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Atmospheric
Chemistry
and Physics
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.

B. J. Majestic et al.

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Comment 1a) 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.

Reply: Page 1365, line 10: In order to clarify the procedure used to determine the total Fe(II) and Fe(III), the following sentence is proposed “Ě Fe(II)/Fe(III) ratio. At low values of Fe(0) (which can be detected by XANES), XANES spectroscopy can be used in conjunction with a method which can measure total iron (such as ICPMS) to estimate the absolute mass of Fe(II) and Fe(III).”

Comment 1b) 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.

Reply: As outlined in the Reply to Comment 1a), The XANES data in and of themselves do not provide absolute amounts of Fe(II) and Fe(III).

Comment 1c) 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.

Reply: Page 1365 line 18-19: We agree with the reviewer that the uncertainty of the XANES measurement should be reported. To clarify this, we propose the following change in the text “The overall uncertainty in the reported Fe(II) values is driven by the uncertainty in XANES determined iron oxidation state ratios (uncertainty associated with the ICP-MS measurements of total iron are significantly lower). The Fe(II) concentration was found to be 24 ś 3%, which equates to a RSD of 12.5%, a value which we consider to be a reasonable estimate of the uncertainty associated with the XANES measurement.”

Comment 1d) 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.

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Reply: Page 1366, lines 20-23: To help avoid confusion, these sentences are proposed to read “The solid bars Ěwere measure by both XANES spectroscopy (coupled with ICPMS measurements) and the Ferrozine methodĚ”

Page 1368, lines 1-2: “In Fig. 6, we show theĚ as measured by XANES spectroscopy and ICPMS.

Page 1368, lines 10-12: “Figure 7 presents the size-resolved total Fe(II) and Fe(III) content (derived from XANES and ICPMS measurements) after aging Ě”

Page 1372, lines 1-3: “In this study, we have developed a XANES spectroscopy method to determine the total Fe(II) and Fe(III) ratios in limited-mass atmospheric personal exposure samples. When applied in parallel with ICPMS, XANES spectroscopy can establish the average iron oxidation state in an aerosol sample.”

Comment 2a) There is not enough description to understand the illumination. What lamps were used? How do their spectral outputs compare with some reference sunlight?

Reply: Page 1363, line 21: For clarification of the light sources, the following sentence is proposed. “Illumination of the samples was achieved using a carefully calibrated mix of fluorescent and incandescent light bulbs. The light output from the combination of these bulbs was similar to the solar spectrum, with some excess light in the near infrared region. The spectra from each type of bulb can be found in the supplemental material.”

Comment 2b) What was the gaseous atmosphere that the samples were exposed to? Was it relative-humidity-conditioned ambient air? Was the air purified at all?

Page 1362, line 21: To clarify this point, the following sentence is proposed. “Air conditioners supply the building with filtered air (95% removal of particles 10-0.3 μm), with another 95% bag filter at the inlet of the experimental room. In addition, we installed additional particle filters on the air discharge vents in the chamber. Overall, the air in the room is supplied with 95% recycled air and 5% outside air and the room air was exchanged approximately every 30 seconds. The filters were transparent to gaseous pollutants, so maximum ozone levels in the room would be around the average outside levels (around 75 ppb); however the actual value is likely lower as significant ozone degradation in the ventilation system is expected."

Comment 2c) Were the samples in containers? Was there anything between the sampled PM and the lamps (e.g., the lid of a container)?

Reply: Page 1362, line 19: To clarify this point, the following modification is proposed "The samples were placed in acid-cleaned polystyrene Petri dishes with the cover removed and were artificially agedĚ"

Comment 2d) 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?

Reply: Page 1363, line 5: Our past work suggests that the iron speciation of unexposed samples does not significantly change. For clarification of this point, the following sentence is proposed. "Our previous work shows that the soluble fraction of Fe(II) does not significantly change over the timeframe of this experiment while the PM is stored in the dark at -20oC (Majestic et al., 2006). Therefore, any change in the iron speciation over the course of this experiment is due to the exposure of PM to the artificial atmosphere."

Comment 3a) The suggested mechanisms for Fe(II) oxidation and Fe(III) reduction should be discussed.

Reply: Page 1373, replace lines 5-10: To help the reader understand potential mechanisms, we agree that a discussion regarding these mechanisms of iron transformations are warranted. However, the study was not designed to definitively resolve a specific mechanism, so we keep the discussion brief. The addition of the following paragraph is proposed.

