

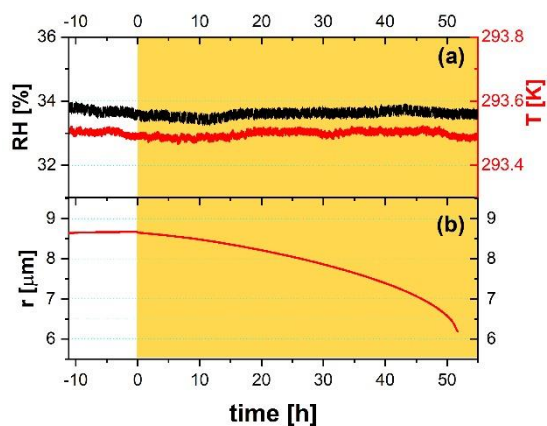
We thank the reviewer for such helpful comments and suggestions of our manuscript. We will answer the questions one by one below and list our planned changes to the manuscript as well.

Major comments:

Line 126-127: Figure 2 shows the data while irradiation, not while the particle is equilibrating. The data for this part of the experiment are shown over a much shorter time than the 10 h stated in the methods section. what is the magnitude of mass loss during the dark equilibration period?

The mass of the particle is quite stable during the dark equilibration period as soon as the RH and T in the trap are stable, since no chemistry happening in the dark. **An example is shown below.** Therefore, we only show a short dark period to indicate that the particle was stable before we turned on the light.

No change to the manuscript.



There are conclusions made in the abstract that did not come across very clearly upon examining the figures and the text. It is important that each major statement on observations in the manuscript is supported by the data analysis in the manuscript. The figures need to be re-made to make conclusions easier to see for connection with the abstract. For example, the conclusion in line 17 was for 10 micron particles over 24 hr, but the modeling results in Figure 13 were for 1 micron to nanometer particles, and their mass loss rate is different. Also, data in Figure 6 show less than 80% mass loss.

We thank the reviewer for pointing out that the reader needs to be more clearly informed which results are experimental observations and which are model results.

Fig. 2 shows that a single, levitated particle with a 12  $\mu\text{m}$  radius loses about 80% of its mass to the gas-phase under the conditions of this particular experiment.

The purpose of Fig. 6 is to show that the PRAD model is able to simulate such experiments reasonably well. We show only the mass loss of the first 40 % here as eventually crystallization of iron citrate occurs within the particle, which is not treated in our model. However, we agree with the reviewer that it may help the reader to see the data of the subsequent mass loss to better understand our statement in lines 302-304:

*“However, the model is not able to capture the full degree of acceleration of the degradation rate, as it does not attempt to include the complete multi-generational oxidation chemistry at the level of individual components after initial radical production.”*

The reviewer is correct, that the model results of Fig. 13 cannot be directly compared to the experimental data shown for example in Fig. 2 as the irradiation conditions and the particles size is quite different. For estimating the effect on atmospheric aerosol particles, we developed the PRAD model.

#### **Planned changes for a revised manuscript:**

To avoid confusion between experimental data and modeling predictions, we will shift lines 17 to 20 of the abstract to directly follow the list of experimental techniques and only then introduces the PRAD model in the abstract so that there is a clear separation between experimental results and modeling predictions.

The figure below shows how the experiments of Fig. 6 evolve subsequently. We will put this figure in the appendix of the paper. And a comparison with PRAD modeling is shown in the same figure as well.

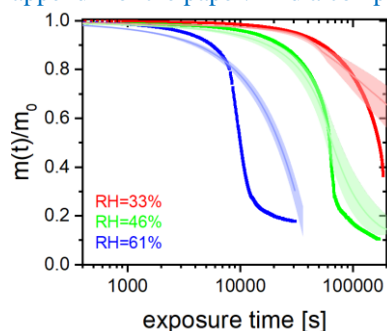


Figure A3.  $\text{Fe}^{\text{III}}(\text{Cit})/\text{CA}$  (molar ratio 0.05) particle mass change with irradiation (log scale) at different RH: 33% (red), 46% (green), and 61% (blue). The irradiation wavelength was 375 nm, its intensity was  $0.25 \text{ W cm}^{-2}$ , and the experimental temperature was 293.5 K. Thick lines are EDB experimental data. Thin lines are PRAD model outputs (with  $\pm 2\%$  RH uncertainty shown as shaded area).

In the abstract, the statement, “The PRAD model was tuned to reproduce all experimental results”: The mass loss data in Figure 2 does not show modeling results specific to the experimental setting to support this sentence. Also, model results in figures 7 and 11 are way off from the experimental data. So, it is not clear how this model reproduced the experimental data.

