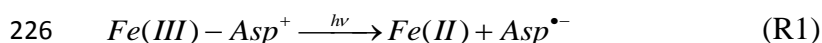
### 188 **3. Results and Discussion**

#### 189 *3.1 Complex formation and phototransformation yields*

190 Stability constants of complexes between ferric ion and amino acids have been reported in  
191 literature (Perrin, 1958) suggesting the formation of stable complex with a stoichiometry 1:1.  
192 High stability constant was found for aspartic acids (logK of 11.4). Vukosav and Mlakar  
193 (Vukosav and Mlakar, 2014) investigated the ferric and ferrous ions complexation with an  
194 excess of aspartic acid using square wave voltammetry. The authors reported the formation of  
195 different iron-aspartate complexes as function of solution pH. In our work, stability constants  
196 reported in Table SM1 are used to predict the iron-aspartate complex form under our  
197 experimental conditions. In Figure SM1 different forms of iron complexes are reported as  
198 function of pH considering 100 μM of Fe(III) and aspartate concentration ranging from 50 to  
199 300 μM. Two main complexes between Fe(III) and aspartate are found : Fe(III)-HAsp<sup>2+</sup> and

200 Fe(III)–Asp<sup>+</sup>. They both have a stoichiometry ratio of 1:1 and are complexes between Fe<sup>3+</sup>  
201 and respectively aspartate monoanion (HL<sup>-</sup>) and aspartate dianion (L<sup>2-</sup>). The latter is expected  
202 to be formed increasing the pH in which L<sup>2-</sup> is the predominant specie (pKa ~3.8)  
203 (Rakhimova et al., 2013). In the presence of aspartate concentration greater than Fe(III), the  
204 main specie present in solution at pH 3.7 (natural pH) is Fe(III)–Asp<sup>+</sup> complex. However, at  
205 molar ratio 1:1, ferric ion is partially present as aquacomplex (Fe(OH)<sup>2+</sup> and Fe(OH)<sub>2</sub><sup>+</sup>).  
206 Increasing the concentration of aspartate (ratio 1:2), about 92% of iron is present as  
207 Fe(III)–Asp<sup>+</sup> and no more Fe(II)-aquacomplexes are present. Moreover, no significant  
208 difference in the iron speciation can be appreciated using higher ratio (1:3).  
209 Laser flash photolysis experiments are performed using Fe(III) mixed with aspartate solutions  
210 and amount of ferric ions disappearance is monitored following the absorption decrease at 290  
211 nm. Iron bleaching is monitored upon 266 nm excitation of iron and iron-aspartate solutions  
212 producing a transient spectrum reported in Figure 2A. Interestingly, when experiments are  
213 performed in the presence of aspartate high decay is observed at ~290 nm (see insert of Figure  
214 2A) indicating a different photoreduction efficiency of Fe(III) in the presence of amino acid.  
215 Absorption decay at 290 nm of Fe(III) [100 μM] solution in the presence of different aspartate  
216 concentrations (Figure 2B) also indicates a non-linearity of experimental data fit with a  
217 plateau value observed near the ration [Asp]/[Fe(III)] = 2.0. For these reasons the next  
218 experiments are performed with 100 μM Fe(III) and 200 μM Asp which correspond to the  
219 formation of almost 100 μM of Fe(III)–Asp<sup>+</sup> complex.  
220 Under monochromatic (313 and 365 nm) and polychromatic (290-450) irradiation, the UV-vis  
221 spectrum of Fe(III)–Asp<sup>+</sup> undergoes a fast decrease, and after about 5 min of irradiation at  
222 365 nm, about 15 % of the complex disappeared (see Figure SM2). Measurements of ferrous  
223 ions in solution confirm that photolysis of Fe(III)–Asp<sup>+</sup> complex leads to the quantitative  
224 photoreduction of Fe(III) into Fe(II) and consequent oxidation of ligand following a well-

225 known ligand-to-metal charge transfer reaction (LMCT) as reported in reaction (R1).



227 In Figure 3 the disappearance of complex monitored at 290 nm and formation of ferrous ions  
228 under polychromatic irradiation are displayed. Similar degradation and formation rates for

229  $Fe(III)-Asp^+$  and  $Fe^{2+}$  (respectively  $R_{Fe(III)-Asp^+}^d = (3.79 \pm 0.33) \times 10^{-6} \text{ M min}^{-1}$  and  $R_{Fe^{2+}}^f =$

230  $(3.71 \pm 0.23) \times 10^{-6} \text{ M min}^{-1}$ ) are determined indicating that ferrous ions are stable in water

231 despite a possible oxidation into ferric ions observed at pH higher than 4.0 (Morgan and

232 Lahav, 2007). Direct hydroxyl radical formation has been observed during iron-

233 aquacomplexes photolysis while photolysis of iron-organic complexes is suggested to lead to

234 the formation of reactive oxygen species (ROS). Reactivity of dissolved oxygen with organic

235 ligand radical ( $Asp^{\bullet}$ ) can lead to the formation of superoxide radical anion ( $O_2^{\bullet-}$ ) that can react

236 with iron complex or, through disproportionation, leads to the formation of hydrogen peroxide

237 (Bielski and Allen, 1977; Wang et al., 2009; Zhang et al., 2009). Hydrogen peroxide can react

238 with ferrous ions in solution generating hydroxyl radical (Fenton reaction). Formation of

239 hydrogen peroxide has been also demonstrated during photolysis of  $Fe(III)$ -oxalate complexes

240 through oxidation of  $Fe(II)$  into  $Fe(III)$  by  $HO_2^{\bullet}/O_2^{\bullet-}$  (Zuo, 1995).

