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Photoreduction of Iron(III) in Marine Mineral Aerosol Solutions

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Although there have been a number of studies of the solubility of Fe in marine mineral aerosols, there have been few studies of the oxidation states of the soluble iron fraction and of the factors that affect the solubility of iron in aerosol solutions. In this paper we present measurements of the concentrations of total Fe (including particulate), total soluble Fe and total soluble Fe(II) in marine aerosol particles. Only 1% of the total Fe and 7.5% of the soluble Fe was in the Fe(II) form. Photolysis experiments were performed with solutions extracted from aerosol filter samples and with solutions of Fe(III) in acidic sodium chloride. In both systems, Fe(II) concentrations increased rapidly when the solutions were exposed to sunlight and they attained steady state within an hour. However, in all cases Fe(II) is only a minor component even when conditions are favorable for photolysis. Fe(II) formation is hindered at the low pH that is believed to be characteristic of marine aerosol solutions. Solutions with added oxalate yielded greatly increased concentrations of Fe(II); this is probably related to the fact that Fe(III) oxalate complexes have strong ligand to metal charge transfer bands in the tropospheric solar UV-visible region. However, the presence of oxalate also leads to the formation of H_2O_2 ; when the radiation level decreased, the Fe(II) was partially or totally oxidized back to Fe(III) due to reactions with H_2O_2 . The photoreduction of Fe(III) to Fe(II) did not appear to significantly increase the dissolution of Fe(III) from the dust mineral matrix.

INTRODUCTION

Iron is essential for photosynthesis and for the growth of phytoplankton in the oceans. In many oligotrophic regions of the ocean, where upwelling of nutrient-rich deep water and fluvial input are minimal, the deposition of atmospheric mineral aerosol may be an important source of iron to the surface waters. Indeed, in these regions iron may be the limiting nutrient and, consequently, productivity may be closely linked to the deposition rate of iron from the atmosphere [Martin and Fitzwater, 1988]. However, the availability of this aeolian iron to the marine biota is partially a function of its solubility which may, in turn, be related to its oxidation state.

In previous studies of the solubility of atmospheric Fe [Hardy and Crecelius, 1981; Moore *et al.*, 1984; Zhuang *et al.*, 1990; Zhu *et al.*, 1992], it has generally been assumed that the iron was present predominantly as Fe(III). Fe(III) oxide is the most common form emitted by both natural and anthropogenic sources. Moreover, Fe(II) is thermodynamically unstable in the oxidizing environment of the atmosphere. Hence, any Fe(II) that is emitted to the atmosphere should be rapidly converted to Fe(III). However, recent work suggests that Fe(II) could, in fact, be an important constituent in aerosols in a variety of areas. For example, Fe(II) reportedly comprised 20-90% of the total dissolved Fe in fog water from a suburb of Zurich, Switzerland [Behra and Sigg, 1990]. Zhuang *et al.* [1992] reported that Fe(II) accounted for volume-weighted means of $56 \pm 32\%$ of the total Fe in aerosols over the North Pacific and $49 \pm 15\%$ at Barbados, West Indies; at the North Pacific sites, the Fe(II)/total Fe ratio ranged from 11% to nearly 100%. The reasons for the high concentrations of Fe(II) are still poorly understood.

In this paper, we present the results of a series of studies to assess the solubility of Fe in marine mineral aerosol solutions, the oxidation state of the dissolved Fe, the mechanism for formation of Fe(II), and the effect of the oxidation state of Fe

on its solubility. We focus on processes that might occur in aerosol solutions rather than in cloud droplets or precipitation. Marine mineral aerosol solutions constitute an extremely complex chemical environment. During their life cycle in the atmosphere, mineral particles accumulate on their surface a variety of oxidation products (including $\text{SO}_4^{=}$ and NO_3^-) and various other salts including sea-salt. As a consequence, marine aerosols exist as complex internal mixtures [Andreae *et al.*, 1986]. Because of the presence of these materials, such particles will be hygroscopic and they will deliquesce under the ambient relative humidity conditions in the marine environment (typically 80-90% RH). The result is that mineral aerosol particles will be constantly wetted by a brine solution. Furthermore, because of the presence of nonsea-salt (nss) $\text{SO}_4^{=}$ and NO_3^- , the solution can be highly acidic, although part of the acid can be neutralized by NH_3 or basic mineral substances such as CaCO_3 .

