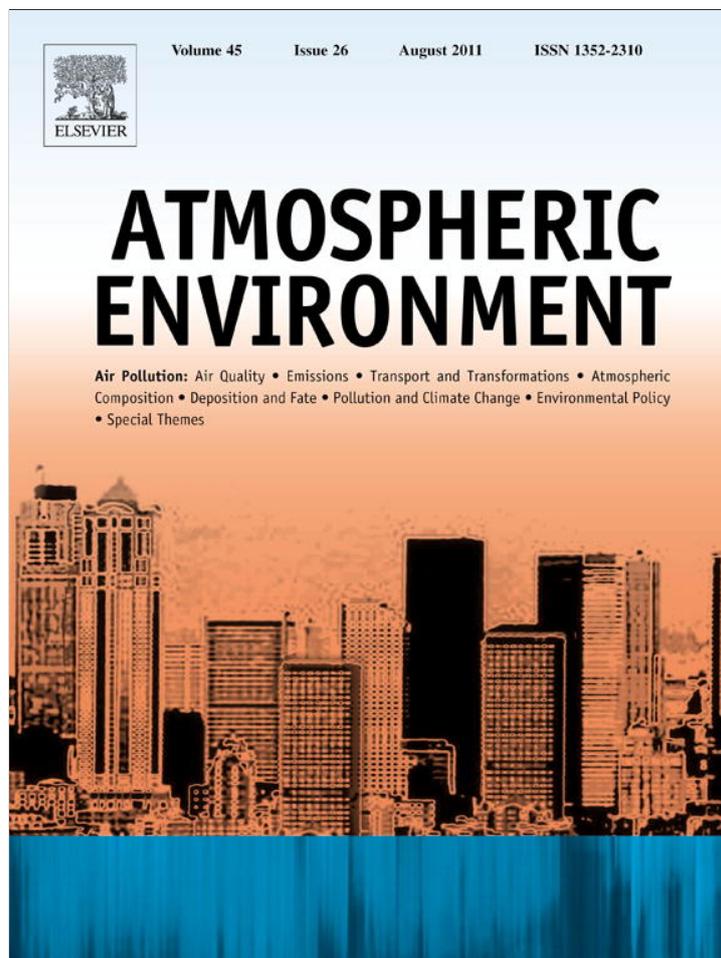


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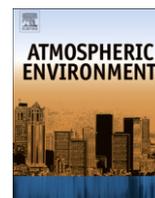
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Short communication

Iron speciation in urban dust

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ARTICLE INFO

Article history:

Received 1 June 2010

Received in revised form

18 April 2011

Accepted 16 May 2011

Keywords:

Urban dust

Iron

Speciation

Micro-focused X-ray absorption spectroscopy

ABSTRACT

An improved understanding of anthropogenic impacts on ocean fertility requires knowledge of anthropogenic dust mineralogy and associated Fe speciation as a critical step toward developing Fe solubility models constrained by mineralogical composition. This study explored the utility of micro-focused X-ray absorption spectroscopy (μ -XAS) in characterizing the speciation of Fe in urban dust samples. A micro-focused beam of $10 \times 7 \mu\text{m}$ made possible the measurement of the Fe *K* edge XAS spectra of individual dust particles in the PM_{5.6} size fraction collected in Newark, New Jersey, USA. Spectral analysis indicated the presence of mixtures of Fe-containing minerals within individual dust particles; we observed significant magnetite content along with other Fe(III)-(hydr)oxide minerals which could not be conclusively identified. Our data indicate that detailed quantitative determination of Fe speciation requires extended energy scans to constrain the types and relative abundance of Fe species present. We observe heterogeneity in Fe speciation at the dust particle level, which underscores the importance of analyzing a statistically adequate number of particles within each dust sample. Where possible, μ -XAS measurements should be complemented with additional characterization techniques such as μ -XRD and bulk XAS to obtain a comprehensive picture of the Fe speciation in dust materials. X-ray microprobes should be used to complement bulk methods used to determine particle composition, methods that fail to record particle heterogeneity.