241 Zhang and coworkers determined that photolysis quantum yield of  $Fe(III)$ -pyruvate complex

242 at 355 nm decreases from 1.0 to 0.46 in deoxygenated and aerated solutions respectively

243 (Zhang et al., 2009). This result demonstrates the key role of molecular oxygen on the

244  $Fe(II)/Fe(III)$  catalytic process in agreement with formation of hydroperoxide/superoxide

245 radical and finally hydrogen peroxide. However, quantification of hydrogen peroxide in

246 solution is difficult due to the fast reactivity with photogenerated ferrous ions. Under

247 polychromatic irradiation ferrous ions formation from 100  $\mu\text{M}$  of  $Fe(III)-Asp^+$  solution is

248 presented in Figure 4 and compared to the data obtained from 100  $\mu\text{M}$  of  $Fe(III)$ -aquacomplex

249 ( $Fe(OH)^{2+}$ ) and iron-monoxalate complex ( $Fe(III)-(C_2O_4)^+$ ). The pH of the solutions is the

250 natural pH : respectively  $3.8 \pm 0.1$  for Fe(III)-Asp<sup>+</sup> and Fe(OH)<sub>2</sub><sup>+</sup> solutions and  $2.6 \pm 0.1$  for  
251 Fe(III)-(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup> solution. Under 290-450 nm irradiation Fe<sup>2+</sup> formation rate ( $R_{Fe^{2+}}^f$ ) for  
252 Fe(III)-Asp<sup>+</sup> is  $(3.79 \pm 0.33) \times 10^{-6}$  M min<sup>-1</sup> while a rate of  $(4.99 \pm 1.43) \times 10^{-7}$  M min<sup>-1</sup> and  
253  $(2.50 \pm 0.17) \times 10^{-5}$  M min<sup>-1</sup> is determined for Fe(OH)<sub>2</sub><sup>+</sup> and Fe(III)-(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup> respectively.  
254 In Table 1 Fe<sup>2+</sup> formation quantum yields are reported and compared with previously  
255 investigated iron complexes adopted as proxies for Fe-complexes in cloud water. Ferrous ions  
256 formation yield from Fe(III)-Asp<sup>+</sup> complex is about 5 times lower than the value measured  
257 for Fe(III)-(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup> under the same irradiation conditions. By complexing with organic  
258 ligands, Fe(III) photolysis is faster than for the aquacomplex form. This leads to higher Fe<sup>2+</sup>  
259 formation rates which modify the speciation of iron in the aqueous phase of cloud and  
260 therefore the iron cycle in clouds.

261

### 262 3.2 Hydroxyl radical formation

263 In order to assess the impact of Fe(III)-Asp<sup>+</sup> complex photolysis on the oxidative capacity  
264 and chemical composition of cloud water, different experiments by varying the initial  
265 concentration of complex and presence of hydrogen peroxide are performed under dark and  
266 polychromatic irradiation as summarized in Table 2. Hydroxyl radical formation rate ( $R_{HO^\bullet}^f$ ) is  
267 quantified spiking the solution with 500 μM of coumarin that quantitatively trap all generated  
268 hydroxyl radical ( $k_{coumarin,HO^\bullet} = 6.4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>) (Singh et al., 2002) generating a fluorescent  
269 intermediate (7-OH-coumarin, 7OHC).

270 In dark experiments no relevant formation of hydroxyl radical is observed for all experiments  
271 excepted for experiment 2 and 4 in which a formation rate of hydroxyl radical ( $R_{HO^\bullet}^f$ ) of  $(2.30$   
272  $\pm 0.12) \times 10^{-8}$  and  $(2.98 \pm 0.12) \times 10^{-8}$  M min<sup>-1</sup> is determined. Under polychromatic  
273 irradiation (Figure 5), a similar formation rate of hydroxyl radical is observed for experiment

274 1 and 3 (ferric ion and Fe(III)-Asp<sup>+</sup> photolysis) with a  $R_{HO}^f$  of  $(1.06 \pm 0.11) \times 10^{-7}$   
275 and  $(9.76 \pm 0.44) \times 10^{-8} \text{ M min}^{-1}$  respectively. In the presence of hydrogen peroxide (1 mM),  
276 as expected, an increase of HO<sup>•</sup> formation rate is observed up to  $(7.18 \pm 0.33) \times 10^{-7} \text{ M min}^{-1}$   
277 for 100  $\mu\text{M}$  of Fe(III)-Asp<sup>+</sup> complex in the presence of 1 mM of hydrogen peroxide.

278

### 279 *3.3 Phototransformation mechanism*

280

281 The mechanisms of Fe(III)-Asp<sup>+</sup> complex transformation under cloud water conditions is  
282 investigated mixing 5  $\mu\text{M}$  of Fe(III) with 200  $\mu\text{M}$  of aspartate and solution was irradiated  
283 under sun-simulated conditions. Fe(III) concentration is typical for aqueous phase of clouds  
284 and aspartate concentration is estimated thanks to HYSS2009 software to obtain more than  
285 90% of Fe(III)-Asp<sup>+</sup> complex. Under these conditions, almost 5  $\mu\text{M}$  of Fe(III)-Asp<sup>+</sup> are  
286 present in solution with an excess of aspartate. In absence of hydrogen peroxide, formations  
287 of ammonia (NH<sub>4</sub><sup>+</sup>) and ferrous ions are proportional to the disappearance of Fe(III)-Asp<sup>+</sup>  
288 complex (Figure 6A) suggesting that irradiation of one complex molecule leads to the  
289 reduction of ferric into ferrous ion and quantitative formation of one NH<sub>4</sub><sup>+</sup> through a complex  
290 mechanism starting from a first ligand-to metal charge transfer (LMCT) reaction between  
291 Fe(III) and Asp.

