Atmos. Chem. Phys. Discuss., 11, C8931–C8938, 2011
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Atmospheric Chemistry and Physics Discussions



*Interactive comment on* "

# Characterization of iron speciation in single particles using XANES spectroscopy and micro X-ray fluorescence measurements: insight into factors controlling iron solubility" *by* M. Oakes et al.

**Anonymous Referee #1**

Received and published: 14 September 2011

1. Does the paper address relevant scientific questions within the scope of ACP?

Yes. This paper addresses iron in atmospheric aerosols and is well within the scope of ACP.

2. Does the paper present novel concepts, ideas, tools, or data

Yes. This paper has employed novel tools, XANES and X-ray fluorescence, to study the oxidation state of iron in individual atmospheric aerosols. The data presented suggested a less important role of abundance in major iron minerals in determining the soluble Fe content in the aerosols.

3. Are substantial conclusions reached?

Yes.

4. Are the scientific methods and assumptions valid and clearly outlined?

The scientific methods and assumptions seem to be valid and outlined.

5. Are the results sufficient to support the interpretations and conclusions?

Mostly. Caution should be made for some of the interpretations. See below.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

The reviewer is not sure about the synchrotron based work but otherwise ok.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

Yes.

8. Does the title clearly reflect the contents of the paper?

Yes.

9. Does the abstract provide a concise and complete summary?

Yes.

10. Is the overall presentation well structured and clear?



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Yes.

11. Is the language fluent and precise?

Yes.

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

Yes, to my knowledge.

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

Yes. See detailed comments.

14. Are the number and quality of references appropriate?

No. Some very recent papers regarding Fe mineralogy/speciation and Fe solubility are not included. One example is Oxalate metal complexes in aerosol particles: implications for the hygroscopicity of oxalate-containing particles, Atmos. Chem. Phys., 11, 4289–4301, 2011.

15. Is the amount and quality of supplementary material appropriate?

Yes.

In general, this is an interesting paper and is well written and well organized. The data presented in this paper are extremely difficult to obtain and are useful to understand the Fe speciation and mineralogy of particles in the atmospheric aerosol particles.

There are some problems in the manuscript which need to be clarified. Particularly, the results are based on single samples in particular season and at particular site but the authors have tried to discuss the spatial and seasonal trends. This is questionable because there is no evidence that such as a single sample could be representative of the whole season or a single site. Also, the uncertainties associated with the limited



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number of particles analyzed should be addressed in the paper (see more detailed comments below).

More particular comments include:

1. Abstract: solubility needs to be defined. It is not clear in the abstract and the paper that where the authors want to mention solubility (in a geochemical sense, which is a thermodynamic parameter) or where fractional solubility. For example, in line 19, what does this solubility refer to? They need to be consistent throughout the paper and the abstract and should be defined the first time it appears.

2. Page 22772, Line 12: What "elemental analyses" with what methodology?

3. Abstract, last sentence: Is this the key point of this paper? If it is, it needs to be strengthened in the paper. A direct comparison of the abundance (should be number abundance by the way) of Al-Fe oxides and Fe-aluminosilicates was only mentioned briefly at the end of a paragraph in 22785. Figure 6 and table 2 showed some data about the Fe(II)/total Fe but not the number abundance. Also, a large part of paper is discussing about Fe(II)/total Fe (for example, Fig. 2) rather than focusing on the key point (i.e., the last sentence). It is suggested that a figure or a table is added to the paper (or add further data on particle abundance in table 2) for a more direct comparison of the Fe-particle abundance with fractional Fe solubility.

4. Page 22773, Line 14-16: There is probably some misunderstanding here. It does not seem to be right to say that "there are ample evidence. . .". Meskhidze et al. (2005) is a modelling study not a laboratory or field study. Shi et al. (2009) is a laboratory and field study but they did not suggest that in-cloud processing has a positive relationship with fractional Fe solubility. They found Fe nanoparticles in the natural clouds, which indirectly suggested that dust had been acid processed before being deposited in the rain.

5. Page 22773, line 17: Baker and Jickells (2006) did not observe an inverse relation-



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ship between size and fractional solubility. What they have showed is that fractional Fe solubility increases with decreasing dust mass concentration (which is likely accompanied by decreasing average sizes).

6. Page 22774: line 5: “association to” should be “association with”?

7. Use either “iron” or “Fe” throughout the paper. Do not mix them.

8. Page 22775, line 1: “Fe particles” should be “Fe-containing” particles. It is very unlikely that a natural particle is composed of Fe only.

9. Page 22777, line 5: Define “NBS”

10. Figure 4: were the spectra of standard minerals taken under the same condition and same time of the XANES analyses of natural aerosol samples? Are they similar or the same to the spectra in literature?

11. Page 22778, line 15: “Fe solubility of the filter samples” cannot be measured by ferrozine. The ferrozine method could only give the soluble Fe concentration, but not the Fe solubility of a sample.