In earlier work [Zhu *et al.*, 1992], we measured the size-dependent composition of marine mineral aerosols based on the analyses of 18 cascade impactor samples collected at Barbados, West Indies. We computed the mean chemical characteristics of marine aerosol solutions in each particle size class at ambient relative humidities. We found that the pH could be lower than 1.0 and the ionic strength could be higher than 3.0. At a relative humidity of 80%, the calculated pH's typically lie between 0 and 1 unless the dust concentrations are very high. Under these extreme conditions, Fe(III) solubilities can be far higher than those normally expected for seawater, fresh water, cloud water and rainwater. Thus, aerosol solution processes could be a major factor affecting the fraction of iron that will readily dissolve when the atmospheric mineral particles enter the ocean.

MARINE AEROSOL SAMPLES

Methods

Soluble Fe(II) [Fe(II)_s], total soluble Fe [T- Fe_s] and total Fe [T-Fe] concentrations were measured in marine aerosol particles collected in the trade winds at Barbados, West Indies (13.17°N, 59.43°W). These winds often transport very high

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concentrations of mineral dust from the arid regions of North Africa [Prospero and Nees, 1987]. The aerosol samples were collected on 20x25 cm Whatman-41 cellulose and Pallflex 2500QAT-UP quartz filters in a sampling system at the top of a 16 m high tower at the easternmost end of the island. Our sampler is controlled by a wind direction sensor which activates the sampling system only when the wind blows off the ocean at speeds greater than 1 m s^{-1} . Because the tradewinds are very strong and steady at this site all year long, in-sector times are rarely less than 90% of the sampling period.

To measure soluble Fe, a quarter section of a filter was leached in 25 mL of acidic NaCl solution for 5 min at ambient temperature (typically $23 \pm 2^\circ\text{C}$). This volume is adequate for extracting a quarter filter without saturating the Fe [Zhu, 1992]. The leaching solution was 1 M NaCl with the pH adjusted to 1.0 with HCl; this solution replicates the pH and ionic strength of typical mineral aerosol particles in the marine boundary layer [Zhu, 1992]. We used a leaching time of 5 min so as to remove only the most mobile fraction of the Fe from the aerosol. Results from a previous study [Zhu, 1992] suggested that the unmodified atmospheric mineral Fe is virtually insoluble in seawater and that a prolonged acid extraction will only leach out the Fe that is bound in the mineral lattice. In contrast, the readily mobilized (5 min leach) Fe fraction will serve as an indication of the extent of processing that the mineral-aerosol Fe has undergone in the atmosphere. This is also the fraction of the Fe that would be most rapidly released if the particle were to be deposited in the ocean; hence, this Fe would be readily available to organisms in the surface waters.

To measure T-Fe in the Whatman-41 filter samples, another quarter section of the filter was dry ashed at 500°C overnight. After weighing, the residue was digested for 30 min at 85 psi in 25 mL of a strong acid solution ($\text{HNO}_3:\text{HCl}:\text{H}_2\text{O} = 10:10:5$) using a CEM Model MDS-81D Microwave Digestion System. With this procedure, we could not measure T-Fe in the quartz filter samples because of the bulk of the filter matrix.

All solutions were filtered through a $0.2 \mu\text{m}$ precleaned Nuclepore filter prior to analysis. Fe(II) was measured spectrophotometrically using ferrozine (3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine). Except where noted, a 10-mL sample aliquot was added to a volumetric flask containing 0.3 mL of 0.1 M ferrozine and 2.0 mL of 5 M acetic acid/ammonia buffer solution (pH 5.5). The absorbance of this solution was measured in a 10-cm cell at 562 nm with a Hewlett-Packard 8452A UV-visible spectrophotometer. Fe(II) standards consisted of electrolyte grade Fe powder dissolved in 0.1 M HClO_4 . This method can measure Fe(II) levels from nanomolar to micromolar [Landing and Westerlund, 1988]. T- Fe_s and T-Fe were measured directly in the leachate and digestion solutions, respectively, using flame atomic absorption spectrophotometry with deuterium arc background correction. Analytical errors were less than 1% for Fe(II) and about 4% for T- Fe_s and T-Fe. The sample and standard preparation were performed in Class 100 clean hood at the Rosenstiel School of Marine and Atmospheric Science, University of Miami.