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1. Introduction

Iron (Fe) speciation is of major interest due to its role in affecting the dissolution of Fe from dust materials, and the input of soluble iron to the ocean is critically important, as Fe serves as a limiting nutrient for phytoplankton growth in the ocean (Coale et al., 1996) affecting oceanic biogeochemical cycles (Falkowski, 1997; Watson and Lefevre, 1999). The primary natural source of Fe is dust material from dry lands. However, recent observations indicate that anthropogenic combustion sources may also contribute substantial amounts of iron (Chuang et al., 2005; Sedwick et al., 2007). At present, the speciation and dissolution of Fe from anthropogenic sources remain poorly understood.

Dust materials are composed of a mixture of minerals (clays, feldspars, metal-(hydr)oxides, etc.), and typically include a variety of Fe-bearing minerals such as Fe-oxyhydroxides (e.g. ferrihydrite, goethite), Fe-oxides (e.g. magnetite, hematite), or phyllosilicates (e.g. Fe-containing illite or kaolinite). Different Fe species found in minerals represent different Fe pools in dust, each with a specific set of physico-chemical characteristics, including Fe solubility.

The dissolution of Fe in dust is thus closely linked to its speciation, and quantitative predictions of Fe release require a fundamental understanding of Fe dissolution from dust as controlled by Fe mineralogy. The notion that aerosol mineralogy constrains Fe solubility from dust materials has been stressed in previous studies (e.g. Dedik and Hoffmann, 1992; Cwiertny et al., 2008; Schroth et al., 2009), but quantifying speciation of Fe in anthropogenic dust remains a challenge.

Assessment of Fe speciation in dust requires the application of techniques capable of providing accurate and quantitative information on the types and abundance of Fe phases present. Spectroscopic tools such as Mössbauer and X-ray absorption spectroscopy (XAS) can provide this type of information for Fe. These 'bulk' methods, however, record the speciation of an entire dust sample, averaging over hundreds or thousands of dust particles. Studies that have successfully applied these bulk techniques to study the speciation of Fe in dust have highlighted the heterogeneity of Fe speciation in dust materials, generally reporting a mixture of Fe²⁺ and Fe³⁺ and the presence of various Fe-containing minerals (Majestic et al., 2007; Tong et al., 2001; Wang et al., 2006; Schroth et al., 2009). O'Day et al. (2004) specifically addressed the utility of Fe *K* edge XAS to determine Fe speciation in mineral samples (soils and sediments) consisting of mixtures of Fe-bearing minerals, and concluded that

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this technique is capable of distinguishing between major classes of iron-bearing minerals (phosphates, oxides, etc.), with a practical detection limit of 5% atomic Fe. However, studies employing bulk spectroscopic methods to assess Fe speciation in dust are scarce, primarily due to the difficulty in collecting sufficient amounts of material to allow analysis by these techniques that are otherwise routinely used to determine the speciation of trace metals in geo-media such as soils and sediments (e.g. Manceau et al., 2000; Ostergren et al., 1999; O'Day et al., 2004; Isaure et al., 2002; Scheinost et al., 2002). Here, we explore the utility of micro-focused X-ray absorption spectroscopy (μ -XAS) to assess Fe speciation in dust materials by applying this technique to urban dust material collected from the Northeastern USA. We argue that the technique, which is capable of interrogating individual dust particles, provides a unique tool for exploring the variability of Fe mineralogy at the particle level, but note that extended energy scans are required to sufficiently constrain Fe speciation, and point out that this micro-focused technique would ideally be used to complement established bulk analyses of dust materials.

2. Materials and methods

2.1. Dust collection

Sampling of urban dust was performed on an elevated platform located on the Rutgers–Newark campus in downtown Newark, New Jersey, USA (40° 44' N., 74° 10' W) in February 2009. Samples were collected using a 10-stage MOUDI (Micro-Orifice Uniform Deposit Impactor, MSP) aerosol sampler with a flow rate of 30 l min⁻¹. Urban dust particles were collected on Teflon filters (Pall Corp., 47 mm diameter, 1 μ m pore size) for a 7-day duration. Further details are provided in Zhao and Gao (2008). The fraction of the 50% cut-off diameters of 5.6 μ m dust particles was used for XANES analysis to ensure particle dimensions similar to the micro-focused beam size allowing interrogation of Fe speciation within individual dust particles.