12. Page 22778, section 2.4: what is the detection limit of the method for soluble Fe? What is the accuracy? What is the lowest soluble Fe concentration in the aerosol sample leach?

13. Page 22779, line 12, end of paragraph: here it is necessary to mention how the fractional Fe solubility is calculated and how the total Fe is measured.

14. Page 22779-22780 and table 2: here the authors showed the total Fe was measured by microscopic X-ray fluorescence. The total Fe data were then compared with literature data. This is a very awkward way of validating the data because it does not provide evidence of the accuracy of the measurements. For example, total Fe ranges by more than an order of magnitude in the Southeastern US, so your total in a particular sample falls in this range does not mean your data are accurate. Obviously, the



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best option was to analyze total Fe using XRF or ICP-MS/ICP-AES. However, it seems that such analyses had not been done on the filter. If the samples are still available, the best way is to analyze them directly. Otherwise, the uncertainty should be addressed.

The authors have mentioned in line 16 of page 22779 that scans were made for 1-4 maps per filter. This gave some indications of the variability or uncertainty of the total Fe measurement, which is shown in Table 2. Since a large part of the paper is dependent on the results in the fractional Fe solubility, it is necessary that such uncertainty is mentioned clearly in the paper and the calculated ranges (or at least standard deviation) of fractional Fe solubility should be plotted in Figure 6 as well.

15. Page 22780, line 4-5: this is a methodology and should have been mentioned in Section 2. See comment 13.

16. Page 22782, line 5: What does “reduced particles” mean? Please clarify. 17. Figure 4: can the authors give some explanations why there are substantially amount Fe(II) in the so-called Fe oxides particles in this study?

18. Page 22783, line 11-12: What “enhanced levels of silicon and aluminium” mean? It is necessary to give some values. Otherwise, readers would not know how you have classified these particles into different groups.

19. Page 22783, line 17-19: Where are the examples of the spectra? Please refer to a figure in the paper. If the authors are referring to Fig. 4b, then the reviewer is unable to find any similarities of the iron-containing aluminosilicates (natural aerosol particle) and standard Fe oxides (maybe this is because I am not an expert of XANES analyses?). If this is true, then the discussion on the Fe oxides as the surface oxidation products of aluminosilicate is not justified.

20. Section 3.4: The data in this paper cannot provide enough evidence to discuss about the spatial and seasonal trends. The reviewer is not even sure the authors could conclude that “whether there are significant variations in the Fe speciation in the



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aerosols collected during different time and at different sites". See major concerns above.

21. Page 22784, line 7: Is "78

22. Page 22784, line 16: why Fe solubility ranges 4.3 to 5.8 ng/m3? It should not have a unit.

23. Page 22784, line 22-25: How could 1-6

24. Page 22784, line 12: "data were collected. . ."? This sentence needs re-written. 25. Section 3.6: This section is less convincing and not immediately relevant to the results of this paper. The reviewer, if was the author, would simply remove this section.

26. Page 22788, line 1: "size" is not mentioned in the main text. It is important to know the size and the mineralogy and therefore such information should be presented and discussed in the main text.

27. Figure 3: it would be better if the positions of the Fe(II) and Fe(III) are shown in the figure.

28. Figure 4: The two figures should be combined to make one figure. Most of the spectra are exactly the same and it is not necessary to use two figures. In the caption, what "horizontal lines" are referred to? Should they be "vertical lines" in the figure? Why there is significant shift to the left for Fe(II) oxalate and Fe(II) sulphate? Are these spectra similar to those in literature?

29. Figure 5: how the two datasets are separated? At the left bottom corner, there are lots of data points which could be either classified to group 1 or 2. What standards have been used to classify them?

30. Figure 6: it would have been much easier to read and interpret if the data are plotted as scatter plot. However, if the standard deviation is also to be plotted, it might still be better to use the original style. Therefore, it is up to the authors to decide what



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would be the best way to present the data.

31. Table 2: the number of particles analyzed for each filter should also be listed in the table. Fig. 2 showed that there are large variations in Fe(II)/total Fe in the individual particles and the number of particles analyzed was very small. The standard deviation and range of Total Fe(II)/Total Fe for each sample should also be listed in the table. The number of particles analyzed is worriedly small, which would have made the direct comparison of the Fe(II)/total Fe with the also to some extent uncertain fractional Fe solubility less useful.

32. Can Total Fe(II)/Total Fe be calculated from the XANES spectra of an area rather than individual particles, like that in Majestic et al. (2007, ACP)? If it can, it will give much more credible data on total Fe(II)/total Fe then what were presented in this table (the average total Fe(II)/total Fe from limited number of particles analyzed). Again, the comparison between number abundance of iron minerals (Al-substituted Fe oxides and Fe-alumnosilicate) and the fractional Fe solubility seems to be the key result the authors wanted to mention and therefore the data should be presented more clearly.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22771, 2011.