Characterization and acid-mobilization study of iron-containing mineral dust source materials

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Received 28 August 2007; revised 1 November 2007; accepted 29 November 2007; published 4 March 2008.

Processes that solubilize iron in mineral dust aerosol may increase the amount of iron supplied to ocean surface waters, and thereby stimulate phytoplankton productivity. In particular, the uptake of acids such as H$_2$SO$_4$ and HNO$_3$ on mineral dust surfaces can produce extremely acidic environments that promote iron dissolution. Here, four samples that represent source materials for mineral dust (Saudi Beach sand (SB), Inland Saudi sand (IS), Saharan Sand (SS) and China Loess (CL)) and one commercial reference material (Arizona Test Dust (AZTD)) were characterized, and examined in dissolution studies in solutions of sulfuric, nitric and hydrochloric acid ranging from pH 1 to 3. Mössbauer spectroscopy revealed Fe(III) in all samples, whereas SB, CL and AZTD also contained appreciable Fe(II). Spectra suggest that both Fe(II) and Fe(III) were substituted into aluminosilicates, although CL, AZTD and IS also contained Fe(III) oxide phases. Total iron solubility measured after 24 h ranged between 4–16% of the initial iron content for each material, but did not scale with either the specific surface area or the total iron content of the samples. Instead, we show that Fe(II)-containing solid phases such as Fe(II)-substituted aluminosilicates represent a significant, and sometimes dominant, source of soluble Fe in acidic environments. Results of dissolution studies also show that the nature of the acid influences iron solubilization, as elevated concentrations of nitrate encountered from nitric acid at pH 1 suppressed Fe(II) formation. We propose a surface-mediated, non-photochemical redox reaction between nitrate and Fe(II), which may contribute to Fe(II)/Fe(III) cycling in the atmosphere.


1. Introduction

Bioavailable iron is thought to limit phytoplankton primary productivity in ocean waters characterized by high macronutrient concentrations yet low chlorophyll levels [Martin, 1990; Martin et al., 1994; Falkowski et al., 1998]. These so-called high nutrient low chlorophyll (HNLC) regions have been suggested to comprise roughly 30% of the world’s oceans [de Baar and Boyd, 2000]. Mesoscale iron fertilization experiments have demonstrated this iron-limitation [Boyd et al., 2007], with the addition of artificial sources of iron stimulating both CO$_2$ drawdown and biomass production [Coale et al., 1996; Cooper et al., 1996; Boyd et al., 2000]. With respect to natural sources of nutrient iron, deposited mineral dust aerosols play an important, if not dominant, role for HNLC surface waters [Duce and Tindale, 1991; Jickells and Spokes, 2001]. A growing body of evidence suggests that deposited dust can be linked to increases in ocean productivity [Bishop et al., 2002; Han et al., 2006; Yuan and Zhang, 2006; Jo et al., 2007].

Mineral dust aerosols typically originate from terrestrial desert regions and contain, on average, approximately 3% iron by mass [Jickells et al., 2005]. Iron contained within these particles is presumed to be predominantly in the form of ferric iron (Fe(III)) that is substituted into aluminosilicate minerals, although it may also be present to a lesser extent as (oxyhydr)oxides such as goethite ($\alpha$-FeOOH) and hematite ($\alpha$-Fe$_2$O$_3$). These latter iron phases have been spectroscopically identified in aerosols from a variety of sources [Dedik and Hoffmann, 1992; Eyre and Dickson, 1995; Hoffmann et al., 1996; Kopcewicz and Kopcewicz, 2001; Arimoto et al., 2002; Shen et al., 2006], and are suggested by some to represent the forms of iron most suitable for solubilization processes and biological utilization [Claquin et al., 1999].

Despite the deposition of several hundred teragrams of mineral dust aerosols into the world’s oceans on an annual basis [Jickells et al., 2005], the concentration of
dissolved iron in HNLC regions such as the subarctic Pacific, equatorial Pacific and Southern Ocean are typically on the order of $10^{-12}$ M [Butler, 1998]. Such low concentrations are in part attributable to iron’s chemical properties and speciation. Fe(III) is the thermodynamically stable oxidation state under most environmental conditions, yet its solubility is extremely limited at pH values encountered in ocean waters [Stumm and Morgan, 1996]. Although the solubility of ferrous iron (Fe(II)) is several orders of magnitude greater at circumneutral pH values [Stumm and Morgan, 1996], it is prone to rapid oxidation by O$_2$ under such conditions [Stumm and Lee, 1961; Millero et al., 1987]. Consequently, the majority of iron contained in mineral dusts is expected to remain as insoluble ferric iron particulates or colloids after oceanic deposition.

It has been proposed that acidification of mineral dust aerosols during atmospheric transport increases the amount of bioavailable iron after deposition [Duce and Tindale, 1991; Zhu et al., 1992; Zhuang et al., 1992a; Zhuang et al., 1992b; Zhu et al., 1993; Zhu et al., 1997; Meskhidze et al., 2003; Meskhidze et al., 2005]. Mineral dust surfaces have been recognized as key reactive components in the troposphere for several years [Dentener et al., 1996; Usher et al., 2003]. Indeed, there are numerous laboratory investigations of acid uptake on mineral dust particles (see review by Usher et al. [2003] and references therein), as well as several field-scale studies illustrating the ability of mineral dust aerosols to serve as scavengers for sulfate and nitric acid (e.g., [Ooki and Uematsu, 2005; Matsumoto et al., 2006; Sullivan et al., 2007]). For example, concentrations of nitrate and non-sea salt sulfate present in Saharan dust collected over Barbados, West Indies corresponded to aerosol pH values lower than 1 at relative humidities typical to that area (>80%) [Zhu et al., 1992]. Similarly, analysis of field measurements by Meskhidze et al. [2003] indicate that the mixing of dust from the Gobi desert with anthropogenic SO$_2$ and HNO$_3$ can produce a deliquescent layer on the aerosol particles and that this aqueous coating could have a pH value less than 2.

Such an extremely acidic deliquescent layer is thought to impact bioavailable iron concentrations because it will enhance the rate of proton-promoted dissolution of Fe-containing solid phases [Kraemer et al., 2005], in turn increasing the concentration of dissolved Fe present in the aqueous phase surrounding the aerosol. This scenario is consistent with previous studies that have shown increased rates of dissolution for Fe-containing aerosols in low pH environments [Spokes et al., 1994; Desboeufs et al., 1999]. Acidification can also influence the speciation of dissolved iron generated from multiphase dissolution processes, as acidic environments will serve to stabilize Fe(II) because its rate of oxidation slows with decreasing pH [Stumm and Lee, 1961; Millero et al., 1987]. Therefore, dissolved Fe(II) generated as a result of the homogeneous photochemical reduction of Fe(III) [Faust and Hoigne, 1990] or the heterogeneous photochemical reductive dissolution of Fe(II)-containing solids [Faust and Hoffmann, 1986; Conklin and Hoffmann, 1988; Faust et al., 1989; Pohkronen et al., 1993; Siefert et al., 1994] should persist in acidic environments, which could explain the numerous observations of dissolved Fe(II) in atmospheric waters (see review by Deguillaume et al. [2005] and references therein). This influence of acidification on Fe speciation would be expected to impact the bioavailable fraction of iron in mineral dust aerosols if Fe(II) were the most bioavailable form of dissolved iron.