2.2. Micro XANES and micro-XAS

Micro-focused X-ray absorption near-edge spectra were collected on beamline X27A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, New York. Filters were mounted on a motorized sample stage positioned at 450 incidence to the beam. The beam was focused with Kirkpatrick–Baez micro-focusing mirrors to produce a 10 \times 7 μ m spot on the sample; energy selection was achieved with a Si(311) monochromator, and a solid state 13-element detector was used for fluorescence detection. Several individual dust particles were selected for analysis of the Fe *K* edge. Scanning was done using 4 s dwell time and steps of 5 eV, 0.1 eV, 0.2 eV and 0.5 eV in the energy regions 7020–7110 eV, 7110–7120, 7120–7140 and 7140–7215 eV, respectively. Three or four scans were collected per spot, and averaged to improve spectral signal-to-noise.

Spectra of reference compounds were collected to assist interpretation of the microbeam data. The spectra were collected in transmission mode at beamline X11A of the NSLS for the following compounds: goethite (α -FeOOH), hematite (Fe₂O₃), ferrihydrite (Fe(OH)₃), lepidocrocite (γ -FeOOH), and magnetite (Fe₃O₄). Goethite, hematite and ferrihydrite were synthesized using standard procedures (Cornell and Schwertmann, 2003); lepidocrocite was obtained from LANXESS (Bayferrox 943; LANXESS Corp., Leverkusen, Germany/Pittsburg, PA, USA), and magnetite from Sigma Aldrich. Three further references were Fe incorporated into the aluminum phyllosilicates kaolinite and montmorillonite, which were purchased from the Clay Minerals Society as KGa2, and SWy-2,

respectively, and “white rust” Fe(OH)₂, which was precipitated from dissolved FeCl₂ by base addition. The phyllosilicates and Fe(OH)₂ were scanned in fluorescence mode at the Fe *K* edge, using an Ar filled Stern–Heald type Lytle detector, and a Si(311) monochromator.

2.3. Data analysis

Averaging and background correction of the raw spectra were performed using WinXAS 3.1 (Ressler, 1997). Iron oxidation states were estimated from the barycenter of the pre-edge features located approximately 15 eV before the main absorption edge, which were isolated by fitting a spline function through the pre-edge region (Wilke et al., 2001) using the XANES dactyloscope software (Klementiev, 2002). A linear calibration function was determined from the barycenters of white rust (Fe(OH)₂), as a reference for Fe²⁺ in octahedral coordination, and hematite as a reference for octahedral Fe³⁺. The energy position of the barycenter was determined by fitting the pre-edge spectrum with up to three Voigt functions and calculating the area-weighted average of the fitted peaks using the software Fityk 0.9.1. Linear combination fits of the experimental spectra were performed using the routine available for this analysis in WinXAS 3.1.

3. Results

Fig. 1 shows an optical image of the dust material analyzed here, where the bulls eye matches the 10 \times 7 μ m dimension of the beam spot on the sample. Clearly, a significant number of dust particles and surrounding open space have dimensions similar to the beam size, which permitted characterization of Fe speciation at the individual particle level. The normalized iron *K* near-edge spectra collected for thirteen individual dust particles are presented in Fig. 2, where they are compared to the near-edge spectra of the various Fe reference compounds. The spectra of the dust particles resemble each other, indicating broadly similar Fe speciation in the particles. Relatively small differences between the spectra, however, do suggest some variation in the types or concentrations of Fe species present. No clear match is found between the experimental spectra and any of the reference spectra, indicating either mixed Fe speciation in the dust particles, and/or the presence of Fe species not represented in the reference spectral set.