292 When the same experiments are performed with addition of 50  $\mu\text{M}$  of H<sub>2</sub>O<sub>2</sub> (Figure 6B), an  
293 important increase of NH<sub>4</sub><sup>+</sup> is observed leading to a significantly higher concentration than the  
294 initial concentration of Fe(III)-Asp<sup>+</sup> complex (about 3 times higher after 100 min of  
295 irradiation). Moreover, formation of short-chain carboxylic acids such as malonic, oxalic and  
296 formic acids is observed during irradiation (Figure SM4). In absence of hydrogen peroxide,  
297 carboxylic acids are not detected in solution suggesting that their formation can be probably  
298 attributed to the oxidation of aldehyde that is generated from deamination of aspartic radical.  
299 Moreover, no relevant formation of NH<sub>4</sub><sup>+</sup> or carboxylic acids has been noticed in absence of

300 ferric ions (i.e. only aspartate and hydrogen peroxide).

301 The addition of 10  $\mu\text{M}$  of ferric ions after 240 min of irradiation shows an important increase

302 of  $\text{Fe(III)-Asp}^+$  complex which is again photo-degraded and leads to an important formation

303 of  $\text{NH}_4^+$ . The increase of ferrous ions concentration is not proportional to the formation of

304 ammonia which suggests a re-oxidation of ferrous ions into ferric ions (Fenton reaction)

305 which is complexed again with the excess of aspartate in solution.

306 To confirm this hypothesis, the same experiment has been performed with an addition of

307 hydrogen peroxide (200  $\mu\text{M}$ ) after 240 min of irradiation. When  $\text{H}_2\text{O}_2$  is added (Figure 6C), a

308 relevant decrease of  $\text{Fe}^{2+}$  concentration (about 0.8 $\mu\text{M}$ ), proportional to the complex

309 formation, is observed confirming a re-oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  (Fenton reaction) which

310 then is re-complexed by aspartate in solution. The irradiation of this solution highlights an

311 important increase of ammonia concentration despite a quite stable concentration of  $\text{Fe}^{2+}$  and

312  $\text{Fe(III)-Asp}^+$  complex. In Figure 7, the proposed mechanisms from  $\text{Fe(III)-Asp}^+$  is presented

313 indicating that different steps leading to the formation of ammonia from Aspartate radical

314 anion. A first decarbonylation of Aspartate radical anion leads to the formation of amine

315 radical. This latter can react with molecular oxygen leading to the formation of ammonia and

316 aldehyde (R-CHO). The formation of short-chain carboxylic acids observed only in the

317 presence of hydrogen peroxide can be attributed to the hydroxyl radical mediated oxidation of

318 aldehyde as reported in the literature (Charbouillot et al., 2012). These different photoinduced

319 steps lead to the formation of carbon dioxide  $\text{CO}_2$  and therefore represent a sink for organic

320 compounds in aqueous phase. As observed for Fe-oxalate, by complexation processes and

321 photoreaction iron is allowing large organic compounds to be transformed into smaller

322 compounds and  $\text{CO}_2$ .

323

#### 324 4. Conclusions

325 The present work investigate, for the first time of our knowledge, the photochemical reactivity  
326 of an Fe(III)-amino acid complex in atmospheric mimic waters. The photolysis of Fe(III)-  
327 Asp<sup>+</sup> complex under sun-simulated conditions leads to the formation of ammonia as main  
328 product and short chain carboxylic acid through a more complex degradation mechanism. In  
329 the presence of hydrogen peroxide the formation of hydroxyl radical is enhanced leading to  
330 the re-oxydation of ferrous into ferric anion during Fenton process and a possible formation of  
331 a new complex. The formation of iron-amino acid complexes can represent a degradation  
332 pathway for amino acids oxidation as well as new photochemical sources of carboxylic acids  
333 and ammonia in cloud aqueous phase. The relevance of this photochemical reactivity needs to  
334 be extended to aerosols. In fact, we can expect that the presence of higher amino acids and  
335 iron found in atmospheric particles can induce these new heterogeneous processes enhanced  
336 by solar irradiation. For these reasons, iron-amino acids photoreactivity can modify the  
337 physico-chemical properties of atmospheric particle (*i.e.* hygroscopicity) but also the  
338 composition of solid and gas phases of atmosphere.

339

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345

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431  
  
432

Conditions	$\phi_{313nm}$	$\phi_{365nm}$	$\phi_{300-450nm}$
Fe(III)-Asp <sup>+</sup>	0.25±0.04	0.11±0.04	0.31±0.06
Fe <sup>3+</sup> aquacomplex (FeOH) <sup>2+</sup>	–	0.027 (Wang et al., 2009)	0.03±0.01
Fe(III)-(C <sub>2</sub> O <sub>4</sub> ) <sup>+</sup>	–	–	1.6±0.2
Fe(III)-(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	0.10 (Long et al., 2013)	0.085 (Long et al., 2013)	–
Fe(III)-(H <sub>2</sub> C <sub>3</sub> O <sub>3</sub> ) <sup>2+</sup>		0.46* (Zhang et al., 2009)	