Although natural pathways for dust acidification exist, such as the biological production of dimethyl sulphide as first discussed by Zhuang et al. [1992b], recent attention has focused on anthropogenic sources, which Meskhidze et al. [2005] argue represent a larger annual source of SO$_2$ and may be more important due to the proximity of emission sites to dust source zones. Meskhidze et al. [2003] even went so far as to suggest a link between anthropogenic SO$_2$ emissions and ocean productivity, and therefore, global carbon and climate cycles. In fact, subsequent modeling studies incorporating the acid-mobilization of iron resulting from the mixing of dusts with anthropogenic SO$_2$ and HNO$_3$ have predicted considerable increases in soluble iron as a result of this mixing process [Meskhidze et al., 2005; Fan et al., 2006].

Despite the extensive body of previous research and the recent interest in dust acidification generated by the proposal of Meskhidze et al. [2003], questions persist as to the relative contribution of the different Fe-containing phases commonly encountered in mineral dust to the rate and extent of Fe dissolution in such low pH environments. Whereas several studies have demonstrated enhanced rates of Fe-containing aerosol dissolution at low pH, there is need for additional studies that attempt to link the solid-phase characterization of mineral dust aerosols with dissolution studies that explore not only the production of total dissolved Fe, but also the speciation of the soluble Fe forms resulting from acid-promoted dissolution.

Such a complementary approach has previously been employed by Dedik and Hoffmann [1992] and Majestic et al. [2007], both of which examined the speciation and solubility of iron in aerosols collected in urban areas. Dedik and Hoffmann used Mössbauer spectroscopy to identify the predominant iron solid phases in aerosol from Darmstadt, Germany, while also using ion chromatography to examine the relative amounts of dissolved Fe(II) and Fe(III) generated in suspensions of 0.1 N HCl. More recently, Majestic et al. [2007] employed synchrotron based spectroscopic methods to determine the relative solid-phase concentrations of Fe(II) and Fe(III) in aerosols from Waukesha, WI, St. Louis, MO and Los Angeles, CA, while also using a colorimetric assay to determine the amounts of Fe(II) and Fe(III) released into pH 4.3 acetate buffer after as much as 40 days of simulated atmospheric processing including relative humidity and light. In both studies, the aerosols were found to contain solid phase Fe(II) and Fe(III), and both iron oxidation states were solubilized during the respective dissolution experiments.

These studies illustrate that Fe(II)-containing solid phases may contribute to the amount of soluble Fe generated from dust dissolution, especially in strongly acidic environments that promote mineral dissolution. While the notion that aerosol mineralogy controls Fe solubility is certainly not new, additional attempts should be made to establish experimentally clear and definitive links between mineralogy and Fe solubility before the biogeochemical impacts arising from aerosol acidification can be fully assessed. In addition, the extreme pH conditions proposed by previous researchers allow for scenarios in which the chemical species causing acidification could also impact
Fe dissolution. In particular, the stability of Fe(II) in environments with high nitrate concentrations merits investigation. The reduction of nitrate by aqueous Fe(II) has been observed at circumneutral pH values [Buresh and Moraghan, 1976; Summers and Chang, 1993; Summers, 2005]. Although measurable rates of nitrate reduction by aqueous Fe(II) have not been observed under acidic conditions [Summers and Chang, 1993; Summers, 2005], Fe(II)-containing surfaces, which are stronger reductants than aqueous Fe(II) [Stumm and Morgan, 1996], can reduce nitrate under acidic conditions [Summers, 2005]. It is possible, therefore, that the mixing of Fe(II)-containing aerosols with nitric acid results in an additional pathway for Fe(II)-Fe(III) redox cycling in the atmosphere, which would certainly have implications for the amount of bioavailable Fe present in chemically processed mineral dust aerosols.

In the current study, we use complementary solid-phase characterization techniques and aqueous-phase solution studies to explore the physical and chemical factors influencing the rate, extent, and speciation of iron dissolution from mineral dust source materials in low pH environments. Authentic source materials from four global regions were considered: Saudi Arabian Beach sand (SB), sand from Inland Saudi Arabia (IS), Saharan desert sand (SS) and China Loess (CL), a material previously shown to contain both structural Fe(III) and Fe(II) [Eyre and Dickson, 1995]. Arizona Test Dust (AZTD), a commercially available material that has also been previously characterized [Vlasenko et al., 2005], was also included for comparision.

Although source materials are generally larger than particles that have been entrained in the atmosphere, they represent valuable proxies for mineral dust aerosol in laboratory studies because they allow enough material to be available for both characterization and dissolution studies. Moreover, the use of source materials enables trends in Fe solubility to be linked entirely to particle mineralogy, as these materials have yet to undergo any chemical processing during atmospheric transport that may enhance or inhibit Fe solubility. We also note a growing interest in understanding the contribution of coarse mode aerosol (>10 μm) to iron bioavailability in light of recent evidence that supports the long-range transport of larger soil materials (see Mackie et al. [2006] and references therein).

A suite of bulk and surface-specific spectroscopic and microanalysis techniques including Mössbauer spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) and computer-controlled SEM-EDX were used to examine the elemental content, as well as the distribution and oxidation state of iron in each source material. Dissolution studies were conducted in solutions of H2SO4, HNO3, and HCl to determine the soluble fraction of iron in each sample at pH 1, conditions specifically chosen to mimic the low pH environments proposed by some previous investigators to increase the amount of bioavailable Fe in aerosols. Trends in the rate and extent of iron dissolution were then examined and compared to results of material characterization to determine whether the amount of soluble iron could be predicted from source material properties. Although HCl is most commonly associated with acidification of sea salt aerosol [von Glasow and Sander, 2001], we included it in our study of mineral dust source materials so that possible trends in Fe dissolution unique to acidification by nitric or sulfuric acid might be identified. In particular, we focused our attention on the role that nitrate, a possible oxidant for Fe(II), may play in Fe(II)-Fe(III) redox cycling.

2. Experimental Section

2.1. Reagents

All chemicals were reagent grade or better. Dissolution studies were conducted in aqueous solutions of sulfuric acid (H2SO4; Fisher), nitric acid (HNO3; Fisher), hydrochloric acid (HCl; EMD), and sodium formate (Sigma Aldrich). All solutions also contained sodium chloride (NaCl; Fisher), while select studies included variable concentrations of sodium nitrate (NaNO3; Fisher). For dissolved iron analysis, 1,10-phenanthroline (Sigma Aldrich), hydroquinone (Sigma Aldrich), an ammonium acetate buffer (Fisher) and ammonium fluoride (Sigma Aldrich) were used. Nitrite quantification was performed using the commercially available Griess reagent (Alexis Biochemicals, Switzerland). Griess reagent is one part 0.1% naphthylethlenediamine dihydrochloride in distilled water plus one part 1% sulfanilamide in 5% concentrated H3PO4.

