Response to comments

Reply to the referee #1:

The authors presented single-particle measurements of iron-containing aerosols to analyze the formation of secondary species. The work conducted in this paper may contribute to improve our understanding of effect of iron on the formation of secondary species, although more careful discussions are required for the iron chemistry in aerosol and cloud water. I have some comments and questions to improve this paper.

We would like to thank the referee #1 for his/her useful recommendations to greatly improve our manuscript. All of the comments have been properly addressed in the revised manuscript.

Specific comments

p.9, l.187, Figure S2: Please indicate the upper size of the particles.

Reply: The upper size of particles was 2.0 μm. We have provided the information on the upper size of the particles. Please refer to Lines 214-216 in the revised manuscript and Figure S3 in the revised Supplement.

p.12, l.249: Please present the references and specify the in-cloud chloride formation and irradiation effect.

Reply: Higher NFs of chloride were found in the Fe-containing cloud residues and interstitial particles compared to the cloud-free particles (16 ± 1% or 13 ± 2% versus 6 ± 1%, by number) (Figure 3). The partitioning of volatile gaseous chloride (i.e., HCl) into the aqueous phase was a major contributor to the increased chloride in cloud droplets (Sellegri et al., 2003). On the other hand, the irradiation effect during daytime would generally result in the reduction of ammonium chloride in the particles due to evaporation at high temperature (Huang et al., 2011). In the case of cloud events, there was no change in NF of chloride in the Fe-containing cloud residues between daytime and nighttime (Figure 4c), suggesting that the amount of in-cloud chloride formation was less affected by irradiation effect. In the case of cloud-free events, no decreased NF of chloride in the Fe-containing cloud-free particles was also observed during daytime relative to the nighttime (Figure 4c), presumably due to the formation of calcium chloride (Sullivan et al., 2007). Please refer to Lines 271-274 and 283-290.

p.12, l.256: Did you measure HCl concentration? What are the sources of HCl in the region?

Reply: The measurement of gaseous HCl has not been conducted in our study. Recently, Fu et al. (2018) reported that the anthropogenic gaseous HCl emission was estimated to be in a range from 20-200 kg/km^2 in southern China, mostly from coal burning, agricultural biomass burning, and waste incineration. The gaseous HCl sources in this region might originate from regional transport of these anthropogenic HCl in southern China. We have clarified them. Please refer to Lines 280-283.

p.15, l.319: The Fenton reaction is a sink of ferric iron. Please consider the redox cycling for the role of the Fenton reaction in the formation of aqueous-phase OH.

Reply: We have added the effect of Fe redox cycling on the formation of aqueous-phase OH through Fenton reaction: “These findings implies that aqueous-phase OH were likely produced by redox cycling of the Fe-driven Fenton reaction (Hems et al., 2017), and thus enhance oxidation of various precursors to form oxalate during cloud processing.” Please refer to Lines 359-361.

p.18., l.378: The photolysis of Fe-oxalate complexes could reduce the net amount of oxalate formation in cloud droplet, even though the Fenton reaction increases the formation rate of aqueous-phase OH (Sorooshian et al., 2013; Lin et al., 2014). Thus, other mechanisms (e.g., strong complexation of iron with organic compounds) are needed to enhance the oxalate concentration in Fe-rich particles. Please consider the effect of Fe chemistry on the net formation of oxalate and discuss the mechanisms to enhance the oxalate concentration in Fe-rich particles.

Reply: We agree with the comment. We have discussed the effect of Fe chemistry on the net formation of oxalate: “Our data showed that aqueous-phase oxidation of the oxalate precursors was an important contributor to the in-cloud formation of oxalate in the Fe-rich particles. The Fe-driven Fenton reaction likely accelerate the conversion of the oxalate precursors to oxalate in the Fe-rich particles during cloud processing. Moreover, the complexation of Fe with oxalate might further increase oxalate content in the Fe-rich cloud residues (Chen and Grassian, 2013), but the photolysis of Fe-oxalate complexes in the Fe-rich cloud residues would lead to the losses of oxalate during daytime.” Please refer to Lines 421-428.

p.18., l.384: The formation of stable complexes (e.g., calcium oxalate) is assumed for the

SOA yield to remain entirely in the particulate phase when the water is evaporated. This is different from the suppression of oxalate-promoted Fe dissolution in the model (Ito, 2015), which is based on the laboratory measurements (Chen and Grassian, 2013). At low concentration of oxalate, complexation of oxalate with iron on the surface of the particle is suppressed through formation of Fe-oxalate complexes in solution. Less content of Ca-containing particles suggests low pH in aerosol water. It was proposed that the competition is more significant at low pH. Thus, excess oxalate is needed to enhance Fe dissolution in aerosols. Please consider the effect of the ligand concentration on Fe dissolution in aerosols and discuss the implications.

Reply: We have emphasized the role of oxalate concentration in Fe dissolution in the revised manuscript: "In this work, nearly 45 ± 1% (by number) of the Fe-rich cloud residues contained only oxalate. The mass concentration of oxalate in the bulk aqueous phase might be overestimated in model simulations. This might suppress Fe dissolution under low concentration of oxalate because of competition of oxalate complexation between dissolved Fe in solution and Fe on the particle surface (Chen and Grassian, 2013)." Please refer to Lines 431-436.

p.19, l.398: Please reconsider this. The Fenton reaction increases the formation rate of aqueous-phase OH, but the net amount of oxalate formation in cloud droplet is reduced by the photolysis of Fe-oxalate complexes. Please also consider the pH upon droplet evaporation when the ammonium species may enhance the SOA yield.

Reply: As suggested by the referee #3, the Sections Atmospheric Implications and

Conclusions have been combined to improve integration of the study results with their impacts. The effect of Fe chemistry on the net formation of oxalate have already been added, as stated above. We have also included the following sentence to mention the contribution of ammonium species to oxalate formation: “Ammonium species possibly enhance oxidation of precursors to form oxalate in the Fe-rich cloud residues through increasing aerosol pH.” Please refer to Lines 421-428.

References

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