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Atmospheric
Chemistry
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Discussions

Interactive comment on "Application of synchrotron radiation for measurement of iron red-ox speciation in atmospherically processed aerosols" *by* B. J. Majestic et al.

Anonymous Referee #2

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The authors use a combination of synchrotron radiation (XANES), ICP-MS, and a ferrozine wet chemistry technique to explore the speciation of soluble and total iron in ambient particles collected from three sites in the U.S. In addition, they have done a series of aging experiments to examine how Fe oxidation states might change during atmospheric transport. While there are several important issues that should be addressed, I support publication in ACP after revision.

Major Comments

1. Information from XANES. The most novel part of this work is its use of XANES (X-ray Absorption Near Edge Structure) spectroscopy to distinguish between Fe(II) and

Fe(III) in ambient particles. This technique has been used extensively in geochemistry, but it has only been used for atmospheric particle applications relatively recently.

(a) Because of its novelty for atmospheric samples, the authors should more explicitly state what information comes from XANES and how this is used to get the reported values. My understanding of XANES is that it provides the relative amounts of Fe(II) and Fe(III) (e.g., as an Fe(II)/Fe(III) ratio) and does not provide absolute amounts of either. Thus it must be combined with data on the total amount of iron (e.g., from the ICP-MS data) in order to determine absolute amounts of Fe(II) and Fe(III). The experimental portion of the manuscript does not make this clear, but rather suggests that XANES gives Fe(II) and Fe(III) amounts directly. The manuscript should be modified to explicitly state what quantities are determined from the various methods.

(b) If XANES is in fact giving absolute amounts of Fe(II) and Fe(III), then the total Fe determined from XANES should be compared to the total Fe from ICP-MS.

(c) Page 1365, lines 15 - 20. This is an example of text that suggests XANES directly gives the amount of Fe(II). If XANES only gives the Fe(II)/Fe(III) ratio, then this report of precision is misleading, as XANES is not giving an amount of Fe(II), but rather a ratio of Fe(II)/Fe(III). Better to report the actual data from the method (i.e. the ratio of oxidation states) rather than a derived quantity based on a fixed ICP-MS Fe amount.

(d) There are a number of other instances where the text should be clarified to indicate that the XANES determination of Fe amounts (as opposed to Fe(II)/Fe(III) ratios) requires a total Fe measurement such as with ICP-MS (e.g., page 1366, lines 20 - 23; section 3.2; first sentence of discussion). The wording should be modified in each case to reflect the overall technique.

2. Artificial aging. More experimental details are needed in order to understand the relevance of the aging to tropospheric conditions.

(a) There is not enough description to understand the illumination. What lamps were used? How do their spectral outputs compare with some reference sunlight?

(b) What was the gaseous atmosphere that the samples were exposed to? Was it relative-humidity-conditioned ambient air? Was the air purified at all?

(c) Were the samples in containers? Was there anything between the sampled PM and the lamps (e.g., the lid of a container)?

(d) Were there any controls that were not aged (e.g., unexposed portions of samples) beyond the time zero point? Was the time zero point re-analyzed after 10 or 40 days of aging?

3. Mechanisms for Fe oxidation and reduction in the Discussion.

(a) The suggested mechanisms for Fe(II) oxidation and Fe(III) reduction should be discussed.

(b) Surface area by itself likely has little bearing on whether Fe will be oxidized or reduced in the atmosphere, as there are atmospheric gases that can oxidize Fe, others that reduce Fe, and some that can do both (e.g., hydroperoxyl radical and its conjugate base superoxide). What mechanisms do you expect are responsible for Fe oxidation and reduction?

(c) What photoreduction mechanisms are you referring to? Photoreduction is probably also a surface-area related process, as light is unlikely to get deep into these particles (especially the coarse PM). Thus I don't believe that you can distinguish the reaction mechanism necessarily by the size dependence of oxidation state changes.

(d) The authors should compare their aging results with those of previous reports for aging of Fe in PM (and cloud drops). These previous reports include the Zhuang et al. (1992) and Zhu et al. (1993) references cited in the introduction as well as the Arakaki and Faust (1998) paper in JGR and some earlier papers by David Sedlak and Jurg Hoigné. Although the latter papers are specifically about Fe (and OH) chemistry in cloud and fog drops, there are many parallels between this chemistry and the PM chemistry studied by the authors.