2.2. Source Materials

Authentic source materials were obtained from four global regions: the Saharan desert (SS), the inland of Saudi Arabia (IS), the beaches of Saudi Arabia (SB), and loess from China (CL). These materials and their source regions have been described previously [Krueger et al., 2004]. In addition to authentic materials, commercially available Arizona fine test dust (Powder Technology Inc., Burnsville, MN, USA) was included in both characterization and dissolution experiments. With the exception of the Arizona Test Dust (AZTD), all source materials were passed through a 212 μm sieve prior to use.

2.3. Characterization of Source Materials

Powder X-ray diffraction (XRD) was performed using a Bruker D-5000 diffractometer with a Cu Kα source. Limited quantities of CL prevented its analysis by XRD. Specific surface areas were obtained from seven-point N2-BET adsorption isotherms performed on a Quantachrome Nova 1200 surface area analyzer. Source material total iron content was determined from the analysis of acid-digested samples via inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP-AES analyses were performed at the University of Iowa Hygienic laboratory in Ankeny, Iowa.

The bulk elemental composition of each source material was determined using a Hitachi S-4000N scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (EDX). Source materials were adhered to carbon tape that had been mounted on an aluminum stub and were subsequently carbon coated. Elemental analyses used an integrated IXRF Systems Inc. X-ray microanalysis system and an accelerating voltage of 10 kV. Spectra were collected at three different locations on the sample stub using a spot size of approximately 700 × 300 μm. Accordingly, reported elemental compositions represent the bulk composition averaged over these three analysis points. The elements present within each sample were quantified using standardless atomic number, absorption,
fluorescence (or ZAF) analysis, which calculates elemental abundance from fundamental parameters of each element.

To examine the distribution of Fe in select source materials, two approaches were used. First, SEM/EDX elemental maps were collected for several AZTD particles. Samples of AZTD were prepared as described above, and maps were generated using an accelerating voltage of 20 kV, a resolution of $256 \times 200$ pixels, and a dwell time of 1 second. At each pixel, an entire EDS spectrum was generated and stored for later processing. The second approach used computer-controlled scanning electron microscopy with energy dispersive X-ray analysis (CCSEM/EDX) to examine the size and elemental composition of individual AZTD and CL particles. CCSEM/EDX allowed the size and relative concentrations of Fe, Al, and Si to be automatically recorded on an individual basis for 4700 AZTD particles and 2900 CL particles, which would be unreasonable to investigate with a traditional SEM/EDX setup.

For CCSEM/EDX analysis, AZTD and CL particles were dispersed onto transmission electron microscopy grids following the procedure described elsewhere [Laskin et al., 2005]. Particles that were poorly adhered to the grid surface were mechanically removed using compressed air. SBS, IS and SS particles were not analyzed, as the larger grains (>2 \(\mu m\)) in these samples poorly adhered to the sample grid.

An FEI XL30 digital field emission gun ESEM was utilized for CCSEM/EDX particle analysis. The system is equipped with EDAX X-ray spectrometer and Genesis\textsuperscript{TM} hardware and software (EDAX, Inc.) for CCSEM/EDX particle analysis. In this work, a magnification of 2000X, a beam current of 400–500 pA, and an accelerating voltage of 20 kV were used. Specific details of the system and microanalysis method can be found elsewhere (see Laskin et al. [2006] and references therein).

Information regarding the oxidation state of iron in the source materials was examined with \(^{57}\)Fe Mössbauer spectroscopy. Mössbauer spectra were collected in transmission mode with a constant acceleration drive system and a \(^{57}\)Co source. Spectra were collected at 298 (room temperature), 140, 77 and 13 K, and all data were calibrated against a spectrum for \(\alpha\)-Fe metal foil collected at room temperature. Spectral fitting was performed with the Recoil\textsuperscript{TM} software package (www.isapps.ca/recoil). Spectral data was modeled using a Voigt-based method as outlined in Rancourt and Ping [1991].

Surface characterization of all samples was performed using a custom-designed Kratos Axis Ultra X-ray photoelectron spectrometer with a monochromatic Al Kα X-ray source [Baltrusaitis et al., 2007]. Source materials were mounted onto a stainless steel stub with a 5 × 5 mm hole at its center that was used to hold the sample. The pressure of the analysis chamber was maintained in the 10\(^{-9}\) Torr range during analysis. Low energy electrons were used to neutralize samples thereby preventing charging of the samples.

Wide energy range survey scans that provide information pertaining to the elemental composition of the source material surface were acquired using the following instrumental parameters: energy range from 1200 to −5 eV, pass energy of 160 eV, step size of 1 eV, dwell time 200 ms, and X-ray spot size \(\sim 700 \times 300\) \(\mu m\). Note that this spot size is identical to that used for bulk elemental analyses performed with SEM/EDX. Survey spectra were collected at three different locations on the sample stub, and reported elemental compositions represent the averages of these three analyses.

XPS data were analyzed using CasaXPS data processing software [Fairley and Carrick, 2005]. All spectra were charge calibrated with respect to the adventitious C(1s) peak at 285.0 eV. A Shirley type background was used to subtract the inelastic background. Mixed Gaussian/Lorentzian (GL(30)) product synthetic components were used to curve fit the selected element envelope when necessary.

### 2.4. Dissolution Experiments

Dissolution experiments were carried out in crimpsealed 70 mL serum bottles (Wheaton) containing 40 mL of an appropriate aqueous solution. Solutions consisted of 0.01 N H$_2$SO$_4$ (pH 1), 0.1 N HNO$_3$ (pH 1), 0.1 N HCl (pH 1), 0.01 N HCl (pH 2), or 25 mM sodium formate (adjusted to pH 3.0) and 0.1 M NaCl. Additional experiments revealed no change in Fe dissolution rates or dissolved Fe speciation for NaCl concentrations up to 1 M (data not shown), suggesting that minor variations in ionic strength did not significantly influence the results of dissolution studies. Experiments exploring the influence of nitrate on the speciation of dissolved Fe resulting from AZTD dissolution were performed by adding variable concentrations of NaNO$_3$ (0.1–100 mM) to solutions of 0.1 N H$_2$SO$_4$ and 0.1 N HCl.

All experimental systems were exposed to oxygen and were performed in triplicate. Dissolution experiments were conducted in the absence of light, accomplished by wrapping all reactors in aluminum foil. The solids loading in most systems was 12.5 g/L, although experiments with AZTD conducted at pH 2 (0.01 N HCl) and pH 3 (25 mM formic acid buffer) used a solids concentration of 3 g/L to minimize pH drift over the course of the experiment. In all cases, solution pH was essentially constant during the dissolution experiments, with at most a 0.2 pH unit increase being observed for a limited number of cases.

Upon addition of the source material to the buffer solution, the reactors were sealed and were mixed end-over-end at approximately 45 rpm. Periodically, the reactors were opened, and an appropriate volume of suspension was withdrawn. Samples were passed through a 0.2 \(\mu m\) PTFE filter (Xpertek) and immediately acidified to a final concentration of approximately 0.2 N HCl in order to preserve the sample for iron analysis. At each sampling event, enough sample volume was taken to allow for analysis of dissolved Fe(II), total dissolved iron, and in select cases nitrate.