434

435 **Table 1:** Formation quantum yields of Fe<sup>2+</sup> under monochromatic (313 and 365 nm) and  
436 polychromatic (300-450 nm) irradiation. Fe(III)-(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup> and Fe(III)-(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>-</sup> are ferric-  
437 mono and di-oxalate complexes respectively while Fe(III)-(C<sub>3</sub>H<sub>3</sub>O<sub>3</sub>)<sup>2+</sup> refers to ferric-  
438 pyruvate species. \* the quantum yields is determined at 355 nm

439

Experiment		Fe(III)( $\mu$ M)	Asp ( $\mu$ M)	H <sub>2</sub> O <sub>2</sub> ( $\mu$ M)	$R_{HO^\bullet}^f$ ( $\times 10^{-7}$ M min <sup>-1</sup> )
1	Dark	100	–	–	0.015 $\pm$ 0.003
2	Dark	100	–	1000	0.230 $\pm$ 0.012
3	Dark	100	200	–	0.017 $\pm$ 0.003
4	Dark	100	200	1000	0.298 $\pm$ 0.012
1	Light	100	–	–	1.06 $\pm$ 0.11
2	Light	100	–	1000	3.47 $\pm$ 0.12
3	Light	100	200	–	0.976 $\pm$ 0.044
4	Light	100	200	1000	7.18 $\pm$ 0.33

440 **Table 2:** Initial chemical composition of solutions for experiments under dark and  
441 polychromatic irradiation and the corresponding HO<sup>•</sup> formation rate  $R_{HO^\bullet}^f$ . The pH was 3.7  
442 and temperature 283 K  
443

444 **Figure Captions**

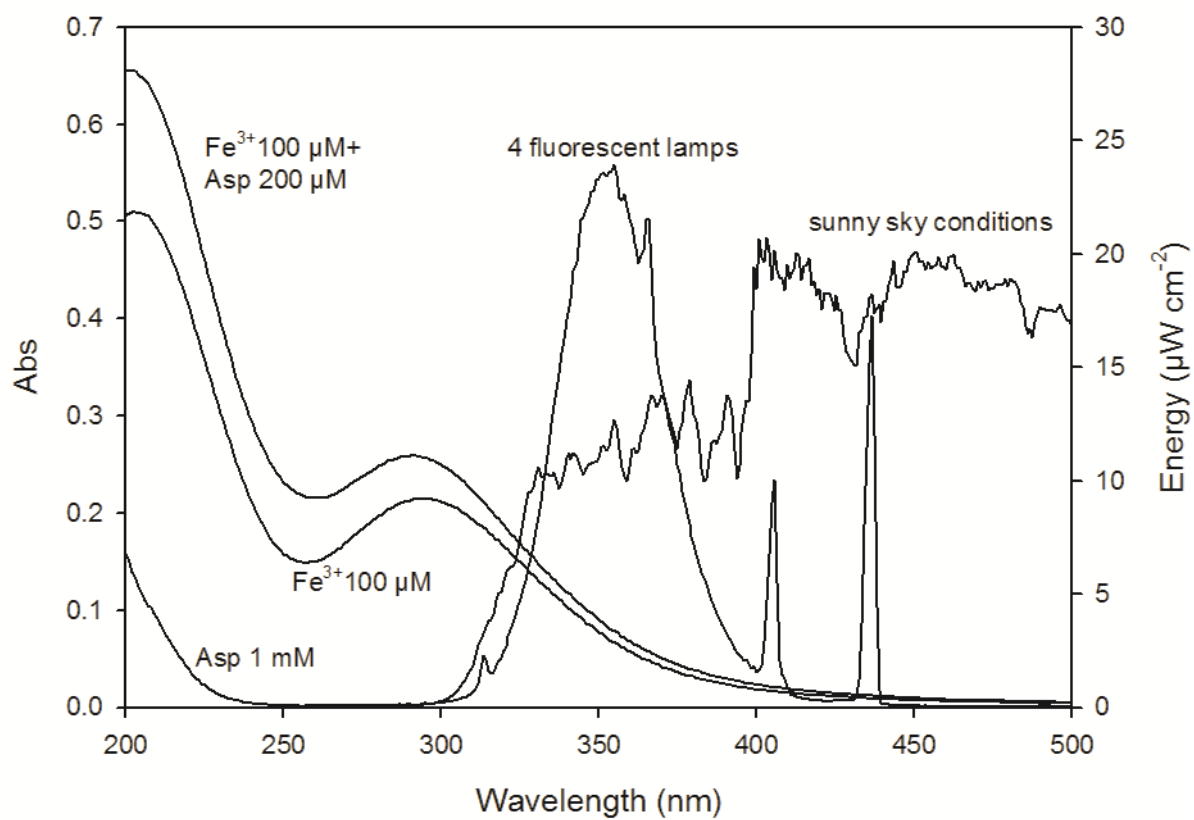
- 445 1) Absorption spectra of  $\text{Fe}^{3+}$  100  $\mu\text{M}$ , aspartate 1 mM and  $\text{Fe}^{3+}$  100  $\mu\text{M}$  + Asp 200  $\mu\text{M}$   
446 solutions at pH 3.7. Emission spectra of four fluorescent lamps reaching the solution  
447 surface and sun spectrum acquired during a spring day at Clermont-Ferrand (France).  
448
- 449 2) **A:** Transient absorption spectra produced upon 266 nm excitation of  $\text{Fe(III)}$  500  $\mu\text{M}$   
450 solution ( $\circ$ ) and  $\text{Fe(III)}$  500  $\mu\text{M}$  + aspartate 500  $\mu\text{M}$  solution ( $\bullet$ ). Solid lines represent  
451 the fit of experimental data with a Gaussian equation. Error bars are determined from  
452 the signal resolution of absorption decay signal. The insert shows the absorption decay  
453 signal monitored at 290 nm. **B:** Absorption decay monitored at 290 nm vs ratio  
454  $[\text{Fe(III)}]/[\text{Asp}]$ . Errors bars are determined considering standard deviation of 3  
455 different experiments. Experiments are performed at  $\text{pH } 3.7 \pm 0.2$ , 293 K and aerated  
456 conditions.
- 457
- 458 3)  $\text{Fe(III)-Asp}^+$  complex (monitored at 290 nm) disappearance and  $\text{Fe}^{2+}$  formation under  
459 polychromatic irradiation (290-400 nm) of  $\text{Fe}^{3+}$  100 $\mu\text{M}$  + Asp 200  $\mu\text{M}$  solutions at pH  
460 3.7. Continuous line represents the exponential fit of experimental results, while  
461 dashed line the 95% confidence of fit.  
462
- 463 4)  $\text{Fe}^{2+}$  formation during polychromatic irradiation of 100  $\mu\text{M}$   $\text{Fe(OH)}^{2+}$ ,  $\text{Fe(III)-Asp}^+$  or  
464  $\text{Fe(III)-(C}_2\text{O}_4\text{)}^+$  at pH 3.7 in aerated solutions.
- 465 5) Hydroxyl radical formation during polychromatic irradiation of  $\text{Fe(III)}$  100  $\mu\text{M}$  in the  
466 presence of hydrogen peroxide and/or aspartate.
- 467 6) Polychromatic irradiation of **(A)**  $\text{Fe}^{3+}$  5 $\mu\text{M}$  + Asp 200  $\mu\text{M}$  solution ; **(B)**  $\text{Fe}^{3+}$  5 $\mu\text{M}$  +  
468 Asp 200  $\mu\text{M}$  + 50  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$  solution with addition of 10 $\mu\text{M}$  of  $\text{Fe}^{3+}$  after 240 min ;  
469 **(C)** Same condition as **(B)** with addition of 200  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$  after 240 min. The pH of