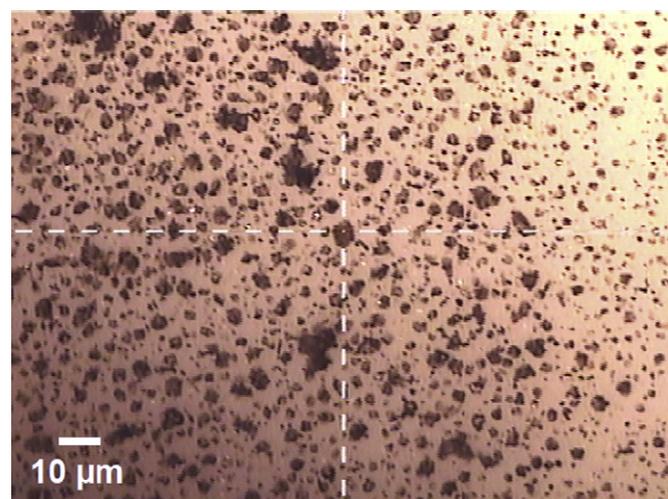


Fig. 1. Optical image of the dust material analyzed in this study. Micro-focused Fe *K* near-edge spectra were collected for individual particles; the beam dimension matched the bulls eye seen in the center of the figure.

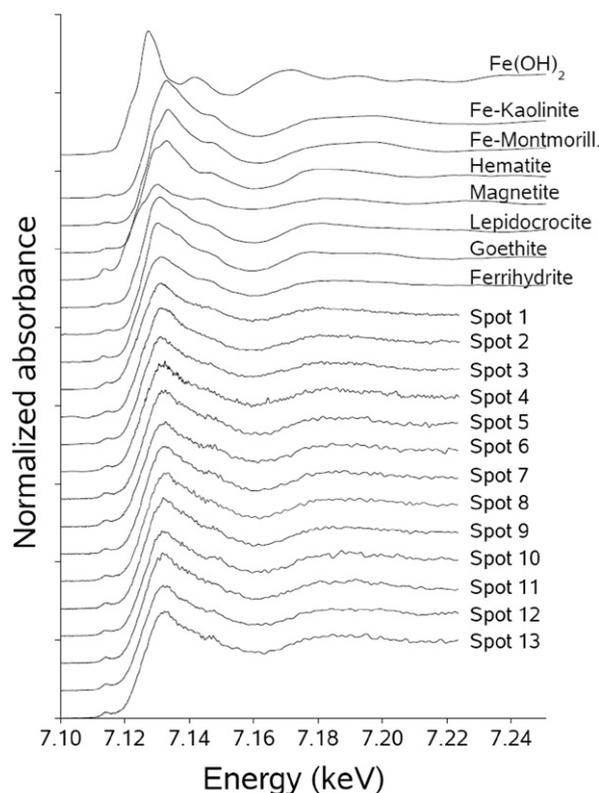


Fig. 2. Comparison of the Fe K near-edge spectra collected for individual dust particles and Fe reference compounds.

Analysis of Fe pre-edge features around 7111–7113 eV using the method described in Wilke et al. (2001) provides estimates of the average Fe oxidation state in mineral samples. Fig. 3 presents the pre-edge features of dust spectra 1 and 2 (which span the range of pre-edge features present in the data set), and those of Fe(OH)₂, hematite, ferrihydrite and magnetite. The pre-edge features were fitted with up to three Voigt peaks, with the area-weighted average energy position of these peaks correlated to the Fe redox state. This method provides only a rough estimate of Fe oxidation state, since the area-weighted centroid energy position is also dependent

on the coordination environment of Fe (Wilke et al., 2001), which is not known for our samples. We further note that for the current data, the energy resolution of the reference spectra (approximately 2 eV at the Fe K edge) is lower than that of the experimental spectra (approximately 0.5 eV), which will further increase the uncertainty in estimated Fe valence. Despite these caveats, we estimated the average Fe oxidation state in the dust particles by using the barycenters of Fe(OH)₂ as a reference for ferrous Fe in octahedral coordination, and hematite as a reference for ferric Fe in octahedral coordination. The barycenters were 7113.06 and 7114.40 eV for Fe(OH)₂ and hematite respectively, and 7114.22 and 7114.37 eV for dust particles 1 and 2, respectively. A linear calibration of Fe²⁺ content based on the barycenters of Fe(OH)₂ and hematite results in estimates of 14% Fe²⁺ for particle 1, and 3% Fe²⁺ for particle 2. While the errors associated with these numbers are expected to be large, these results do indicate a substantial difference in Fe²⁺ content between these particles, which is consistent with the near-edge spectra of these samples discussed below.