### 2.5. Analytical Methods

Ferrous iron was measured colorimetrically with 1,10-phenanthroline, which forms a complex with Fe(II) that absorbs at 510 nm [Schlüt, 1969; Stucki, 1981; Stucki and Anderson, 1981; Komadel and Stucki, 1988]. For Fe(II) analysis, 200 \(\mu L\) of a 5 mM 1,10-phenanthroline solution and 200 \(\mu L\) of an ammonium acetate buffer were added to 1 mL of sample. To avoid possible interference from Fe(III), which can also form a complex with 1,10-phenanthroline when present at high concentrations, 50 \(\mu L\) of 0.43 M ammonium fluoride was added to the sample prior to 1,10-
Table 1. Properties of Mineral Dust Source Materials Investigated in the Current Study

<table>
<thead>
<tr>
<th></th>
<th>Arizona Test Dust (AZTD)</th>
<th>Saudi Beach Sand (SB)</th>
<th>China Loess (CL)</th>
<th>Saharan Sand (SS)</th>
<th>Inland Saudi Sand (IS)</th>
</tr>
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<tbody>
<tr>
<td>Specific Surface Area (m²/g from N₂-BET)</td>
<td>4 ± 1⁺</td>
<td>1.8 ± 0.2</td>
<td>7.6²</td>
<td>3.1 ± 0.6</td>
<td>2.7 ± 0.5</td>
</tr>
<tr>
<td>Total Iron Content (% mass from ICP-AES)</td>
<td>1.48 ± 0.06</td>
<td>0.41 ± 0.03</td>
<td>2.2</td>
<td>0.24 ± 0.04</td>
<td>0.39 ± 0.04</td>
</tr>
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¹All uncertainties represent one standard deviation from quadruplicate measurements.
²Due to limited sample, only one analysis was performed.

We operationally define the dissolved Fe(III) concentration as the summed concentrations of aqueous Fe(III) and all colloidal Fe(III) particles less than 0.2 µm present in our systems.

Nitrite was quantified colorimetrically using the commercially available Griess reagent according to the protocol provided by the manufacturer (Alexis Biochemicals). Briefly, 40 µL of Griess reagent was added to 1 mL of aqueous sample. The mixture was allowed to react for 30 min, over which time the presence of nitrite resulted in the development of a pink hue. This color results from the reaction between nitrite and sulfonamide, and the subsequent reaction of the diazonium salt produced via this first reaction with naphthylethylenediamine, which yields an azo dye that absorbs light at 548 nm. Absorbances were converted to aqueous nitrite concentrations using standard solutions of sodium nitrite (Fisher Scientific) that were prepared daily. Standard solutions were prepared in 0.1 N HNO₃, which was the matrix used to explore the reduction of nitrate by Fe(II)-containing source materials, and our detection limit for nitrite was 1 ppm.

We report the presence of iron in the solid phase as TOTFe(s), total iron content initially present in our experimental solids. Values are reported as percentages.

3. Results and Discussion

3.1. Physical Properties of Source Materials

Results of N₂-BET surface area measurements and ICP-AES total iron analyses are shown in Table 1. All source materials exhibited specific surface areas on the order of several m²/g, with CL representing the highest surface area source material. With respect to total iron content, a range of values was obtained. By mass, CL and AZTD contained the highest percentage of Fe (on the order of 2%), whereas the iron contents of SB, IS and SS were nearly an order of magnitude smaller (ranging between 0.24 and 0.41%). X-ray diffraction patterns provided little information as to the iron-containing phases present in these source materials. Rather, XRD patterns for all samples were consistent with the predominance of quartz, although smaller amounts of aluminosilicates phases, i.e., clay minerals, were distinguishable for AZTD and SB. Finally, secondary electron images revealed that CL and AZTD particles possessed a relatively narrow size distribution, with particles all less than two microns in diameter. In contrast, a much wider distribution of grain sizes ranging up to several hundred microns was observed for SS, SB and IS samples.

3.2. Bulk and Surface Elemental Composition of Source Materials

For both XPS and SEM/EDX characterization, the analysis area (700 × 300 µm) contained multiple source material particles. Thus, reported elemental compositions represent an average determined from the analysis of several particles. The key distinction between these two spectroscopic approaches is that information from XPS is specific to the near surface region of the source materials, whereas SEM/EDX provides information pertaining to their bulk composition. Typically, triplicate SEM/EDX and XPS analyses produced standard deviations on the order of 10% for
Greater deviations were observed for the larger source materials because of the fewer number of particles included per XPS or SEM/EDX analysis. Figure 1 compares the elemental compositions from XPS to compositions determined with SEM/EDX. Generally, Si and Al were most abundant, followed by lesser quantities of Fe, Ca, Mg, K, and Na (note that C, N and O were not included in this analysis). Differences in the composition of these materials were readily observed, however. SB particles contained S and Cl, whereas Ti was detected in trace quantities for AZTD and CL particles. We also observed that SB and CL particles were enriched in Mg and Ca relative to the other materials.

The data in Figure 1 reveal reasonable agreement between the surface composition and bulk composition for most samples, especially for AZTD and CL particles. On the other hand, the relationship for the SB particles was particularly poor, likely indicative of greater particle-to-particle compositional differences for this sample. Reasonable correlations between surface and bulk elemental concentrations were not anticipated, as the surfaces of source materials are subject to processes (e.g., chemical weathering) that could cause their composition to vary considerably from that of the particle bulk. The existence of such correlations, however, indicates that for the most part the bulk composition of these source materials reasonably reflects the elemental composition of their surface.
3.3. Distribution of Iron in Source Materials

Elemental maps revealed that iron is unevenly distributed in AZTD particles (Figure 2). Although some grains were entirely free of iron, others exhibited high (Figure 2a) or more moderate (Figure 2b) iron content. The elemental maps in Figure 2 also provided some useful, albeit limited, information pertaining to the mineralogy of AZTD particles. The iron in Figure 2a was found in a particle primarily free of Si and Al (perhaps indicative of an iron oxide), whereas the iron in Figure 2b was located within grains also containing Si and Al (most consistent with Fe substitution into an aluminosilicate mineral).

Single particle analysis with CCSEM/EDX also indicated that Fe is unevenly distributed among AZTD and CL particles. The relative atomic concentrations of Fe, Al, and Si in individual AZTD and CL particles are shown as ternary composition diagrams in Figures 3a and 3b, respectively. Each point illustrates the relative Fe, Al, and Si concentra-
tions determined for a single particle, calculated according to the relationship \([\text{Fe}] + [\text{Al}] + [\text{Si}] = 100\%\). These diagrams include only those particles with a Fe concentration greater than 2% (relative atomic percent out of Na, Mg, Al, Si, S, Cl, K, Ca, Ti, and Fe elements). This corresponded to 1226 out of 4700 particles analyzed for AZTD (26%) and 475 out of 2900 particles analyzed for CL (16%), relatively low percentages that are consistent with the nonuniform Fe distribution depicted for AZTD particles in Figure 2.