470 the solutions was set to 3.7.

471 7) Mechanism of Fe(III)-Asp<sup>+</sup> photolysis and formation of main products.

472

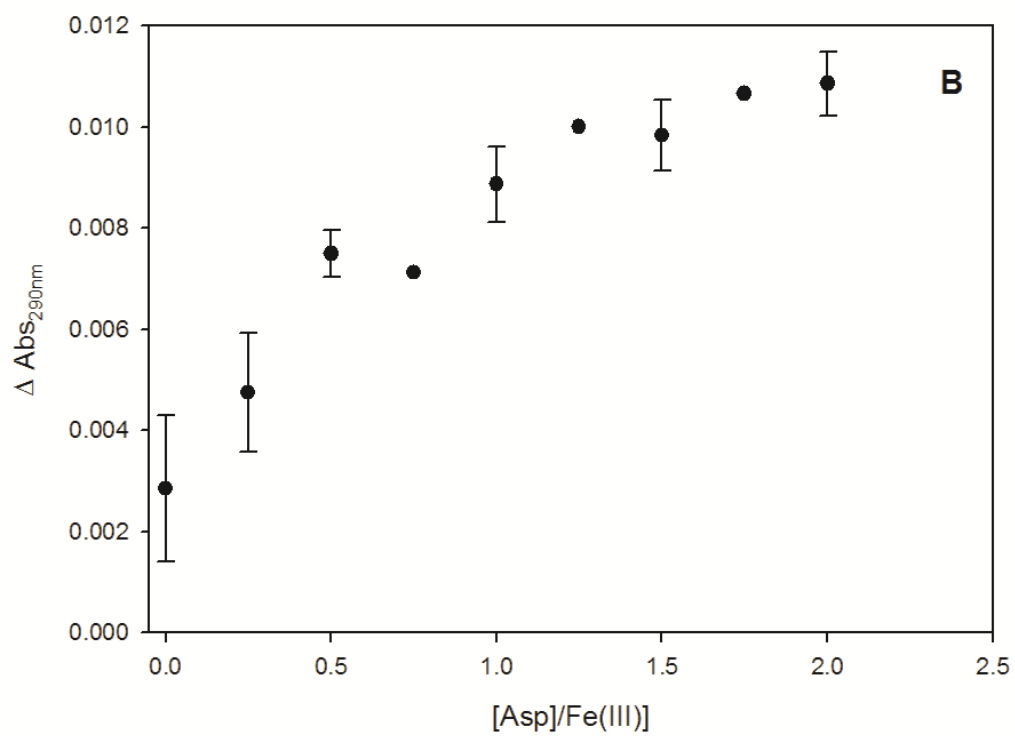
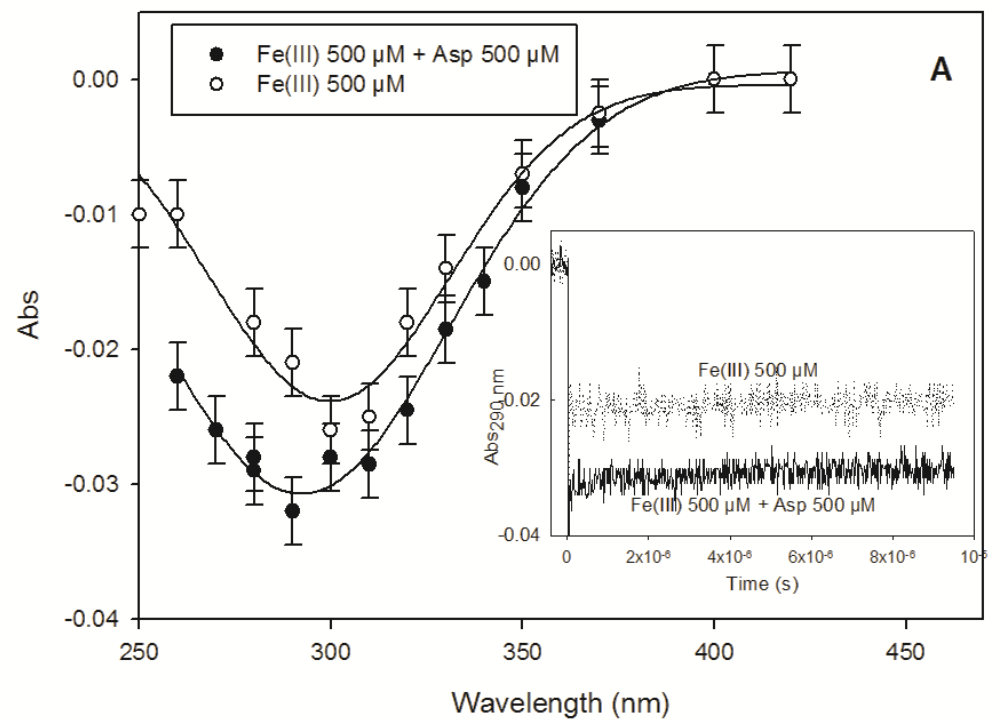
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474

