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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-cloud formation of secondary species in iron-containing particles" *by* Qinhao Lin et al.

Anonymous Referee #3

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Lin et al present an important measurement study of the presence of Fe in individual cloud residual particles, compared to clear air, as well as the presence of secondary species expected to be formed via cloud processing. Given the current interest in Fenton chemistry and importance of considering what fraction of cloud droplets actually contain Fe, this study is quite timely and needed. Overall, the study is well done; however, significant technical corrections and clarifications are needed, as described below.

Major comments:

- As a point of caution in wording, the SPAMS measures the presence of a particular species, but without calibration taking into consideration matrix effects, the mass of that species is not quantified. While much of the paper uses the phrasing of "number

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Discussion paper

fractions", there are many places (e.g. lines 30-31 of abstract, line 394 in conclusions, and many other places) where a reader would expect the authors to be discussing mass concentration, as is the traditional norm of the atmospheric aerosol community. Phrasing should be revised to avoid this potential confusion. For example, on line 32 of the abstract and line 394 of the conclusions, the phrasing "extremely high amounts of sulfate" and "no enhancement in sulfate" is used, but sulfate mass was not measured in this study, rather the number fraction of particles containing sulfate was measured. This distinction is important, as it impacts the interpretation of results, for example that the authors state "no distinct changes in sulfate during cloud events" (lines 33-34), where the authors did not measure sulfate mass to evaluate this result. The authors need to fix this phrasing (assumption of mass rather than number fraction) and associated conclusions throughout the manuscript. The phrasing such as "number fraction of Fe-containing particles internally mixed with sulfate" would be clearer, for example. Wherever percentages are stated, the phrasing "number fraction", "by number", or similar should be used to avoid confusion. For another example, the authors stated on line 176 "Lithium (m/z 7[Li]+) was found to account for 7% of the Fe-rich type"; I believe the authors mean "7%, by number,", rather than "7%, by mass,", as the typical reader would assume.

- Lines 147-152: In the screening for Fe-containing particles, were particles required to contain m/z 54, to ensure the presence of Fe? This is important and not clear here. It would seem that a range of 56Fe/54Fe is most appropriate, rather than simply a ratio >10, which could mean little m/z 54 present.

- At the beginning of the Results & Discussion, I highly encourage the authors to add a section or several sentences addressing the number fraction of Fe-containing particles out of the total measured for the categories of cloud, interstitial, and clear air. It is important for those modeling Fenton chemistry to understand the fraction of cloud droplets that contain Fe, and so, I think this information will be very useful to the community.

- Due to matrix effects in LDI, it is not valid to compare peak areas between particle types (e.g. Line 173, Figure S5, Lines 211-213, and other locations). I refer the authors to Hatch et al (2014, Aerosol Sci. Technol.), Gross et al (2000, Analytical Chem.), and Reinard & Johnston (2008, J. Am. Soc. Mass Spectrom.).

- Lines 209-214 and 259-260: Please check that the percentages being compared are indeed statistically significant. Please report errors in the text as well to provide greater context.

- Section 3.3: A main result is that Fe-dust particles were more likely to containing oxalate precursors; however, I am concerned about potential ion peak interferences as follows: m/z -59 (HCNO2-, AlO2-), m/z -87 (AlCO3-), m/z -103 (AlSiO3-), and m/z -117 (CaCO3OH-). Either the simultaneous presence of related peaks (e.g. Al+, Ca+, SiO3-, CNO-) should be investigated, or these ion peaks should not be included when screening for oxalate precursors.

- Lines 345-346: Since both nitrate and sulfate were present, how can the presence of ammonium nitrate be ruled out?

- Figure 3: Given the similarities between the cloud residues and interstitial particles, is it possible that the interstitial particles are already cloud processed?

Technical Comments:

- Please clarify the sentence on Lines 38-41.

- Please add a reference to the sentence on Line 47, and provide quantitative and location-based context for “frequently detected”. This is surprising to me.

- Line 54: Change “contained” to “can contain”.

- Lines 61 & 72: Change “aerosol Fe” to “Fe-containing particles”. Watch this phrasing throughout. It is not correct to say that another chemical species is “in the aerosol Fe”.

- Lines 75-76: The Sullivan & Prather 2007 paper describes a shipboard study, which

would not have been a low RH, as stated here.

- Lines 85-87: Vague sentence; please clarify.

- Lines 89-92: The authors have published several other manuscripts on GCVI-SPAMS measurements at this field site. It would be helpful for the reader for these manuscripts to be described briefly and cited here to provide greater context for the current work.

- Lines 100-101: Please clarify this sentence and what is meant by “measured area”.

- Lines 121-122: Was a cyclone used? Please state.

- Section 2.1: Move the dates of the study (Lines 122-123) to Section 2.1; also move up the sentence on lines 123-124 that gives the time in cloud during the study. What was the cloud type and temperature? State whether these were liquid-only clouds. Refer to Figure S1.

- Line 125: How were interstitial particles sampled?

- Line 133: Please clarify that the triggers was (I assume) based on the calculated velocity of the particles, rather the intensity of the light scattered, as implied here.

- Line 135: Change “fragments is” to “ions are”.

- Lines 136-139: Fix grammar throughout sentence.

- Lines 145-146: Change “ranged” to “ranging”. Change “bipolar ion mass spectra” to “with the SPAMS”.

- Line 147-148: Change sentence starting with “Because the Fe ion peak at m/z 56 may be contaminated. . .” to “Since other species, such as. . .., may also contribute to m/z 56, the natural isotopic composition. . .”. The phrasing “may be contaminated” is not correct.

- Line 168: Change “averaged mass” to “averaged single-particle mass”.

- Lines 186-189: Please clarify these sentences. The size transmission of the SPAMS

needs to be stated in Section 2.2 to provide context for this statement as well.

- Line 206: Note that temperature and RH also typically follow diurnal patterns.

- Line 234: Please clarify this sentence. It is not clear what “was compared” means in the context of this sentence.

- Line 244: Please quantify what is meant by “barely detected”.

- Line 250: Please clarify what is meant by “overwhelm the simultaneous irradiation effect.”

- Lines 262-261 and 267-270: Please clarify these sentences.

- Make sure all figure captions are clear to a reader not familiar with single-particle measurements.

- While up to the authors’ discretion, I suggest combining the Atmospheric Implications and Conclusions sections to improve integration of the study results with their impacts.

- Figure 1 caption: Change “averaged mass spectra” to “average single-particle mass spectra” for clarity.

- Figure 2 caption: The reference to Pratt et al. is not needed in the caption.

- Figure 5 caption: Should “its precursors” be “the sum of the peak areas of its precursors”?

- Figure 6 caption: More information is needed here for the non-SPMS reader to understand the figure.

- Figure S1: What does “alternate sample” mean? What does “used to correct interstitial particles” mean?

- Figure S4 & S7: Please clarify the captions and include the m/z peaks used in these analyses.

- Figure S6 caption: Change “of oxalate in the non-Fe” to “oxalate-containing non-Fe”.

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