For AZTD and CL, a range of Fe/Al/Si ratios was observed. The presence of aluminosilicates in the Fe-containing particles is unambiguously inferred from the ternary diagrams. Typical aluminosilicates come in compositional units of the following stoichiometry: \([\text{AlSiO}_4]^-\), \([\text{AlSi}_2\text{O}_3]^-\), \([\text{AlSi}_4\text{O}_{10}]^-\), \([\text{Al}_2\text{Si}_2\text{O}_8]^2^-\), and \([\text{Al}_2\text{Si}_3\text{O}_{10}]^2^-\) [McBride, 1994]. This leads to an expected range of Si/Al ratios between 1 and 4, which is marked by the shadowed area in the ternary plots. As can be seen, a majority of particles fall within this compositional range, consistent with Fe being predominantly substituted into aluminosilicate minerals. However, particles with very high relative Fe content (>90%) and minimal Si and Al (<10%) were also observed. These data likely pertain to a smaller fraction of particles containing Fe in some other form such as (oxy-)hydrates (e.g., goethite and hematite).

As the size of aerosol particles has recently been implicated as a primary control of Fe solubility [Baker and Jickells, 2006], Figure 3 also considers whether the relative
concentration of Fe is a function of particle size. In the ternary diagrams, solid symbols correspond to particles with a diameter greater than 0.75 μm, whereas open symbols represent particles less than 0.75 μm in diameter. In addition, Figures 3c and 3d plot the relative Fe concentration from the ternary diagrams as a function of particle diameter for AZTD and CL, respectively. Consistent with the ternary diagrams, open symbols in Figures 3c and 3d correspond to particles with diameters less than 0.75 μm.

[40] CCSEM/EDX data suggest that smaller particles have a greater tendency to be enriched with Fe. To illustrate this point, we consider the percentage of AZTD and CL grains with a relative Fe concentration greater than 50%. For AZTD, only 5% of particles with a diameter greater than 0.75 μm have a relative Fe concentration exceeding 50%. On the other hand, this value increases to 15% for AZTD particles less than 0.75 μm in diameter. Similar trends are observed for CL, as only 5% of particles greater than 0.75 μm meet this criterion compared to 20% of the particles less than 0.75 μm.

[41] Our analysis suggests that the iron content in some source materials may increase systematically with decreasing particle size, which may result from differences in the grain size of the various iron-containing solid phases typically found in soils (e.g., iron (oxyhydr)oxides and iron-containing aluminosilicates). Consequently, smaller dust particles, which are more susceptible to long range atmospheric transport, may yield increased amounts of soluble Fe relative to larger particles. Although this scenario is consistent with the proposal of Baker and Jickells [2006], they attributed their relationship between iron solubility and particle size to the high surface area to volume ratio of smaller aerosol particles, rather than possible variations in iron-containing aluminosilicates.

3.4. Mössbauer Spectroscopic Analysis

[42] Mössbauer spectra collected at 13 K (Figure 4) were used to identify the oxidation states of iron within each source material. All spectra revealed the presence of a Fe(III) doublet (labeled A in Figure 4). This doublet did not magnetically order to a sextet at our lowest achievable analytical temperature of 13 K, consistent with the presence of Fe(III)-substituted aluminosilicates in all samples. The lack of magnetic ordering is typical of most Fe-substituted aluminosilicates, as the Fe concentration of these materials is generally too low to allow for the interaction of neighboring Fe atoms that is necessary for magnetic ordering to occur [Coey, 1984]. Estimates of the isomer shift (~0.5 mm/s) and quadrupole splitting (~0.6–0.9 mm/s) values associated with this Fe(III) doublet were also in good agreement with those reported for octahedral Fe(III) substituted into aluminosilicate minerals [Coey, 1984].

[43] Spectra of SB, CL and AZTD particles also contained a Fe(II) doublet (labeled B in Figure 4). This Fe(II) doublet did not magnetically order at 13 K and is therefore indicative of Fe(II)-substitution into aluminosilicates [Coey, 1984]. While other Fe(II)-containing phases cannot be ruled out entirely, it is likely that Fe(II)-substituted aluminosilicates represent the dominant Fe(II)-containing phase in CL and AZTD particles based upon the results from complementary CCSEM/EDX individual particle analysis. [44] Spectral features indicative of other iron species were also observed for select source materials. For instance, spectra for AZTD, IS and CL at 13 K contained multiple ferric iron sextets (labeled C in Figure 4), suggesting that some fraction of the Fe(III) in these source materials is present as ferric iron oxides such as hematite or goethite [Murad and Cashion, 2004]. Unfortunately, the low absorption signals, as well as the lack of complementary information from XRD, did not allow us to distinguish definitively between these two and other possible iron (oxyhydr)oxide phases.

[45] The low absorption signals coupled with the overlapping components of the Mössbauer spectra also prevented us from providing a quantitative comparison of the relative amounts of Fe(II) to Fe(III) present in each source material. Qualitatively, however, the prominence of the Fe(II) doublet in SB, CL, and AZTD relative to the Fe(III) doublet and sextet indicate that an appreciable concentration of iron in these source materials exists as ferrous iron substituted into aluminosilicates.

3.5. Influence of pH on Iron Dissolution and Dissolved Iron Speciation

[46] The relationship between Fe dissolution and pH was investigated using 3 g/L suspensions of AZTD particles in pH 1 (0.1 N HCl), pH 2 (0.01 N HCl) and pH 3 (25 mM formic acid buffer) solutions. Figure 5a illustrates the evolution of total dissolved Fe as a function of time in these experimental systems. As anticipated from established dissolution trends for iron minerals [Martin, 2005] and aerosols [Spokes et al., 1994; Desboeufs et al., 1999], increasing from pH 1 to pH 2 produced roughly a 70 (±5)% decrease in total dissolved Fe concentration, whereas the total dissolved Fe concentration at pH 3 was approximately 90 (±1)% less than that measured at pH 1. These percentages represent the mean (and standard deviation) of the ratio of total dissolved Fe concentrations determined at each sampling point shown in Figure 5a.

[47] Not only did the concentration of total dissolved Fe change with pH, but so too did the speciation of dissolved Fe produced from AZTD dissolution. Specifically, the fraction of total dissolved Fe present as Fe(II) increased with increasing pH, ultimately resulting in ferrous iron representing the dominant soluble form of Fe at pH 2 and pH 3 (Figure 5b). In fact, the relative proportion of dissolved Fe(II) increased over time at these pH values, behavior most pronounced at pH 3 where nearly all of the Fe mobilized from AZTD after 120 h was present as Fe(II).

[48] Such changes in dissolved Fe speciation are likely linked to the greater solubility of Fe(II) relative to Fe(III) in aqueous solutions. Based on reported solubility products for ferrous and ferric hydroxide, the maximum dissolved concentration of Fe(II) at pH 2 and 3 is orders of magnitude greater than that of Fe(III) [Stumm and Morgan, 1996]. We therefore expect such changes in the relative concentrations of dissolved Fe(II) and dissolved Fe(III) in our systems both over time and with increasing pH. For our pH 3 suspension, however, we cannot rule out the possibility that the formic acid buffer used to maintain system pH may have in some way influenced the speciation of dissolved Fe in these experimental systems.
We note that experiments with AZTD were also conducted in aqueous solutions buffered at pH 7.0, a value chosen to more closely mimic the aquatic environment encountered after mineral dusts are deposited in the ocean. As expected from the limited solubility of iron at near-neutral pH values, the concentrations of all dissolved Fe species were below the detection limits of our analytical method.