“Iron redox reactions may occur within the aerosol water layer and/or at the particle-air and particle-water interfaces. The absorption spectrum of [Fe(III)OH]2+ overlaps the solar spectrum, and therefore, as studies have shown, cloud processing can play an important role in the reduction of iron in atmospheric waters (Faust and Hoigné, 1989). However, at low pH values (similar to those found in hydrated atmospheric aerosols), [Fe(III)OH]2+ is not present in large amounts (Zhaung et al., 1992) and the dominant Fe(III) species at these conditions is [Fe(III)(H2O)6]3+. Direct photoreduction of [Fe(III)(H2O)6]3+ is likely only a minor mechanism as its absorption spectrum does not significantly overlap with the solar spectrum (Faust and Hoigné, 1989). Therefore, it is likely that other components of the aerosol are responsible for the reduction of [Fe(III)(H2O)6]3+ under environmental conditions usually associated with aerosols. It is known that iron plays an integral role in the sulfur cycle and this may lead to the oxidation and reduction of iron. A discussion of possible mechanisms is discussed in detail elsewhere (Zhuang et al., 1992, Conklin and Hoffmann, 1988). Iron is also known to interact with organic carbon in aerosols where iron red-ox changes have been observed to occur (Kieber et al., 2005; Pehknoen, et al., 1993). For example, photo-reduction of Fe(III)-carboxylic acid complexes has been shown to be a major source of Fe(II) (Okada et al. 2000). Zhuang et al., (1992), and Conklin and Hoffmann, (1988) discuss, in detail, potential redox mechanisms. Further oxidation of iron may occur from interaction with atmospheric oxygen, as detailed elsewhere (Valavanidis et al., 2000).”

Comment 3b) 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?

Reply: Please see the Reply to Comment 3a.

Comment 3c) What photoreduction mechanisms are you referring to? Photoreduction

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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.

Reply: We agree with the Reviewer that we cannot distinguish the reaction mechanism based on the size fraction. We have, therefore, propose to remove any references related to size-specific mechanisms (Page 1373, line 5-10) and replace them with the mechanistic discussions from the Reply to Comment 3a.

Comment 3d) 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.

Reply: Page 1371, following the Reply to Comment 3a: We agree that an expanded comparison to past aging studies would benefit the reader; therefore, we propose the following passage to be added.

“Only a few published studies have examined the red-ox transformations of PM-associated iron during atmospheric transport. Although an estimate of aerosol transport time was not given, Zhuang et al. (1992) found that significant conversion between Fe(II) and Fe(III) can occur during transport, with reduction of Fe(III) to Fe(II) being more significant than oxidation of Fe(II) to Fe(III) in marine aerosols. A number of studies have sought to measure the photoreduction of Fe(III) in aqueous leaches or suspensions of aerosols (Okada et al., 2006 and Zhu et al., 1993). These studies found that, in the leachate, the Fe(II) levels quickly increase upon irradiation of the aerosol solution, with the levels reaching a pseudo steady-state within 45 minutes. Irradiation studies performed on atmospheric cloud water have reported similar results (Arakaki and Faust, 1998). It should be noted that, in all of these irradiation studies, the aerosols were "trapped" in a leaching solution, and therefore unavailable to atmospheric oxygen."

Comment 4a) 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?

Reply: Page 1365, line 14: For clarification, the following sentence is proposed. "Due to the shallow slope of the calibration curve below 20% Fe(II), there is a potential for greater uncertainty in Fe(II) estimates where Fe(II) $<$ 20%. Replicate standards of 20% Fe(II) and 50% Fe(II) were analyzed to quantify the extent of this uncertainty. We found that the relative standard deviation (RSD) for the 20% Fe(II) sample was 3.3% (n = 4) while the RSD for the 50% Fe(II) sample was 2.0% (n = 5), a 65% relative decrease in uncertainty. It should be noted, however, that the uncertainty due to sampling (RSD $>$ 12%) is far greater than the analytical uncertainty of this measurement."

Comment 4b) 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.

Reply: The legibility of Figure 6 would be compromised by inclusion of multiple uncertainty estimates, therefore we have instead proposed to incorporated a discussion of the uncertainty the XANES measurement in the text in Section 2.4 (Total Fe(II) and Fe(III) Determination, Page 1365).

Comment 4c) 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.

Reply: For clarification of the XANES uncertainty, the following passage is proposed after the Reply to Comment 1c: “For each of these trials, total Fe(II) was determined by multiplying the fraction of Fe(II) by the total iron content (from ICPMS). For this sampling day, we found an average of 5.94 ś 0.84 ng m-3 (n=5), where the uncertainty is the standard deviation of all of the trials. This corresponds to a RSD of 14.2%, which takes into account the uncertainty from the XANES measurement and the ICPMS measurement. It is this uncertainty estimate that was applied to all Fe(II) concentration values.”