#### Planned changes for a revised manuscript (changes in bold):

We will rephrase the sentences in the abstract and add a sentence: “The PRAD model was tuned to **simultaneously** reproduce all experimental results as closely as possible and captured the essential chemistry and transport during irradiation. In particular, the photolysis rate of  $\text{Fe}^{\text{III}}$ , the re-oxidation rate of  $\text{Fe}^{\text{II}}$ ,  $\text{HO}_2$  production, and the diffusivity of  $\text{O}_2$  in aqueous  $\text{Fe}^{\text{III}}(\text{Cit})/\text{CA}$  system as function of relative humidity and  $\text{Fe}^{\text{III}}(\text{Cit})/\text{CA}$  molar ratio could be constrained. **This led to satisfactory agreement within model uncertainty for most, but not all experiments performed.**”

It is not clear how the molar ratio of  $\text{Fe}(\text{III})(\text{Cit})$  to citric acid (CA) was controlled. The manuscript shows that it was not fixed in the experiments, and the chemical composition was calculated. Section 2.1 does not describe solution preparation from which aqueous droplets were taken for the EDB measurements. The caption of the figures reported 0.01, 0.05, 0.07, and 1. How does these calculated molar ratios correlate with the solution prepared in the lab?

We agree with the reviewer and wish to make it more clear which mole ratio was used for each experiment and each PRAD model run. To summarize, the initial mole ratio was 0.05 for all EDB experiments shown in the manuscript. For all STXM/NEXAFS experiments, the initial mole ratio was 1.0. For all CWFT experiments, the initial mole ratio was 0.07. The PRAD model of these experiments used the same initial mole ratio, respectively. We performed one additional PRAD model simulation (Fig. 13) using a mole ratio of 0.01. **We have added an addition section (new section 2.1) that details our solution preparation:**

Citric acid ( $\geq 99.5\%$ ) and Iron(III) citrate tribasic monohydrate (18–20% Fe basis) were purchased from Sigma-Aldrich. Iron(II) citrate ( $\text{Fe}^{\text{II}}(\text{HCit})$ ) was purchased from Dr. Paul Lohmann GmbH KG. Dilute aqueous solutions of  $\text{Fe}^{\text{III}}(\text{Cit})/\text{citric acid}$  and  $\text{Fe}^{\text{II}}(\text{HCit})/\text{citric acid}$  were made in ultrapure water ( $18 \text{ M } \Omega \text{ cm}^{-1}$ , MilliQ). Since  $\text{Fe}^{\text{III}}(\text{Cit})$  only dissolves slowly in water, citric acid solution with  $\text{Fe}^{\text{III}}(\text{Cit})$  crystals inside has to be put in an ultrasonic bath for at least 24 hours, the same dissolving procedure was also applied to the  $\text{Fe}^{\text{II}}(\text{HCit})$  powders. Note that all the procedures were done under red light illumination because  $\text{Fe}^{\text{III}}(\text{Cit})$  is light sensitive. Molar ratio between  $\text{Fe}^{\text{III}}(\text{Cit})$  and CA was different for each experimental methods used in this study. For EDB, STXM/NEXAFS and CWFT experiments, stock solutions were prepared with molar ratios of 0.05, 1.0 and 0.07, respectively.

What is the pH of the solution prepared in the lab and that calculated from the chemical composition model? What is the effect of pH on mass loss? Photochemical degradation of iron complexes is pH dependent, not only wavelength dependent. This is a major issue that is not addressed in the current version of the manuscript.

We thank the reviewer for pointing out and agree strongly with her/him about the importance of pH.

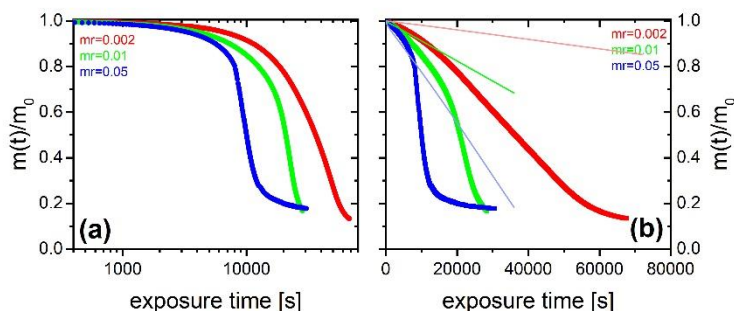
For all three kinds of experiments, CA is highly concentrated in the aqueous system at the relative humidities considered. Its presence dominates the pH (to values in the range of 1 – 2), i.e. the conditions considered in the paper are always acidic. We checked on pH changes predicted by the PRAD model, as it treats the relevant equilibria. According to model outputs, the pH value changes less than 5% during the whole photochemical processes under constant RH.