3.6. Comparing Iron Dissolution From Source Materials at pH 1

Results comparing the dissolution of each source material in pH 1 suspensions of 0.1 N H₂SO₄ are shown in Figure 6, which presents solubility data for total dissolved Fe (Figure 6a), dissolved Fe(II) (Figure 6b) and dissolved Fe(III) (Figure 6c) as a function of time for each material. Generally, the rate of soluble Fe generation was greatest initially (t < 5 h), followed by a more gradual, yet steady, rate of change over longer time intervals. Commercial AZTD yielded the highest solubility of each dissolved Fe species, whereas SB tended to produce the largest amounts of soluble Fe species among the authentic source materials. We note that for all source materials, observed concentrations of dissolved Fe(III) and dissolved Fe(II) were generally well below the solubility limits of common ferric (e.g., goethite, hematite, and amorphous ferric hydroxide) and ferrous (e.g., ferrous hydroxide) (oxyhydr)oxides, which were determined from published solubility products for the respective phases [Morel and Herring, 1993].

Figure 6b reveals significant production of dissolved Fe(II) in suspensions of AZTD, SB and CL particles. As these reactions were conducted in the absence of light, this dissolved Fe(II) cannot be the result of Fe(III) photoreduction and must, therefore, be generated from the Fe(II)-containing solid phases present in these source materials. Interestingly, small amounts (approximately 2 μM) of dissolved Fe(II) were also detected in IS and SS suspensions, even though features characteristic of Fe(II) were not observed in Mössbauer spectra for these materials (see Figure 3). Likely, the phases responsible for this trace Fe(II)
dissolution are not present at high enough concentrations to be clearly resolved by Mössbauer spectroscopy.

As in Figure 5b, an important consideration pertains to how the dissolved iron speciation varied over time in each system (Figure 6d). Although the fraction of dissolved Fe(II) in AZTD and CL systems remained relatively constant (at approximately 0.3 and 0.2, respectively), it steadily decreased over the entire duration of the SB dissolution experiment. This behavior suggests that differences exist in the relative rate and extent of dissolution of the various Fe(II)- and Fe(III)-containing solid phases present in SB particles.

Notably, the trends in Fe solubility observed in Figure 6 do not scale with the source material properties summarized in Table 1. The trend in total dissolved Fe solubility (Figure 6a) did not correlate with the total iron content of the samples ($R^2$ value of 0.004), supporting previous studies (e.g., Lafon et al. [2004] and Chuang et al. [2005]) that have also demonstrated that the amount of soluble iron in aerosols does not necessarily correlate with total iron content. Additionally, no correlation ($R^2$ value of 0.08) was obtained on the basis of source material specific surface area. It appears, therefore, that a simple solubility relationship developed from basic source material characteristics does not exist for the samples considered herein.
although we cannot rule out such a trend for atmospherically transported materials. We did not attempt to examine correlations on the basis of Fe(II) and Fe(III) solubility, as such relationships necessitate accurate quantification of the relative abundances of these species in each source material.

3.7. Influence of Different Acids on Iron Dissolution at pH 1

We also examined the effect of different atmospherically relevant acids on the generation of soluble Fe species in source material suspensions at pH 1. These dissolution results are shown in Figure 7 for AZTD (Figure 7a and 7b) and CL (Figure 7c and 7d) suspensions in 0.1 N H₂SO₄, 0.1 N HNO₃ and 0.1 N HCl. In addition, Table 2 summarizes values of total Fe solubility, soluble Fe(II), and soluble Fe(III) calculated at $t = 24$ h for each source material and acidic medium considered.

Among the three acids investigated, two key differences were observed. The first relates to the amount of Fe(II) generated in the presence of nitric acid. As is clearly
Figure 7. Comparison of total dissolved Fe and dissolved Fe(II) solubility as a function of time in suspensions of AZTD (a and b, respectively) and CL (c and d, respectively) particles at pH 1. Data are presented for acidification resulting from 0.1 N H$_2$SO$_4$, 0.1 N HNO$_3$, and 0.1 N HCl. Reactors contained a solids loading of 12.5 g/L and 0.1 M NaCl. When present, uncertainties represent one standard deviation from triplicate experiments.

Table 2. Solubility of Fe(II), Fe(III) and Total Fe Determined at $t = 24$ h for Dissolution Experiments at pH 1 in H$_2$SO$_4$, HNO$_3$ and HCl

<table>
<thead>
<tr>
<th></th>
<th>H$_2$SO$_4$</th>
<th>HNO$_3$</th>
<th>HCl</th>
<th>Fe(II)</th>
<th>H$_2$SO$_4$</th>
<th>HNO$_3$</th>
<th>HCl</th>
<th>Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZTD</td>
<td>15.7 ± 0.8</td>
<td>11.9 ± 0.5</td>
<td>13.6 ± 0.6</td>
<td>5.1 ± 0.2</td>
<td>1.8 ± 0.1</td>
<td>5.1 ± 0.3</td>
<td>11 ± 1</td>
<td>10.1 ± 0.6</td>
</tr>
<tr>
<td>SB</td>
<td>9.7 ± 0.7</td>
<td>10.5 ± 0.8</td>
<td>9.5 ± 0.8</td>
<td>2.2 ± 0.3</td>
<td>0.35 ± 0.04</td>
<td>2.6 ± 0.3</td>
<td>8 ± 1</td>
<td>10.2 ± 0.9</td>
</tr>
<tr>
<td>CL</td>
<td>7.5</td>
<td>6</td>
<td>6</td>
<td>1.7</td>
<td>0.1</td>
<td>1.5</td>
<td>5.8</td>
<td>5.9</td>
</tr>
<tr>
<td>SS</td>
<td>8 ± 1</td>
<td>6 ± 1</td>
<td>7 ± 1</td>
<td>0.3 ± 0.1</td>
<td>0.06 ± 0.02</td>
<td>0.5 ± 0.1</td>
<td>8 ± 1</td>
<td>6 ± 1</td>
</tr>
<tr>
<td>IS</td>
<td>6.4 ± 0.7</td>
<td>4.4 ± 0.5</td>
<td>4.4 ± 0.5</td>
<td>0.5 ± 0.4</td>
<td>0.03 ± 0.01</td>
<td>0.23 ± 0.04</td>
<td>6 ± 1</td>
<td>4.4 ± 0.5</td>
</tr>
</tbody>
</table>

$^a$Reactors contained a solids loading of 12.5 g/L and an electrolyte of 0.1 M NaCl.

$^b$When present, uncertainties represent one standard deviation for triplicate experiments. Values without uncertainty were obtained from a single experiment.
observed in Figure 7b and 7d, a considerable decrease in soluble Fe(II) was measured in AZTD and CL systems with 0.1 N HNO₃ relative to the amount produced in solutions of 0.1 N H₂SO₄ or 0.1 N HCl. In fact, values of soluble Fe(II) determined after 24 h were substantially lower in experiments with nitric acid for all source materials considered (Table 2). Because the soluble Fe(II) produced in H₂SO₄ and HCl suspensions were essentially equivalent for all source materials, it seems that the depressed concentrations of dissolved Fe(II) measured in 0.1 N HNO₃ suspensions results from the high nitrate concentration in these systems. This hypothesis will be explored more fully in the following section.