Results

The concentrations of Fe(II)_s, T- Fe_s and T-Fe in our samples are listed in Table 1. The ratio of T-Fe to ash weight ranged from 6.1% to 10.6% with a mean of 8.2%. The value of 8.2% is somehow higher than the average crustal abundance, 5.6% [Taylor, 1964; Moore et al., 1984]. The difference is

largely attributable to the loss of volatiles upon heating, about 25%. Similarly, the ratios of the Al concentrations measured by neutron activation analysis (R. Arimoto, University of Rhode Island, personal communication, 1992) to our ash weights in concurrent samples averaged 11% ($n=158$, $r^2=0.992$) compared to an average soil value of about 8%. Thus, the effective T-Fe concentration in the pre-combusted dust is about 6%, a value that is in good agreement with the average crustal abundance.

The T- Fe_s /T-Fe ratios in the Whatman-41 samples were very consistent, ranging from 6.9% to 9.2%, even though the samples were collected over a time span of three months and the dust load on the filters varied by a factor of five. Only a small percentage of the T- Fe_s was in the form of Fe(II), 6.8-12.4% with a mean of 9.2%. The excellent agreement between both the absolute concentrations and the ratios in the leachates from the Whatman-41 samples and those collected concurrently on quartz filters indicates that the filter matrix itself did not significantly affect either the solubility or the speciation. The Fe(II)_s/T-Fe ratio was always less than 1%. These results indicate that Fe(II)_s was only a minor component of the Fe concentration in both the soluble fraction and the total aerosol.

PHOTOCHEMICAL EXPERIMENTS

Many Fe(III) complexes can absorb radiation in both the near-UV and the visible region of the solar spectrum with subsequent reduction of Fe(III) to Fe(II) [Graedel et al., 1985]. Consequently, the Fe(II)_s/T- Fe_s ratio in aerosol solutions and fog droplets could be a strong function of their solar irradiation history. To test this possibility, we measured the change of Fe(II)_s in a variety of solutions during their exposure to solar radiation and after their return to a darkroom.

Methods

Irradiations were carried out in single neck round bottom quartz photolysis flasks which were cleaned with 6 N HCl solution and then thoroughly rinsed and stored filled with Millipore Super-Q ($18 \text{ M}\Omega \text{ cm}^{-1}$) water. The flasks were rinsed with an aliquot of the test solution immediately prior to the irradiation of the final volume of test solution. The irradiation experiments were performed on the roof of Science and Administration Building, RSMAS, University of Miami, where the flasks were immersed in a water bath at a temperature of $301\text{-}303^\circ\text{K}$. Dark control samples, identical to the irradiated samples with the exception that the flasks were wrapped with aluminum foil, were maintained in the same bath. An Eppley Integrating Radiometer (Model 411), located adjacent to the bath, provided a continuous record of the clear-sky solar flux for wavelengths from 290 nm to 385 nm. The flux was quite constant during sunny days in Miami during the summer, $0.3344 \text{ W m}^{-2} \text{ h}^{-1}$.

Filter Leachates

Because the Whatman-41 cellulose filters are leached with a strongly acidic solution, organic ligands might be formed that could complex either Fe(II) or Fe(III) and, hence, alter the reactions occurring during irradiation. However, the results from irradiations of the leachates from the concurrent Whatman-41 and quartz filter samples (Table 2) are quite comparable, indicating that the presence of the cellulose did not create a significant artifact. Before the irradiation, the Fe(II)_s concentrations in the leachates from the two Whatman-41 samples were 0.02 and $0.04 \mu\text{mol}$, respectively, while those in the quartz samples were 0.03 and $0.05 \mu\text{mol}$.

TABLE 1. The Concentrations of Soluble Fe(II), Total Soluble Fe, and Total Fe (μ moles) in Barbados Aerosol Samples

Sample Date in 1991	Filter Type	[Fe(II)] _s	[T-Fe] _s	[T-Fe]	Ash, mg	[Fe(II)] _s /[T-Fe] _s , %	[Fe(II)] _s /[T-Fe], %	[T-Fe] _s /[T-Fe], %	[T-Fe]/Ash, %
Aug. 3-4	W	0.11	0.91	13.0	11.64	12.4	0.87	7.0	6.3
Aug. 4-5	W	0.14	1.43	15.5	14.33	10.0	0.92	9.2	6.1
Oct. 21-22	W	0.02	0.34	4.89	2.72	6.8	0.47	6.9	10.1
Oct. 22-23	W	0.04	0.48	6.95	3.68	7.7	0.53	6.9	10.6
Oct. 21-22	Q	0.03	0.42			6.9			
Oct. 22-23	Q	0.05	0.56			9.3			

W, Whatman-41 filter; Q, Quartz filter.