475 **Figure 1**

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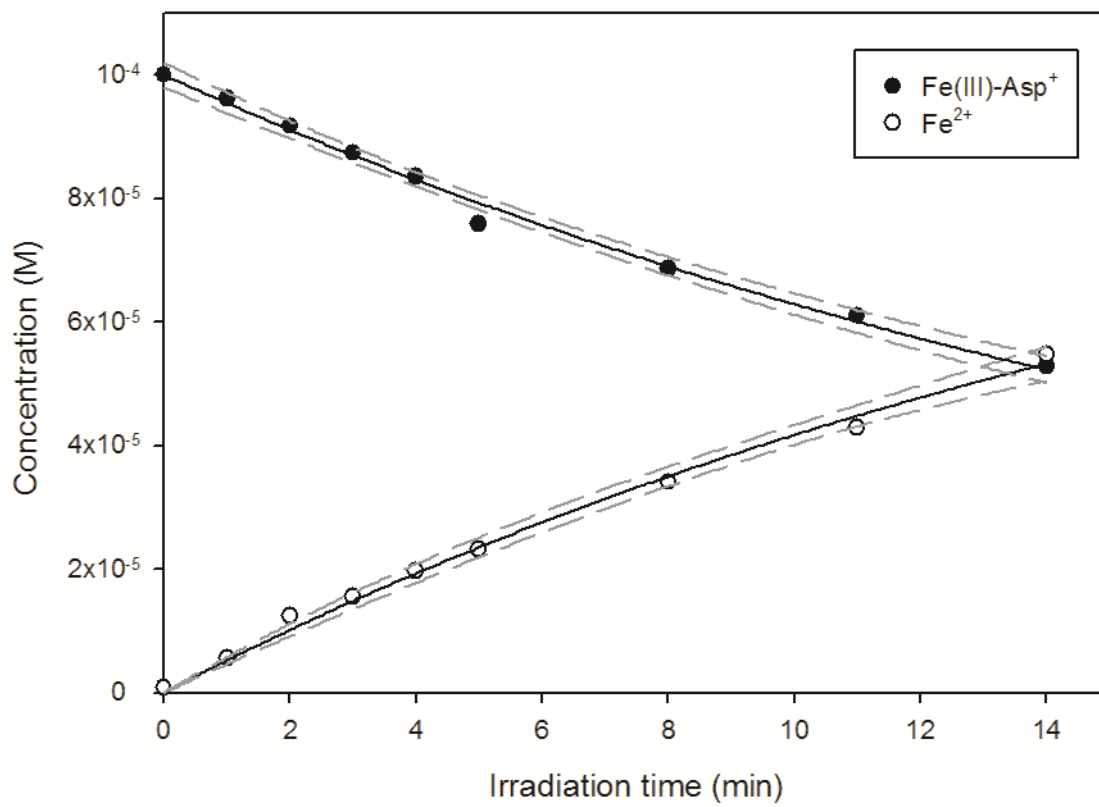