[56] The other notable difference pertains to the amount of total dissolved iron produced in H₂SO₄ solutions. For AZTD and IS particles, a statistically relevant increase in total Fe solubility was observed in 0.1 N H₂SO₄ suspensions relative to measured solubilities in 0.1 N HNO₃ and 0.1 N HCl (Table 2). A similar increase in total Fe solubility was also observed for CL particles (see Figure 7c), but triplicate experiments were not performed due to limited sample quantity. Although these differences in total Fe solubility may seem small, the increases in dissolved Fe concentration necessary to generate such changes in percent solubility in H₂SO₄ systems were actually rather large. For example, the total dissolved Fe concentration in IS suspensions of either HNO₃ or HCl was 37 ±1 µM after 24 h, compared to a total dissolved Fe concentration of 56 ±1 µM in H₂SO₄ systems at the same point in time, an increase of over 50%. Because similar increases in soluble Fe(II) were not observed for H₂SO₄ relative to HCl systems (Table 2), the change in total iron solubility for AZTD, IS and CL particles in the presence of 0.1 N H₂SO₄ must result from the enhanced dissolution of the Fe(III)-containing solid phases present within these materials.

[57] Interestingly, a statistically relevant change in total Fe solubility was not observed for the other source materials investigated (i.e., SS and SB; see Table 2). From our Mössbauer characterization, AZTD, IS and CL differ from SS and SB in that they contain detectable concentrations of Fe(III) oxide phases. Consequently, our results comparing Fe dissolution in different acidic media could be interpreted to suggest that H₂SO₄ promotes Fe(III) oxide dissolution more than the other acids investigated. Additional work is required, however, to further explore if such a link between source material mineralogy, iron dissolution rates, and the nature of acidification truly exists.

[58] Finally, it should be noted that all of the total iron solubilities reported in Table 2 are relatively high when compared to average iron solubilities typically reported for mineral dust aerosols (~2–3% [Jickells et al., 2005]). This is not entirely surprising given the extremely low pH used in our dissolution studies. However, comparable [Baker et al., 2006b] and even higher [Zhuang et al., 1992a] iron solubilities have been reported for aerosols collected in field-scale experiments, and these solubilities have in some cases been determined using far milder extraction conditions (e.g., pH 4.7 ammonium acetate buffer) and shorter dissolution timescales (e.g., 1–2 h) (e.g., Baker et al. [2006b]). Such variability in iron mobilization can be attributed in part to differences that exist between source materials and transported aerosol particles. For example, aerosol particles will typically be smaller than source materials as a result of size segregation during transport, and previous studies have reported greater iron solubilities in fine mode aerosol fractions relative to coarser materials [Siefert et al., 1999; Johansen et al., 2000; Chen and Siefert, 2004; Hand et al., 2004; Luo et al., 2005; Baker et al., 2006a; Baker and Jickells, 2006; Baker et al., 2006b]. In addition, transported aerosols can be subjected to additional physical and photochemical processes that could increase their iron solubility relative to source materials that have yet to undergo such processes.

3.8. Influence of Nitrate on the Speciation of Solubilized Iron

[59] To further investigate the depressed production of dissolved Fe(II) in 0.1 N HNO₃ suspensions, additional experiments were conducted with AZTD in which variable concentrations of nitrate (ranging up to 0.1 M) were added to solutions of 0.1 N H₂SO₄ and 0.1 N HCl. In both acids, the concentration of total dissolved iron was essentially independent of the nitrate level present in the reactor (Figures 8a and 8c). In contrast, experiments conducted in HCl systems revealed that increases in nitrate concentration between 1 and 100 mM produced a concomitant decrease in Fe(II) production (Figure 8b). The influence of nitrate on Fe(II) production in H₂SO₄ systems was far less (Figure 8d), as only a modest yet statistically significant decrease in the concentration of dissolved Fe(II) was observed in solutions with 0.1 M NO₃⁻.

[60] We propose that these results are evidence of a non-photochemical redox reaction between Fe(II) and nitrate in our systems; in the presence of high nitrate concentrations, Fe(II) is oxidized to Fe(III) while nitrate is reduced to nitrite (equations 5–7).

\[
2\text{Fe(II)} \rightarrow 2\text{Fe(III)} + 2e^- 
\]

\[
\text{NO}_3^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}
\]

Net Reaction: \[
2\text{Fe(II)} + \text{NO}_3^- + 2\text{H}^+ \rightarrow 2\text{Fe(III)} + \text{NO}_2^- + \text{H}_2\text{O}
\]

This reaction is consistent with the comparable amounts of total dissolved iron observed in systems with and without nitrate. Furthermore, we detected as much as 10 µM nitrite in AZTD systems with 0.1 N HNO₃ via a colorimetric method using the commercially available Griess reagent, whereas nitrite was not detected in any of our control studies, which included AZTD in 0.1 N HCl or 0.1 N H₂SO₄, and a reactor of 0.1 N HNO₃ without any AZTD. This concentration is far less than that predicted from the Fe(II) loss in Figures 7b and 8b, and the reaction stoichiometry in equation 7. Thus, additional reduction products are likely being generated. One possibility is NH₄⁺, which has previously been observed as a product of nitrate and nitrite reduction by Fe(II) [Summers and Chang, 1993; Summers, 2005], although attempts to develop an analytical method to quantify ammonium in our systems were unsuccessful. In particular, ion chromatography was not
helpful in probing the reaction between nitrate and Fe(II) because the products of reduction (e.g., nitrite) were generated at very low concentrations ($\approx 10 \mu$M) relative to nitrate ($\approx 100$ mM). Consequently, such small changes in nitrate concentration over time could not be observed, and the detection of reduction products was obscured as a result of the large nitrate background signal.

Based on published standard reduction potentials for the Fe(II)/Fe(III) ($E^0 = 0.771$ V) and nitrate/nitrite ($E^0 = 0.94$ V under acidic conditions) redox couples, the reduction of nitrate by Fe(II) is thermodynamically favorable. However, additional control studies conducted herein revealed that 400 $\mu$M of aqueous Fe(II) was stable in oxygenated solutions of 0.1 N H$_2$SO$_4$, 0.1 N HCl and 0.1 N HNO$_3$ over the duration of our dissolution experiments ($\approx 30$ h), suggesting that the proposed reaction between Fe(II) and nitrate does not occur over the kinetic timescales of our dissolution experiments in homogeneous solution. We interpret this result as evidence that the reduction of nitrate by Fe(II) must be surface-mediated. Ferrous iron associated with iron-containing mineral [Elsner et al., 2004] and clay [Hofstetter et al., 2003; Hofstetter et al., 2006] surfaces represents a stronger reductant than aqueous Fe(II), and Fe(II)-containing mineral phases have previously been shown to reduce nitrate [Summers, 2005]. A surface-mediated reaction is consistent with our observation that dissolved Fe(II) formation was suppressed in AZTD suspensions with nitrate concentrations in excess

![Figure 8](image_url). Influence of nitrate concentration on the production of total dissolved Fe and dissolved Fe(II) in pH 1 suspensions of AZTD particles in 0.1 N HCl (a and b, respectively) and 0.1 N H$_2$SO$_4$ (c and d, respectively). Variable concentrations of nitrate (up to 0.1 M) were added in the form of NaNO$_3$. Reactors contained a solids loading of 12.5 g/L and 0.1 M NaCl. When present, uncertainties represent one standard deviation from triplicate experiments.
of 1 mM. If this reaction were to occur in solution, then even the lowest concentrations of dissolved nitrate investigated in this study (100 μM) would have depressed the concentration of dissolved Fe(II) produced in our experimental systems with AZTD, which was not observed. Whether the surface-associated Fe(II) responsible for nitrate reduction is structural Fe(II) present within the aluminosilicate mineral lattice or Fe(II) that has readSORBED on the source material surface after an initial acid-promoted dissolution step remains unclear.