**Planned changes for a revised manuscript (changes in bold):**

We will add this clarification to the section of the PRAD model.

There was no experimental studies looking at the extent of mass loss as a function of molar ratio, as there was for particle radius and %RH (e.g., figure 13).

We did the experiments to look at the effect of molar ratio (thick lines), and compare the data with PRAD model (thin lines). However, the data was not taken into account when we were optimizing the model.



In addition, CWFT experiments were performed as a function of mole ratio and are included in our another manuscript, showing an increasing HO<sub>2</sub> production with the molar ratio of Fe<sup>III</sup>(Cit) to CA, which is captured by PRAD model (Alpert et al., 2020).

*Alpert, P. A., Dou, J., Corral Arroyo, P., Schneider, F., Xto, J., Luo, B., Peter, T., Huthwelker, T., Borca, C. N., Henzler, K. D., Herrmann, H., Raabe, J., Watts, B., Krieger, U. K., and Ammann, M.: Anoxic aerosol particles leads to preserved radicals, under review of Nature Communication, 2020.*

Figure 10: per the mechanism in Figure 1, and the abstract line 4,5 “In the presence of O<sub>2</sub>, ensuing radical chemistry leads to further decarboxylation, and the production of .OH, HO<sub>2</sub>, peroxides, and oxygenated volatile organic compounds, contributing to particle mass loss”, I expected the opposite result for the ‘mass remaining’ data in the right axis: that the mass remaining for the particle recovered in O<sub>2</sub> for 45 min is lower than irradiating fresh particle under N<sub>2</sub> since the photolysis and loss of CO<sub>2</sub> is driven by the chemistry of dissolved O<sub>2</sub>. I did not find an explanation in the text for this part of the figure.

We think the reviewer misunderstood Fig. 10. Fig. 9 is intended to illustrate the experimental procedure. We agree with the reviewer that the uptake of O<sub>2</sub> leads to further oxidation and thus more mass loss. However, both data sets (black and red) shown in Fig. 10 are mass loss due to photochemistry in N<sub>2</sub>. The black one is for the irradiation of fresh particle, and the red one is for another irradiation of the particle after recovery in O<sub>2</sub> in the dark for 45 min, which shows less mass loss due to less photochemically reactive Fe(III) contained in the particle than it initially had.

**Planned changes for a revised manuscript (changes in bold):**

We need to stress stronger that the data shown in Fig. 10 are due to loss in a nitrogen atmosphere where only the decarboxylation is occurring with no further chemistry. We will rephrase the corresponding section.

Minor comments:

Line 418: The reference Duo et al 2020 is not published. The sentence citing this reference does not refer to unknown information. There are book chapters and numerous review articles on this topic, which should be cited.

We thank the reviewer for the suggestion, and change the reference to:

George, C., D'Anna, B., Herrmann, H., Weller, C., Vaida, V., Donaldson, D. J., Bartels-Rausch, T., and Ammann, M.: *Emerg-605ing areas in atmospheric photochemistry*, in: *Topics in Current Chemistry*, vol. 339, pp. 1–53, Springer, Berlin, Heidelberg, [https://doi.org/10.1007/128\\_2012\\_393](https://doi.org/10.1007/128_2012_393), 2012.

George, C., Ammann, M., D'Anna, B., Donaldson, D. J., and Nizkorodov, S. A.: *Heterogeneous photochemistry in the atmosphere*, *Chem. Rev.*, 115, 4218–4258, <https://doi.org/10.1021/cr500648z>, 2015.

Figure 2: for consistency with the text, change the y-axis to hours instead of seconds for time since rates and time discussed in the text are expressed in hours.

In the text, we discussed in both seconds and hours.