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478 **Figure 2**

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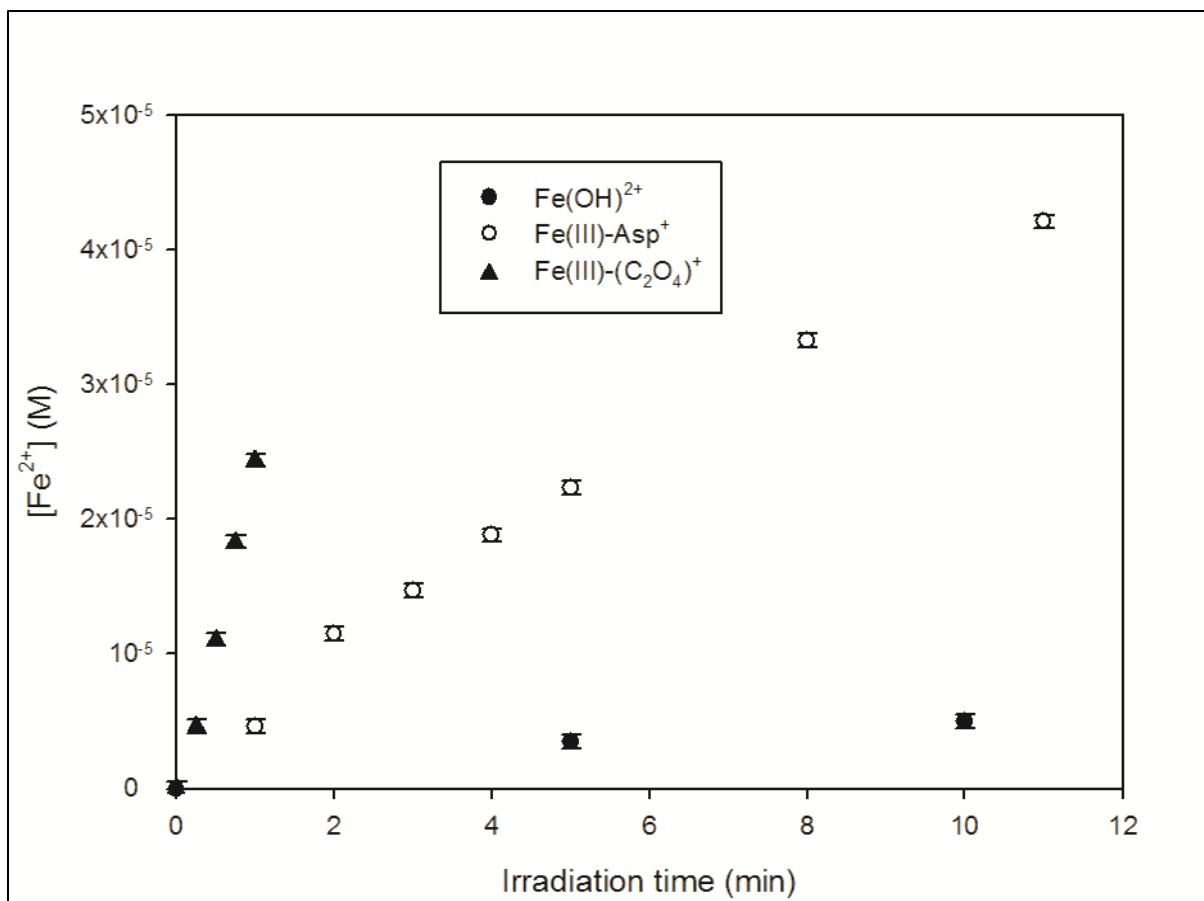
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482 **Figure 3**