TABLE 2. The Fe(II)_s Concentrations (μ moles) and Fe(II)_s/T-Fe_s Ratios Before and After the Exposure of Barbados Sample Extracts to Solar Radiation for 60 Min

Sample Dates in 1991	Filter Type	Before Irradiation		After Irradiation	
		[Fe(II)] _s	[Fe(II)] _s /[T-Fe] _s , %	[Fe(II)] _s	[Fe(II)] _s /[T-Fe] _s , %
Oct. 21-22	W	0.02	6.8	0.07	19.6
Oct. 22-23	W	0.04	7.7	0.12	24.2
Oct. 21-22	Q	0.03	6.9	0.09	22.6
Oct. 22-23	Q	0.05	9.3	0.16	28.4

W, Whatman-41 filter; Q, Quartz filter.

After 60 minutes irradiation, the Fe(II)_s concentrations in each of the leachates increased by a factor of three: to 0.07 and 0.12 μ mol for the Whatman-41 samples; and to 0.09 and 0.16 μ mol for the quartz samples. However, despite the substantial increases in the Fe(II)_s concentrations during irradiation, they still accounted for less than 30% of the T-Fe_s in each of the samples.

To more clearly define the rate of change of the Fe(II) concentration, we exposed the NaCl/HCl leachate of one of our filter samples to sunlight for six hours beginning at about 0930 LT. Fe(II)_s increased sharply from about 0.1 to 1.3 μ mol during the first 20 min of irradiation (Figure 1, open circles), but then remained virtually constant throughout the remainder of the exposure period. When the sample solution was returned to the darkroom, the Fe(II)_s concentration declined very rapidly (by about 25%) during the first 30 min. Thereafter, the concentration decreased relatively slowly, by only 20% during the next 24 hours (Figure 1, solid circles), to a final concentration that was about 60-65% of the maximum.

Effect of pH and Inorganic Anions

Aerosols are complex internal mixtures that often contain relatively high concentrations of inorganic species. Complexes between Fe(III) and these species could, potentially, play an important role in the photochemistry of Fe in aerosols as well as fog and rain drops. However, few measurements have been made of the photochemical properties of Fe(III) complexes with ligands other than the hydrated Fe³⁺ and FeOH²⁺, sometimes referred to by others as Fe(H₂O)₆³⁺ and

FeOH(H₂O)₅²⁺ [Graedel et al., 1985; Faust and Hoigné, 1990]. To assess the potential effects of the most abundant inorganic ligands, irradiation studies were performed on aqueous Fe(III) solutions containing Cl⁻, NO₃⁻ and SO₄⁼.

Five Fe(III) solutions (87 μ M) were made up in Q-H₂O. The pH of two of the solutions was adjusted to 1 and 3 by adding HCl. The final three solutions were made 0.1 M in NaCl, NaNO₃, and Na₂SO₄, respectively, and then adjusted to pH 1 with HCl. All of the solutions were irradiated for about 3 hours and then placed in a darkroom. During both the irradiation and the darkroom periods, aliquots were periodically removed for Fe(II) analysis.

In all solutions the Fe(II) concentration increased rapidly for about an hour and then reached steady state (Figure 2). In the H₂O solutions, Fe(II) formation at pH 3 was about double that at pH 1. This is consistent with the absorption cross sections of the dominant Fe(III) complexes. The absorption spectrum of hydrated Fe³⁺, the dominant complex at pH 1, overlaps only a small portion of the solar spectrum and its absorption cross section in the photochemically important 290-400 nm band is at least an order of magnitude less than that of FeOH²⁺ which is the dominant complex at pH 3.

