

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2022-134

Akinori Ito (Referee)

Referee comment on "Iron (Fe) speciation in size-fractionated aerosol particles in the Pacific Ocean: The role of organic complexation of Fe with humic-like substances in controlling Fe solubility" by Kohei Sakata et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-134-RC2>, 2022

General comments

Organic ligands have been postulated to enhance aerosol iron solubility, but the chemical speciation of Fe complexes in size-resolved aerosols is not characterized well. The authors analyzed Fe species in size-fractionated aerosol particles over the Pacific. The X-ray spectrum analysis using reference materials indicated that fine particles contained ferric organic complexes with humic-like substances. The Fe(III)-HULIS was suggested to be formed during transport to the Pacific. The results presented in this paper contribute to better understanding of Fe cycles. I have some comments and questions to improve this paper.

Specific comments

P2., l.30: Even though EF of Fe is close to one, L-Fe in fine particles can be derived from anthropogenic sources due to much higher solubility, as is indicated by Fe stable isotope ratios and the model estimates over the northwestern Pacific. This lower Fe solubility for mineral dust is partly because the high dust/liquid ratio due to low water content in

mineral dust could suppress the Fe dissolution even in acidic condition over polluted regions, in addition to the buffering capacity of calcite. Moreover, the Fe dissolution rate for mineral dust is much slower than fly ash. Please see below and consider rephrasing L-Fe for mineral dust in PM1.3 throughout the paper.

p.3, l.72: Please define the average pH.

p.4, l.81: Please specify previous studies for HULIS on mineral dust or other types. How does it form on mineral dust or other types?

p.4, l.83: Please specify previous studies for siderophore on mineral dust or other types. How does it form on mineral dust or other types?

p.6, l.137: Please specify the filter. Sub-micron particles for Stage 6 samples might penetrate the filter regardless its chemical form including nano particulate form. How do you consider this?

p.6, l.157: How do you consider the external mixing of Fe-bearing particles with the main component of the marine aerosols mentioned in introduction?

Figure 6: Fig. 6 appears before Fig. 2. Please also correct the caption (d) and check the consistency of Fe species with (a).

p.7, l.176: Please also describe the distinction of Fe(III)-HULIS from ferrihydrite and goethite.

p.8, l.202: These equations are not valid at the high dust/liquid ratio due to low water content in mineral dust, which could suppress the Fe dissolution even in acidic solution. How do you consider the degree of the suppression?

p.8, l.210 and l.211: The cloud cycle and dissolution time depend on the transport pathway of the particles. Please specify the method and references to justify the 12 hours and half of the transportation time.

p.8, l.214: The dissolution curve is fitted to the mass concentration. Please specify the dissolution rates of biotite and illite after normalizing the dissolution rates to the mineral mass.

p.8, l.225: How do you consider calcite? How do you also consider the external mixing of Fe-bearing particles with the main component of the marine aerosols mentioned in introduction?

p.9, l.251: Please show the enrichment factors for Beijing aerosol and NOTOGRO.

p.10, l.276: How do you reconcile non-anthropogenic Fe source with the positive correlation between Fe solubility and EF of Pb?

p.10, l.280: How do you reconcile the positive correlation between Fe solubility and non-sea-salt sulfate with non-anthropogenic Fe source?

p.10, l.284: Please show Fe solubilities for Beijing aerosol and NOTOGRO.

p.10, l.287: How do you confirm this before the 7-day backward trajectories?

p.10, l.290: How do you reconcile this with the positive correlation between Cd or Pb and non-sea-salt sulfate? How do you explain low non-sea-salt sulfate concentrations over SPO? Please show non-sea-salt sulfate concentration which can be attributed to biogenic S emission alone.

p.11, l.315: Please show biotite fraction for Beijing dust quantitatively.

p.11, l.319: The biotite fraction in S6-WPO2 is higher than that in S6-NOTOGRO. The biotite fraction in the S5-WPO3 is also higher than that in S5-NOTOGRO. These results rather suggest that biotite in fine particles is relatively insoluble. How do you explain higher biotite fraction over the oceans than NOTOGRO?

p.11, l.335: Please show the fraction of Al species quantitatively.

p.12, l.360: Non-spherical dust particles can be converted to spherical particles when they are intensely altered. Thus, the irregular shapes rather suggest that phyllosilicate particles in S6-WPO2 are relatively unaltered. How do you reconcile this intensely altered particles with irregular shapes?

p.13, l.375 and Fig. 9: Why don't you show the dissolution curve from the Beijing dust? In the laboratory experiments, Fe solubility for mineral dust has not reached more than 15% at pH 1 for the proton-promoted dissolution time up to 120 (h), in contrast to fly ash. Moreover, Eq. 7 is not valid at the high dust/liquid ratio due to low water content in mineral dust, which could suppress the Fe dissolution even in acidic condition over polluted regions. Thus, it is extremely hard to accept such high Fe solubility for the samples with no evidence from the laboratory experiments and field observations for mineral dust near the source regions. The results presented in this paper rather suggest that L-Fe in fine particle is mainly derived from anthropogenic source.

p.14, l.412: How do you reconcile this with the acidifications of mineral dust by sulfate derived from biogenic S mentioned in this paper?