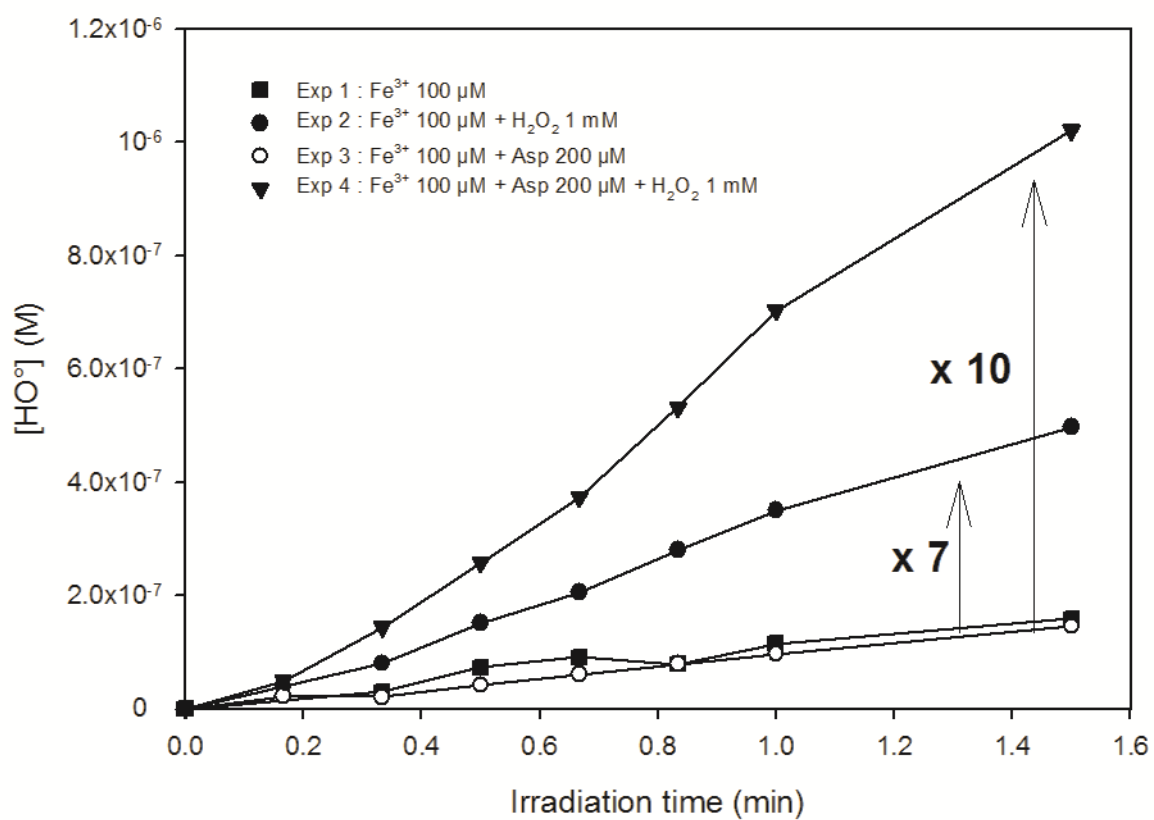




483

484 **Figure 4**

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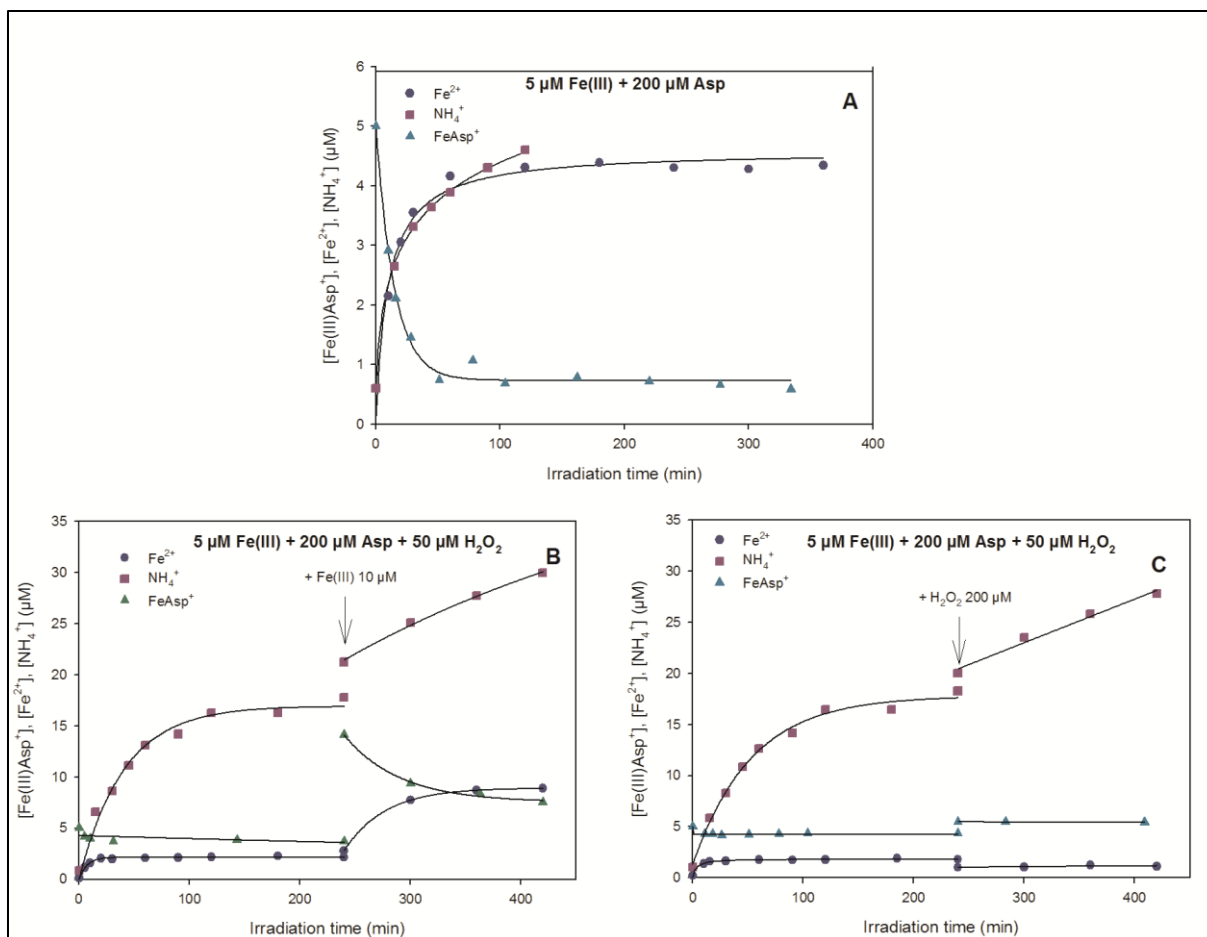
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487 **Figure 5**

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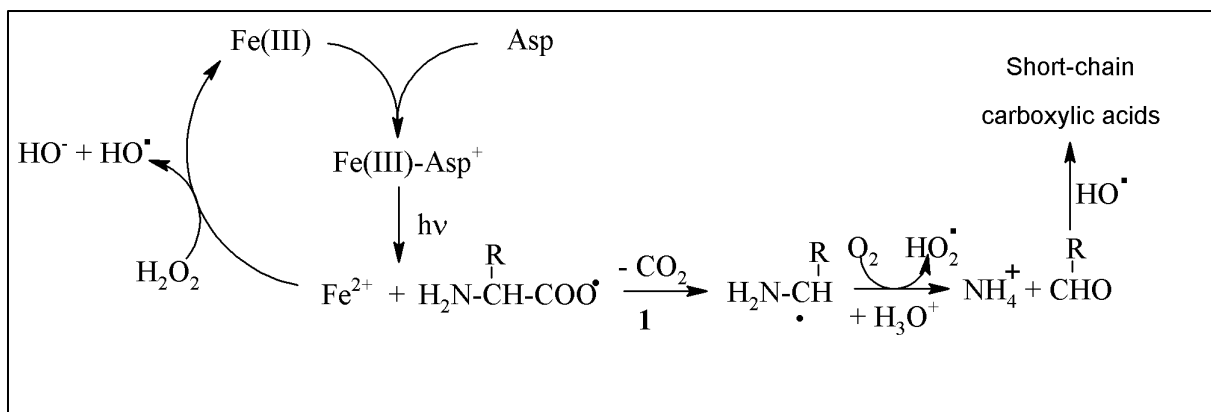
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492 **Figure 6**

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494

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497 **Figure 7**