In the 0.1 M Cl⁻, NO₃⁻ and SO₄⁼ solutions, Fe(III) reduction was significantly less than that in the pH 1 solution without added anions. The difference is particularly pronounced for the SO₄⁼ solution in which the Fe(II)_s is more than a factor of two lower. Notably, even the maximum reduction of Fe(III) at pH 1 produced a Fe(II)_s/T-Fe_s ratio of only about 15%. In the SO₄⁼ solution, the ratio was only about 6%.

Several important conclusions may be drawn from the results of these experiments. The pH dependence of Fe(II) formation indicates that the Fe(II)/T-Fe_s may be much higher in fog and cloudwater which typically have pH's of 3±1 [Jacob et al., 1985] than in aerosol solutions which may have pH's of about 1 or less. Moreover, high concentrations of Cl⁻, NO₃⁻ and SO₄⁼ in the mixed aerosols, e.g. those with sea salt, will tend to inhibit rather than enhance the reduction of Fe(III) to Fe(II).

The results from these studies with inorganic species at pH 1 differ in two major ways from those with the aerosol extracts. First, the steady state Fe(II)/T-Fe_s ratios attained during irradiation are a factor of two or more higher with the aerosol extracts. Second, Fe(II)/T-Fe_s ratios in the aerosol extracts declined rapidly after being returned to the darkroom. In contrast, the ratio in the test solutions remained essentially constant at the irradiated maximum when only H₂O and inorganic ions were present. These observations suggest that constituents other than water molecules and major inorganic

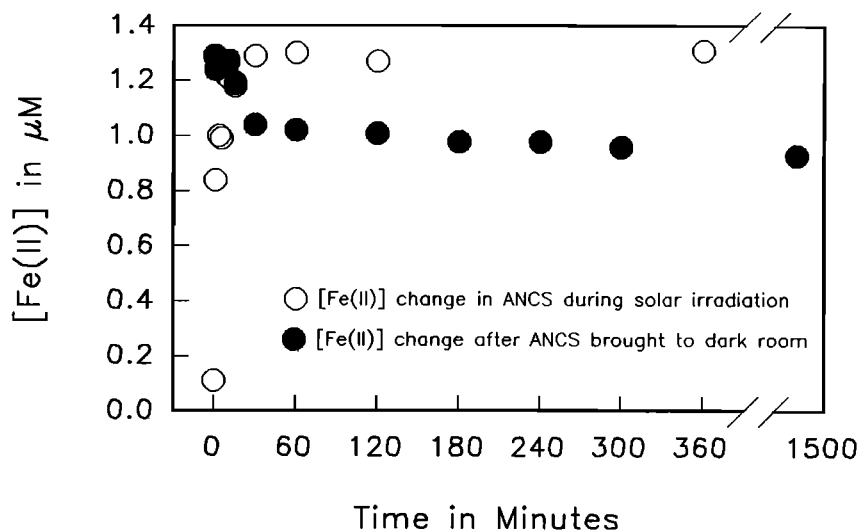


Fig. 1. Temporal changes in the Fe(II) concentration in the acidic NaCl solution extract of a Barbados aerosol sample during exposure to solar radiation (open circles) and after return to a darkroom (solid circles).

ligands must be involved in the Fe(II)/Fe(III) equilibria in the aerosol extracts.

Effect of Organic Anions

Organic species may well be an important factor in explaining the discrepant behavior of Fe in the inorganic solutions and the aerosol extracts. Many organic species are themselves photochemically active as are their complexes with a variety of metals. Organics, being derived from both natural biogenic sources and anthropogenic emissions, are ubiquitous components of atmospheric aerosols. In heavily polluted areas, e.g., Los Angeles, organics can comprise 30% or more of the total aerosol mass [Gray *et al.*, 1984] compared to about 10% in areas which are heavily impacted by soil dust [Mamane *et al.*, 1982]. However, quantitatively evaluating the influence of organic species on atmospheric aqueous phase chemistry is very difficult because of the large variations in both the concentrations and the composition of the organic matter and the tremendous variety of organic species that could potentially be present.

For this investigation, we used oxalate because it is a common constituent in both aerosol particles and atmospheric water droplets. Oxalate can be produced from hydrocarbons by incomplete combustion, ozonolysis or photooxidation [Zuo and Hoigné, 1992]. Its concentration is often about 100 ng m⁻³ in the atmosphere and frequently exceeds 10 μM in fog water and rain [Norton *et al.*, 1983; Joos and Baltensperger, 1991].