We change the upper x-axis to hours:

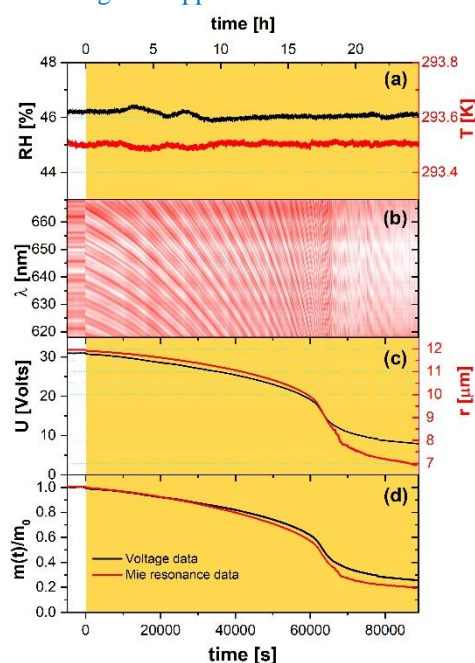


Figure 3: there are two shaded areas in dark and light green, and only the light green is described in the legend. There seems to be a missing compound that describes the dark green shaded area. Also, it is not clear why there are references in the caption? Were some of the spectra shown adapted from these references?

We will change the caption in Fig. 3 to be easier to understand and referenced correctly. First, we clarify that there is only green shading and blue shading. We do not have different shades of green shading.

**We will change the caption to be:**

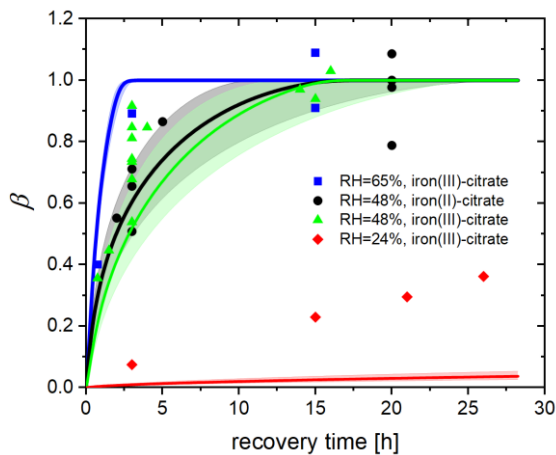
Figure 3. Iron L-edge NEXAFS spectra of Fe<sup>III</sup>(Cit)/CA particles before and after irradiation with UV light shown as orange and red, respectively. The previously recorded spectrum from mixed xanthan gum (XG) and FeCl<sub>2</sub> particles exposed to ozone is shown as the purple line, and a spectrum from FeCl<sub>2</sub> particles is shown as the blue line (Alpert et al., 2019). FeCl<sub>2</sub> and FeCl<sub>3</sub> spectra from Moffet et al. (2012) are shown as the blue and green shading, respectively. The vertical dashed lines indicate peak X-ray absorption at 707.9 shifted to 708.3 eV for Fe<sup>II</sup> and 709.6 eV shifted to 710.0 eV for Fe<sup>III</sup>.

Figure 6: the color description for RH does not match the actual colors of the markers. For example: in the figure, data for RH=33% is red, and in the caption it is mentioned as '(black)'. In be, there are markers and lines, for experimental data and model results. Modify the legend to reflect that to avoid confusion which is which.

We thank the reviewer for pointing out this mistake. The color descriptions in the caption have been corrected.

Figure 11: use different marker shapes for different RH, chemicals. Take into account that this figure might be printed on a black and white printer and will be hard to read as is. Why is here more than one data point at t~3 min for the RH = 48%? Same at t~ 15 min and 20 min for 48% and 65% for iron(II) and iron (III) citrate?

We use different marker shapes but also keep different colors to indicate model simulations under corresponding conditions.



The reason for more than one data point is that we repeated the same procedure several times to be confident of the experimental results.

Figure 12: add a legend defining the markers and lines

Adapted accordingly.

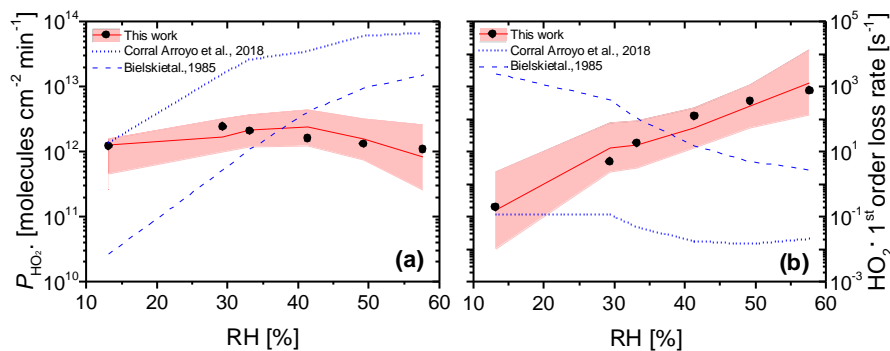


Figure 13: add 'RH=40%' to legend in (a), and '100 nm' to legend in (b).

Adapted accordingly.