Further analysis of the Fe speciation in the dust particles involved an examination of the Fe K near-edge spectra, which provides information on the bonding environment of the Fe atoms in the particles. Close inspection of the spectral data set reveals subtle (relative to the differences seen between the reference spectra) yet notable differences between individual particle spectra, as exemplified by the comparison between the spectra of particles 1 and 2 shown in Fig. 4. An important difference between these spectra is the slight shift of the edge position of spectrum 1 to lower energy relative to spectrum 2, suggestive of a higher fraction of Fe²⁺ in spectrum 1 as compared to spectrum 2, which is consistent with the analysis of the pre-edge features described above. In addition, notable differences in the oscillation patterns of the spectra indicate differences in Fe bonding environments in these particles. Similar (subtle) differences in energy position and oscillation patterns were observed for other spectra in the data set.

Quantitative analysis of the near-edge spectra was attempted through linear combination fitting, which involves combining the spectra of reference compounds in proportions optimized to fit the experimental spectra. Two main observations were made from these linear combination fits:

- (1) The majority of spectra in the data set could not be successfully reproduced with any combination of the reference spectra that were included in the current study (Fig. 1), indicating the

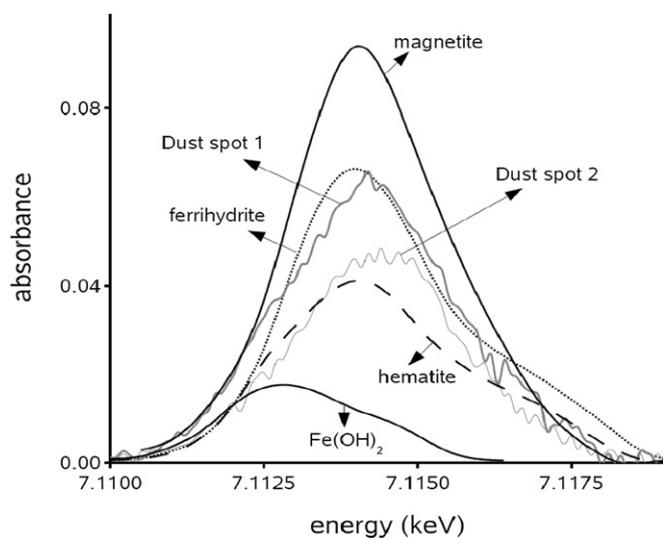


Fig. 3. Pre-edge features of dust particles 1 and 2 and select Fe reference compounds.

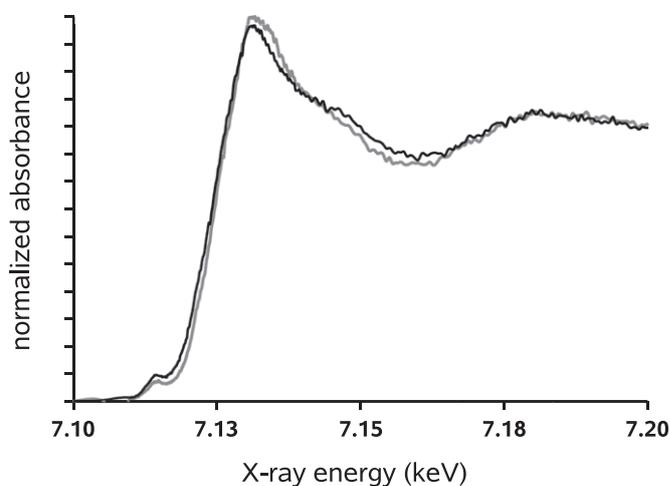


Fig. 4. Direct comparison of the Fe K near-edge spectra collected for dust particles 1 (black line) and 2 (gray line).