The conditions of this experiment were comparable to those for the inorganics: a solution containing 0.1 M Na₂C₂O₄, 87 μM Fe(III), and HCl to adjust the pH to 1. The concentration of Fe(II)_s increased rapidly in the irradiated solutions with added oxalate and the Fe(II)_s/T-Fe_s ratio reached a steady state (Figure 2) that was about 60%, 4-10 times higher than that obtained in the inorganic solutions. As soon as the oxalate solution was placed in the dark, the Fe(II) concentration decreased rapidly to undetectable levels. This result (i.e., the high Fe(II) concentrations during irradiation and rapid decline in the dark) contrasts sharply with the Fe behavior in the solutions of inorganic ions but it is similar to that obtained with our aerosol extracts.

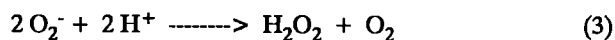
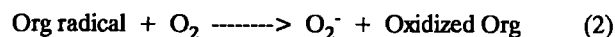
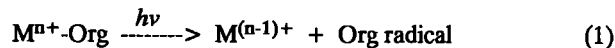
The oxalate experiment was repeated at pH's ranging from 1 to 5 (Figure 3). The same general behavior was observed

except that, at the higher pH's, more Fe(II) was produced during irradiation and more remained after the samples were returned to the darkroom.

There are several possible reasons for the observed dark decrease in Fe(II)_s in the presence of oxalate. In this regard, it is important to note that the standard potential between the oxalate complexes of Fe(III) and Fe(II) is, reportedly, at least two orders of magnitude lower than that between their aquo complexes [Heusler and Lorenz, 1985]. Consequently, when Fe(II) is complexed with oxalate, it can be oxidized much more readily.

When the solutions are exposed to sunlight, the oxalate itself could react to yield products that could subsequently oxidize Fe(II). However, results from additional experiments indicate that this does not occur. A 120 μM sodium oxalate solution in 1 M NaCl (pH adjusted to 1 with HCl) was irradiated under sunlight for 30 min and then returned to the darkroom. The solution was immediately spiked with 10 μM Fe(II). Periodic measurements over the next hour reveal no significant decrease in the Fe(II) concentration (Figure 4). In fact, the change of Fe(II) concentration was essentially identical to that in unirradiated 1 M NaCl (pH 1) solutions with or without added oxalate.

Another possibility is that H₂O₂ is produced during irradiation of a solution containing both iron and oxalate. This H₂O₂ could then rapidly oxidize Fe(II) back to Fe(III) in the dark. Zuo and Hoigné [1992] proposed the following mechanism for H₂O₂ production:



where M and Org represent, respectively, the central metal ion and the complexing organic ligand in the complex. Fe(III)-oxalate complexes were used in their study as a model system.

Several tests were performed to test the possibility that the Fe(II) was indeed oxidized by H₂O₂. In test 1, 100 mL of the 1

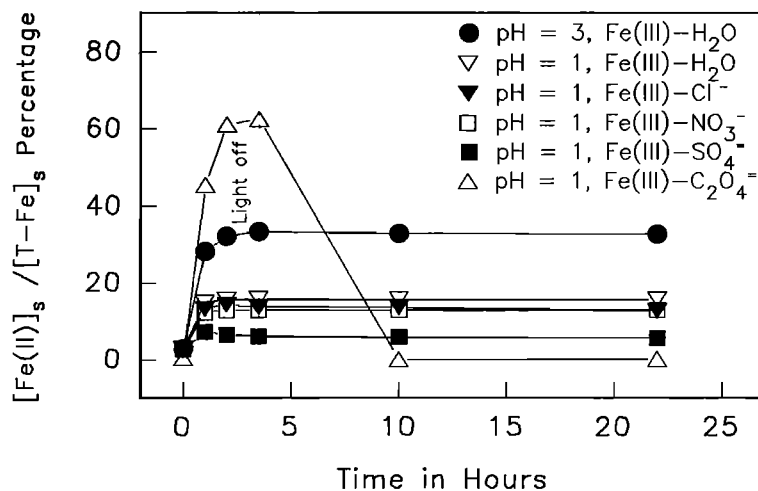


Fig. 2. Temporal changes in Fe(II) as a percentage of the total soluble Fe in a variety of solutions initially containing 87 μM Fe(III) during exposure to solar radiation and after return to the darkroom.