Page 1366, line 8: For clarification of the labile Fe uncertainty, the following sentence is proposed. “In a previous study, we found the uncertainty associated with this measurement (including sampling and analysis uncertainty) to be 7.1% (Majestic et. al. 2006). This propagated uncertainty was globally applied to all soluble Fe(II) data as this metric exhibited only minor variation with concentration.”

Comment 5a) 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?

Reply: Page 1365, line 7: For clarification of this point, we propose to add the following sentences. “Ě the LIII edge was used as a reference. As the apparent peak energy fluctuate due to temperature changes and the accuracy of the monochromator, we often observed variations in the energy at which the Fe(II) and Fe(III) peaks appear. Therefore, the sample energies were normalized to known values in frequently run mixed Fe(II) and Fe(III) standards. In general, this required an energy shift of the raw spectra of about 6 eV. Next, the LIII edge (or “white-line) portion of the spectrumĚ”

Comment 5b) 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.

Reply: Page 1370, lines 28-29: We agree with the Reviewer that there is very little change in total soluble iron from day 0 to day 3. To help clarify that overall iron is not changing rapidly, the we propose the following modification “This leads to an overall decrease in soluble iron in the coarse fraction after 3 days of aging.”

Comment 5c) 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.

Reply: Page 1372, line 15-16 is proposed to read “The reason for this apparent contradiction could be three-fold.”

Page 1372, beginning line 25: We agree that this discussion should be expanded to focus on the LA 2/13 data. Therefore, the following passage is proposed. “Aging trends observed in the XANES (total Fe(II)) results differ from those apparent in the Ferrozine (soluble Fe(II)) on the 13 Feb 2006 sampling day in Los Angeles. Fig. 8 and Fig. 11 show that total Fe(II) in the coarse fraction increases at a significant rate while the soluble fraction of Fe(II) sharply decreases prior to 10 days of aging. This implies that, overall, Fe(II) is being formed, however the specific form of Fe(II) is not soluble or addressable to our leaching solution. Studies by Zhu et al. (1992) documented that photochemical reduction of goethite (α-FeOOH) from Fe(III) to Fe(II) does occur, and that this reduction has no effect on the solubility of the goethite. Because this effect in this study is pronounced in the coarse particle fraction, which likely has a strong crustal component, these data indicate the strong possibility that significant amounts of goethite may be present in the coarse fraction on this sampling day.”

Minor Comments

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

Reply: This sentence should be changed to “Ě as compared to Fe(II) (Zuo and Deng 1997).”

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.

Reply: This sentence should be modified to read “Ěwhen compared to other common electron donors such as acetate and butyrate.”

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

Reply: For clarification, we propose the following modification “Ěsignificant sample mass is needed, which makes application of this technique to ambient and personal PM exposure samples extremely difficult.”

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

Reply: On Page 1363, line 9, we proposed the following correction: “polypentene” to be replaced with “polymethylpentene.”

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.)

Reply: There was a slight energy shift for each XANES spectrum. This has been addressed in the Reply to Comment 5a.

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.

Reply: Following the Reply to Comment 4c on page 1366, line 8, the following sentence is proposed. “The detection limit of this technique was found to be $<$ 0.1 μg L-1 which equates to 0.08 ng Fe(II) m-3 air when sampling for 24 hours at 9 liters per minute.”

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.

Reply: For clarification, this sentence is proposed to read “On 12 July 2006 in Waukesha and on 14 February 2006 in Los Angeles, a smaller portion of the crustal elements (Fig. 4) are present in the coarse fraction, which is consistentĚ”

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

Reply: Page 1367, line 23: For clarification of the sources at the Waukesha, WI sampling site, the following is proposed. “At the East St. Louis and Waukesha sampling sites, a significantly greater fraction of copper (45-60%) is found in the submicron fraction in comparison with mobile-source dominated Los Angeles site ($<$ 20%). Therefore, at these two sites, there is another source contributing significant levels of copper excess of that from motor vehicles. Likely sources in Waukesha are a casting foundry less than 1.5 km directly east of the sampling site and a stainless steel fabrication facility approximately 0.3 km south of the site.”

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

Reply: The sentence is proposed to read “A summary and comparison of percent

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leachable iron in the coarse and PM2.5 fractions measured at East St. Louis, Los Angeles, and Waukesha is presented in Table 1..”