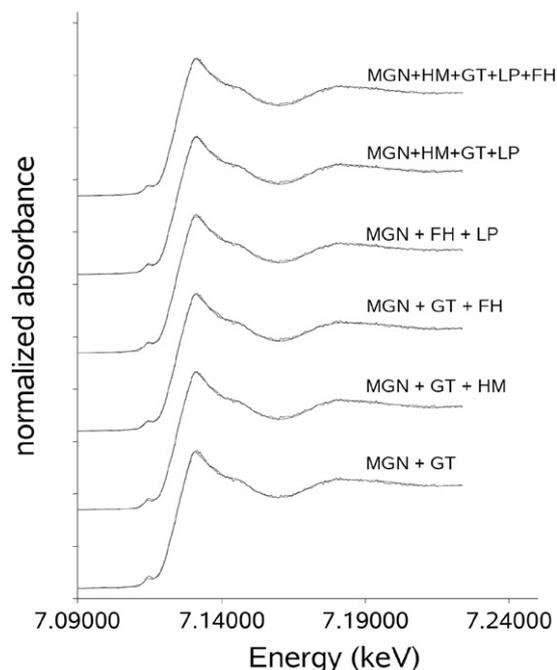


Fig. 5. Overlay of the spectrum of spot 1 with various linear combination fits of this spectrum with reference compound spectra; corresponding fit results are presented in Table 1. MGN = magnetite; GT = goethite; HM = hematite; FH = ferrihydrite; LP = lepidocrocite.

presence of Fe species/compounds that are not accounted for in the current reference data set.

- (2) For the experimental spectra where reasonable fits could be obtained with the current set of reference spectra, the number and contributions of Fe components were overall poorly constrained. This is well illustrated by the linear combination fit results of spectrum 1 presented in Fig. 5 and Table 1. For this particle, we found that magnetite needed to be included to obtain successful fits, contributing approximately 45–60% of total Fe in all cases (Table 1). Similarly, successful linear combination fits to spectra 6 and 12 required inclusion of magnetite as a component as well (not shown). Contributions from other Fe components remained, however, ill-defined, and reasonable fits could be obtained with anywhere from 1–3

Table 1
Results from linear combination fits of dust spectrum 1 using various combinations of Fe(II, III)-(hydr)oxide reference compounds.

Scheme	Magnetite	Hematite	Goethite	Ferrihydrite	Lepidocrocite	Residual
2 components						
1	0.56	0.43				1.42
2	0.59		0.4			1.25
3	0.37			0.62		1.31
4	0.53				0.45	1.18
3 components						
1	0.52	0.19	0.28			1.08
2	0.42	0.14		0.42		1.28
3	0.49	0.15			0.35	1.06
4	0.45		0.23	0.31		1.15
5	0.51		0.17			1.1
6	0.44			0.22	0.33	1.08
4 components						
1	0.48	0.13	0.24	0.13		1.09
2	0.5	0.12	0.12		0.25	1.04
3	0.42	0.05		0.22	0.3	1.03
4	0.46		0.09	0.16	0.28	1.07
5 components						
1	0.46	0.09	0.11	0.09	0.24	1.03

additional Fe(III)-(hydr)oxide components in various combinations (Fig. 5, Table 1). The presence of magnetite ($\text{Fe}_2^{\text{II}}\text{Fe}^{\text{III}}\text{O}_4$) in spectrum 1 is consistent with the pre-edge analysis of this particle indicating the occurrence of Fe^{2+} . Magnetite has been noted in previous studies characterizing urban dust material (e.g. Matzka and Maher, 1999; Morris et al., 1995; Wang et al., 2006; Xia et al. 2008), and is believed to form (along with hematite) during combustion of fossil fuels, which often contain iron as an impurity, and may also be generated by abrasion or corrosion of engine or vehicle body material. The presence of magnetite is therefore consistent with the urban origin of this dust material. The other Fe-bearing components of this particle could not be conclusively determined, but the fitting results allow the conclusion that these additional components most likely are Fe(III)-(hydr)oxide minerals.