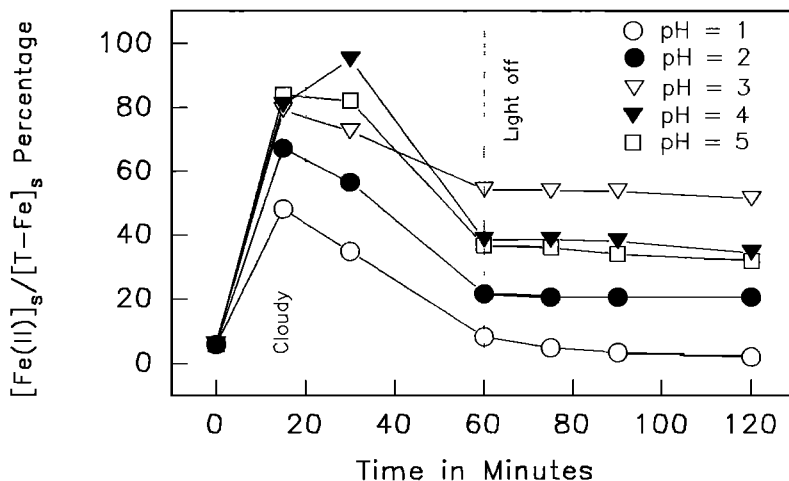


Fig. 3. Temporal changes in Fe(II) as a percentage of the total soluble Fe in solutions initially containing 87 μM Fe(III) and 0.1 M $\text{Na}_2\text{C}_2\text{O}_4$ with pH's adjusted to various levels with HCl. The plots show the changes which occur during exposure to solar radiation and after return to the darkroom. Note that when the sun was blocked by cloud, the Fe(II) percentage in many of the solutions began to decrease.

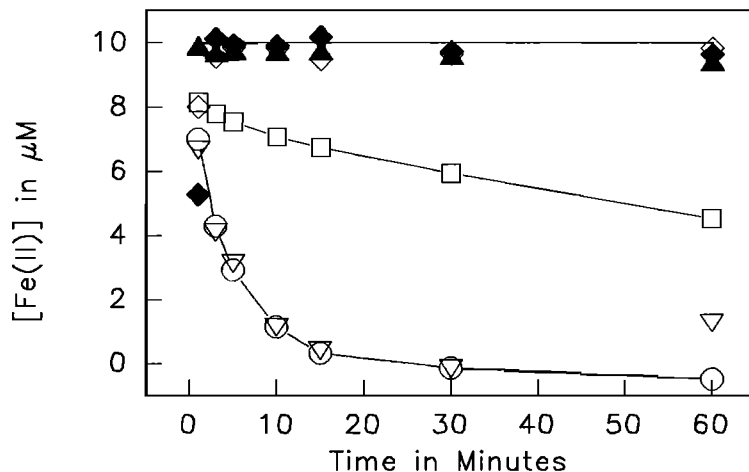
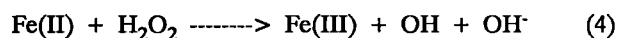


Fig. 4. Temporal changes of the Fe(II) concentration in dark samples in various solutions without prior exposure to solar radiation and with 30 min of exposure. Unexposed acidic NaCl solution (ANCS) spiked with Fe(II) (solid triangles); unexposed ANCS and 120 μM $\text{Na}_2\text{C}_2\text{O}_4$ spiked with Fe(II) (open diamonds); ANCS and 120 μM $\text{Na}_2\text{C}_2\text{O}_4$ exposed to solar radiation and subsequently spiked with Fe(II) (solid diamonds); ANCS/120 μM $\text{Na}_2\text{C}_2\text{O}_4$ solution that was spiked with Fe(II) and then irradiated (open circles); unexposed ANCS spiked with Fe(II) and to a concentration of 5 μM H_2O_2 (open squares); unexposed ANCS spiked with Fe(II) and to a concentration of 50 μM H_2O_2 (open triangles).

M NaCl (pH 1) solution was spiked to 10 μM Fe(II) and 120 μM $\text{Na}_2\text{C}_2\text{O}_4$ and irradiated in sunlight for 30 min. The Fe(II) concentration in this solution dropped very rapidly after the solution was returned to the darkroom (Figure 4). After 15 min, its concentration was only 5% of that measured after the first minute in the dark.