4. Quantitation and uncertainty.

(a) Figure 2. The flatness of the XANES calibration curve between approximately 0 - 20% Fe(II) suggests that speciation assignments in this region are highly uncertain, with an uncertainty dependent upon the amount of Fe(II) in the sample. This is especially important since a large fraction of the samples fall within this range. What are the uncertainties in the calibration in this range? What does this mean about the uncertainties in the XANES sample values? (b) On Figure 6 it would be useful to have error bars at the Fe(II)/Fe(III) "interface" to show the uncertainty in the Fe speciation measurements. These error bars should reflect the fact that the Fe(II)/Fe(III) ratios become less certain at lower values.

(c) How were error bars calculated for the various data points in each figure? That is, what do the error bars represent? This should be indicated either globally in the experimental section or on each figure.

4. Other significant issues

(a) Page 1364, lines 25 - 28. The cited peak energy values in the text don't correspond to the peaks in Figure 1. Are they all incorrect?

(b) Figure 10. I wonder how much of these small changes in the coarse, soluble Fe are real and how much is due to experimental variability. Perhaps there is a difference between day 0 and day 6, but it seems unlikely that the intermediate days are showing real trends.

(c) I appreciate the portion of the discussion that examines the consistency between the XANES and ferrozine results for changes in total and soluble Fe(II) with aging. This should be expanded somewhat to describe what appears to be the largest inconsistency: XANES results for LA on 2/13 show a significant increase in the total Fe(II) in the coarse fraction with aging while the ferrozine technique shows a dramatic decrease in soluble Fe(II) in this size fraction with aging. This seems hard to reconcile based on the offered explanations.

Minor Comments

1. Page 1359, line 10. The sentence is missing a period at the end.

2. Page 1359, line 22. The description of the Pehkonen et al. (1993) work is, I believe, incorrect (although it accurately summarizes the wording of their abstract). From a quick read of the paper it appears that the authors never directly compare the oxalate system with the other Fe-ligand solutions and thus it cannot be claimed that formate is more effective than oxalate.

3. Page 1360, lines 15 - 16. The current wording makes it sound as if Mossbauer can only be used for ambient and personal PM exposures, but I believe the intended meaning is the opposite of this.

4. Page 1363, line 9. I believe the Teflo support ring is made of polymethylpentene (rather than polypentene).

5. Page 1365, line 7. Were sample and standard spectra shifted to normalize the energies of the Fe peaks? (For example, to account for slight differences in peak positions between runs.)

6. Page 1366, top paragraph. Given that some very low soluble Fe results are reported (e.g., Figure 12 for Fe(II)), the detection limit for the ferrozine method should be included in the text.

7. Page 1367, lines 1 - 3. The phrase "small portion" doesn't appear to be true for the Feb. 14 LA sample, where it appears that 30 - 40% of the crustal elements are in the coarse mode.

8. Page 1367, end of last paragraph. Do wind data corroborate identifying the foundry and steel fabrication facility as possible sources?

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9. Page 1369, lines 26 - 28. This is an awkward sentence, especially the phrase "...fractions of per cent leachable...".

10. Page 1370, lines 1 - 2. Based on the last column of Table 1, this range should be $<$ 1 - 23%. The stated number is for the percent of total iron that is soluble Fe(II), rather than soluble Fe.

11. References. (a) Not all references are compatible with ACP style (e.g., in some cases all of the title words are capitalized). (b) There are several minor typographic and formatting errors (e.g., missing subscripts in chemical formulas).

12. Figure 1. (a) It would be very useful to show separate spectra for Fe(II) and Fe(III) standards since the text describes determining the Fe(II) and Fe(III) peak heights. (b) It would be useful to show the baselines on one or more of the spectra so that reader can understand the baseline subtraction.

13. Figure 4. (a) The legend here (and in other figures) is small and somewhat difficult to read. (b) It would be more intuitive if the order of the legend bars matched the vertical order of the elements in the plots (rather than being in inverted order). (c) The same is true for the other figures.

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