[62] Another question pertains to why nitrate impacts Fe(II) production so differently in 0.1 N HCl systems relative to 0.1 N H2SO4 systems (compare Figures 8b and 8d). This is not entirely understood, but may be related to competition between nitrate and sulfate for adsorption sites on the AZTD surface.

4. Conclusions and Potential Global Implications

[63] As expected from established trends in iron mineral dissolution [Martin, 2005] and prior investigations with Fe-containing aerosols [Spokes et al., 1994; Desboeufs et al., 1999], the solubility of iron in dust source materials was greatest at extremely low pH. Accordingly, the amount of dissolved iron in deliquescent aerosols or nucleated cloud droplets should be considerably increased if atmospheric processing with SO2 and HNO3 were to result in pH values on the order of 1, and this result should be applicable regardless of whether acidification results from anthropogenic or natural sources.

[64] We were unable to identify simple predictors of iron solubility for these source materials as a result of the relatively small fraction, uneven distribution, variable mineralogy and possible size-dependent content of their iron-containing particles, properties that are also likely to be exhibited by mineral dust aerosols. Rather, based upon our characterization studies, particularly Mössbauer spectroscopy and CCSEM/EDX individual particle analysis, we reiterate the recommendations of previous researchers (e.g., Dedik and Hoffmann [1992], Zhu et al. [1992], Spokes et al. [1994], and Pehkonen et al. [1993]) that the mineralogy and speciation of iron must be considered when attempting to predict the rate and extent of iron dissolution in all aqueous environments. These mineralogical considerations will likely have to extend beyond generalized classification schemes such as Fe oxide phases or Fe-containing aluminosilicates, as our dissolution data suggest that solubility predictions based solely upon the abundance of iron oxide phases in a material may not be sufficient. Specifically, SS particles have a lower total iron content than IS particles (Table 1), and unlike the IS sample, SS contains no detectable iron oxides (Figure 4). For this specific case, IS particles must contain a greater mass fraction of Fe oxide phases relative to SS particles, yet the IS material exhibited the lowest total iron solubility and Fe(III) solubility of all materials considered.

[65] The data presented herein also highlight the significant contribution of Fe(II)-containing solid phases to total iron solubility in low pH environments. For CL, SB, and AZTD suspensions in H2SO4 and HCl, measured concentrations of dissolved Fe(II) comprise nearly 20–30% of the total iron solubility. Results presented in Figure 5 also suggest that the contribution of dissolved Fe(II) tends to increase with increasing pH over the range of pH values from 1 to 3. As our dissolution experiments were conducted in the absence of light, this soluble Fe(II) must arise from the dissolution of Fe(II)-containing solids. These results are particularly noteworthy for dissolved Fe(II) concentrations, as although numerous studies have observed dissolved Fe(II) in atmospheric waters (see Deguillaume et al. [2005] and references therein), dissolved Fe(II) production is most often attributed to the photochemical reduction of Fe(III). Here, we show that soluble Fe(II) can also be generated from the acid-promoted dissolution of Fe(II)-containing solid phases, and that for such acid-promoted dissolution reactions, Fe(II) can represent the dominant species of dissolved Fe under certain environmentally relevant conditions (e.g., see Figure 5 for pH-dependent results with AZTD).

[66] Complementary CCSEM/EDX and temperature-dependent Mössbauer spectroscopy suggest that the solid phases responsible for dissolved Fe(II) generation may be Fe(II)-substituted aluminosilicates. Although we cannot entirely rule out other Fe(II)-containing solid phases that may be present at levels below detection by Mössbauer spectroscopy, our characterization results indicate that Fe-substituted aluminosilicates are components of these source materials. As the dissolution of common aluminosilicates such as albite and kaolinite is enhanced at extremely acidic pH values (see Walther [1996] and references therein) and the dissolution of aluminosilicates has previously been implicated as a source of dissolved aluminum in ocean surface waters [Maring and Duce, 1987], it seems reasonable to propose that Fe-substituted aluminosilicates may also represent an important source of soluble Fe in certain aquatic environments.

[67] Our results also serve to illustrate the complex interplay between source material mineralogy, the mechanism of acidification, and iron dissolution, as the high concentration of nitric acid necessary to promote iron dissolution is also capable of suppressing the release of dissolved Fe(II). Consistent with our experimental results, we propose nitrate as an electron acceptor in the redox cycling of Fe(II) via a non-photochemical reaction. We also found that acidification by 0.1 N H2SO4 tended to produce greater concentrations of total dissolved Fe than other acids at pH 1, but additional experimental work is needed to further explore the possibility that H2SO4 promotes the dissolution of Fe(III)-containing solids in source materials.

[68] With respect to the impact of acidification on bioavailable iron formation, our results yield two significant results that require further consideration. Evidence from our dissolution experiments suggest that Fe(II)-containing solid phases may represent an important source of dissolved Fe(II) in deliquescent, acidified mineral dust aerosol. Experimental evidence also suggests that nitrate on the surface of mineral dust aerosol is likely an important sink of Fe(II) in these same systems. Because Fe(II) may represent a more bioavailable form of iron, models attempting to determine the impact of HNO3 and H2SO4 uptake on soluble Fe(II) concentrations will likely need to account for these additional sources and sinks in order to properly predict bioavailable Fe concentrations in acidified mineral dust aerosol plumes.
Finally, we should mention that the experimental conditions for dissolution applied in this study, as well as those commonly employed in other investigations (e.g., [Sarthou et al., 2003; Baker et al., 2006b]), will not prevail upon deposition of mineral dust particles into the ocean. Low pH aqueous layers associated with mineral dusts will be replaced by circumneutral pH conditions upon deposition in oceans. Thus, any Fe(II) generated during atmospheric transport will be rapidly oxidized to Fe(III), which will then precipitate as some form of colloidal or nanoparticulate hydrous ferric oxides. It remains to be seen whether atmospheric processing of mineral dusts influences the stability of this colloidal phase, thereby making it more readily bioavailable via either some form of ligand-promoted dissolution (e.g., siderophore-mediated dissolution; [Morel and Price, 2003; Borer et al., 2005; Kraemer et al., 2005]) or greater photochemical reactivity.

Acknowledgments. This material is based upon work supported by the National Science Foundation under NSF EAR-0506679 and CHE-0503854. The CCSE/EDX particle analysis was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy’s Office of Biological and Environmental Research at Pacific Northwest National Laboratory. PNNL is operated by the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RL01 1803.

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