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.

Reply: The proposed modification to this sentence is “Ě total soluble iron fraction ranging from <1-23% of the total iron.”

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)

Reply: The following references will be corrected:

Conklin M. H., Hoffmann M. R.: Metal-Ion Sulfur(IV) Chemistry.3. Metal ion-sulfur chemistry. 3. Thermodynamics and kinetics of transient iron(III)-sulfur(IV) complexes, Environ Sci Technol, 22(8), 899-907, 1988.

Faust B. C., Hoffmann M. R.: Photoinduced reductive dissolution of alpha-Fe2O3 by bisulfite, Environ Sci Technol, 20(9), 943-948, 1986.

Garvie L. A. J., Buseck P. R.: Ratios of ferrous to ferric iron from nanometre-sized areas in minerals, Nature, 396, 667-670, 1998.

Hoffmann P., Sinne R. T., Dedik A. N., Karandashev V. K., Malyshev A. A., Weber S., Ortner H. M.: Iron in atmospheric aqueous and particulate samples, Fresenius J Anal Chem, 350(1-2), 34-37, 1994.

Jacob D. J., Waldman J. M., Munger J. W., Hoffmann M. R.: Chemical-composition of fogwater collected along the California coast, Environ Sci Technol, 19(8), 730-736, 1985.

Majestic B. J., Schauer J. J., Shafer M. M., Turner J. R., Fine P. M., Singh M., Sioutas

C.: Development of a wet-chemical method for the speciation of iron in atmospheric aerosols, Environ Sci Technol, 40, 2346-2351, 2006.

Papaefthymiou V., Kostikas A., Simopoulos A., Niarchos D., Gangopadyay S., Hadjipanayis G. C., Sorensen C. M., Klabunde K. J.: Magnetic hysteresis and Mossbauer studies in ultrafine iron particles, J Appl Phys, 67(9), 4487-4489, 1990.

Parkhomenko V. D., Kolodyazhnyi A. T., Galivets Y. D., Pokholok K. V.: Mossbauer-spectroscopy applied to surfaces of ultrafine iron powders, Soviet Powder Metallurgy and Metal Ceramics, 29(2), 165-167, 1990.

Pehkonen S. O., Siefert R., Erel Y., Webb S., Hoffmann M. R.: Photoreduction of iron oxyhydroxides in the presence of important atmospheric organic-compounds, Environ Sci Technol, 27(10), 2056-2062, 1993.

Torok S., Faigel G., Jones K. W., Rivers M. L., Sutton S. R., Bajt S.: Chemical characterization of environmental particulate matter using synchrotron-radiation, X-ray Spectrometry, 23(1), 3-6, 1994.

van Aken P. A., Liebscher B.: Quantification of ferrous/ferric ratios in minerals: new evaluation schemes of Fe L2,3 electron energy-loss near-edge spectra, Physics and Chemistry of Minerals, 29, 188-200, 2002.

van Aken P. A., Liebscher B., Styrsa V. J.: Quantitative determination of iron oxidation states in minerals using Fe L2,3 - edge electron energy-loss near-edge structure spectroscopy, Physics and Chemistry of Minerals, 25, 323-327, 1998.

Zhu X., Prospero J. M., Savoie D. L., Millero F. J., Zika R. G., Saltzman E. S.: Photoreduction of iron(III) in marine mineral aerosol solutions, J Geophys Res, 98(D5), 9039-9046, 1993.

Zhuang G. S., Yi Z., Duce R. A., Brown P. R.: Link between iron and sulfur cycles suggested by detection of Fe(II) in remote marine aerosols, Nature, 355(6360), 537-539, 1992.

Zuo Y. G., Hoigne J.: Photochemical decomposition of oxalic, glyoxalic and pyruvic-acid catalyzed by iron in atmospheric waters, Atmos Environ, 28(7), 1231-1239, 1994.

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.

Reply:

a) Fig. 1 shows a mixed Fe(II) / Fe(III) spectra. To avoid reader confusion, we propose modification to the text as follows “As can be seen in Fig. 1 (example spectra showing a 70% Fe(II) / 30% Fe(III) standard and an actual ambient sample),”

b) So that the reader can see a typical baseline, we propose to add raw (unmodified) spectra to the Supplementary Material.

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.

Reply: We agree with the reviewer and the legends in Fig. 4, Fig. 5, Fig. 6, Fig. 7, Fig. 9, and Fig. 10 will be enlarged. Further, the legends in all of these Figures will be placed in the order of the plot elements.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1357, 2007.