4. Discussion

The results presented here highlight a number of benefits and limitations of μ -XAS to study the speciation of dust materials. The current successful application of this technique to collect interpretable Fe *K* near-edge spectra of individual dust particles indicates that the technique may be used to analyze even the smallest amounts of aeolian samples that are not readily accessible for analysis with bulk techniques. The spot size of the focused beam in the current study was approximately $10 \times 7 \mu\text{m}$, as limited by the instrumental setup at X27A. Current and future synchrotron-based hard X-ray microprobes with optics providing even higher spatial resolutions will allow for analysis of smaller particles, and will further enable mapping and speciation of elements (including Fe) within individual dust particles.

The current results indicate a mixture of Fe species in individual dust particles, and point to a potentially important role for Fe(II, III)-oxides in regulating the Fe solubility of this anthropogenic dust material. The confirmed presence of magnetite in the material provides an important source of Fe^{2+} , which has a higher solubility than Fe^{3+} , and therefore is of major importance in determining overall Fe solubility. Studies involving dusts collected from a wide variety of urban centers are required to assess the general importance of magnetite as an Fe^{2+} source in urban dust. The solubilities and surface areas of the Fe(III)-(hydr)oxides ferrihydrite, lepidocrocite, goethite and hematite differ substantially, with amorphous ferrihydrite having much higher Fe solubility and specific surface area than crystalline hematite, goethite and lepidocrocite (Cornell and Schwertmann, 2003). Iron dissolution and the potential of Fe solubilization through atmospheric processing are therefore much higher for ferrihydrite than for hematite and goethite, which illustrates the importance of dust mineralogy when predicting Fe solubility. Future application of μ -XAS to delineate which Fe(III)-hydroxides are present will benefit from extending the energy range of the Fe *K* edge spectra, which will help constrain linear combination fits of the experimental data, and thus improve the quantitative estimates of Fe speciation. Quantitative analysis will further benefit from expanded Fe reference datasets containing additional Fe compounds of both natural and anthropogenic origin (e.g. Fe-sulfates, Fe-bearing primary minerals, and additional Fe(II,III)-(hydr)oxides). Further constraints on Fe speciation in dust particles can be provided by additional characterization techniques; of particular note is the capability of micro-focused X-ray diffraction (μ -XRD) at select synchrotron X-ray probes, where the micro-focused beam is used for XRD measurements (e.g. Manceau et al., 2004; Arai et al., 2007). Combining μ -XRD measurements with μ -XAS analyses of the same particle would represent an especially powerful way of characterizing Fe speciation at the individual dust particle level.

As a final remark, we note the differences in the μ -XAS spectra collected for the various dust particles, which indicate heterogeneity in Fe speciation at the dust particle level (Fig. 4). Because of this heterogeneity, extrapolation of results obtained from single particle analysis should be done with caution, especially for materials where multiple Fe sources may have contributed, e.g. in samples obtained from areas with both anthropogenic and natural dust inputs; conversely, application of μ -XAS may prove useful in studies aimed at delineating source contributions (e.g. anthropogenic versus geogenic contributions) to specific dust samples. Capturing the degree of heterogeneity within a dust sample will require analysis of multiple individual particles, for which μ -XAS is uniquely suited. For relatively large samples, it is recommended to complement micro-focused analyses aimed at characterizing the level of heterogeneity at the particle size scale with bulk XAS analyses, which provide the average Fe speciation within the dust material. Characterizing the degree of heterogeneity of Fe speciation within individual dust particles will require micro-focused beam spots smaller than the dust particle dimensions.

Acknowledgments

This work was performed at Beamline X27A, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). X27A is supported in part by the U.S. Department of Energy (DOE) - Geosciences (DE-FG02-92ER14244 to The University of Chicago - CARS) and BNL - Environmental Sciences. Use of the NSLS was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. We further thank Kumi Pandya (NSLS beamline X11A) for assistance during XAS data collection of the references, and two anonymous reviewers whose comments helped improve this paper.

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