We could not directly verify the mechanism of Fe(II) oxidation by measuring the concentration of H_2O_2 in the test solution during the course of the reaction. As an alternative, we prepared two solutions identical to that used in the irradiation experiment but kept them in the darkroom. H_2O_2 was directly injected into the solutions to final concentrations of 5 μM and 50 μM . The Fe(II) concentrations which were measured at various time intervals after the H_2O_2 injection are shown in Figure 4. In both of these solutions, the Fe(II) concentrations decreased significantly with time. For the solution containing 5 μM H_2O_2 , the Fe(II) concentration decreased by only about 20% in the time interval from 1 to 15 min after the H_2O_2 injection. During the same 14-min interval, the Fe(II) concentration in the 50 μM H_2O_2 solution decreased by 95%. The striking difference between the Fe(II) decreases in these two solutions strongly indicate that the destruction of Fe(II) was controlled by reaction with H_2O_2 . Interestingly, the rate of destruction of Fe(II) in the radiation experiment, test 1, was virtually identical to that in the 50 μM H_2O_2 solution.

The primary reaction of Fe(II) with H_2O_2 in solution is given by



Hence, the lifetime (τ) of Fe(II) is obtained from the equation:

$$\tau = \frac{[\text{Fe(II)}]}{d[\text{Fe(II)}/dt]} = \frac{1}{k_4 [\text{H}_2\text{O}_2]} \quad (5)$$

where k_4 is the rate constant of reaction (4).

In a plot of the logarithm of the Fe(II) concentration remaining in solution versus time, the slope is equal to $k_4 [\text{H}_2\text{O}_2]$, and hence k_4 is equal to slope/ $[\text{H}_2\text{O}_2]$. The results from our measurements with the 50 μM H_2O_2 solution (Figure 5) yield a value of $\log_{10}(k_4) = 1.8$ in our 1 M NaCl (pH 1) solution. Previous extensive studies [Millero and Sotolongo,

1989; Millero *et al.*, 1991] indicate that k_4 is a strong function of pH and solution composition. In acidic solutions, the rate constant is independent of the composition, and the value of $\log_{10}(k_4)$, 2.0 ± 0.1 , is in good agreement with our measurements at pH 1.

The Fe(II) decay curve of the irradiated solution in test 1 is nearly identical to that in the 50 μM H_2O_2 solution. Consequently, if the decay of Fe(II) in the irradiated solution is, in fact, due solely to reaction with H_2O_2 , then the concentration of H_2O_2 in the irradiated sample must be comparable. Such H_2O_2 concentrations are, in fact, fairly typical in atmospheric water drops. In marine rainwater, for example, H_2O_2 concentrations are typically about 10-100 μM [Zika *et al.*, 1982].

The following mechanism is proposed to explain the above phenomena. Under solar irradiation, the photochemical reduction of Fe(III) can occur in atmospheric aqueous solutions. If certain organic materials such as oxalate are present in the solution, H_2O_2 will also be formed during irradiation. Initially, the concentrations of both Fe(II) and H_2O_2 will increase as they are usually low in the solution. As their concentrations increase under continued irradiation, they will begin to react with each other. Under constant solar intensity, a steady-state is established in which Fe(III) is photoreduced to Fe(II) as quickly as Fe(II) is oxidized to Fe(III) by H_2O_2 . When the solar radiation starts to decrease in the late afternoon, photoreduction of Fe(III) decreases and the continued reaction of Fe(II) with H_2O_2 results in a decrease in the concentration of Fe(II). After sunset, only the Fe(II) reaction with H_2O_2 is significant. The final Fe(II) concentration in the dark will depend on the relative amounts of H_2O_2 and Fe(II) in the solution. Depending on the relative concentrations, Fe(II) could be partially or totally oxidized back to Fe(III).

Effect of Photochemical Reduction on Iron Solubility

The above results strongly indicate that substantial reduction of Fe(III) to Fe(II) could and probably does occur in atmospheric water droplets and aerosol solutions. Changes in the oxidation state of dissolved Fe could potentially influence the solubility of Fe. To address this issue, we added $\alpha\text{-FeOOH}$ (goethite), one of the most common iron-containing minerals during the weathering process, to 1 M NaCl (pH 1) solutions

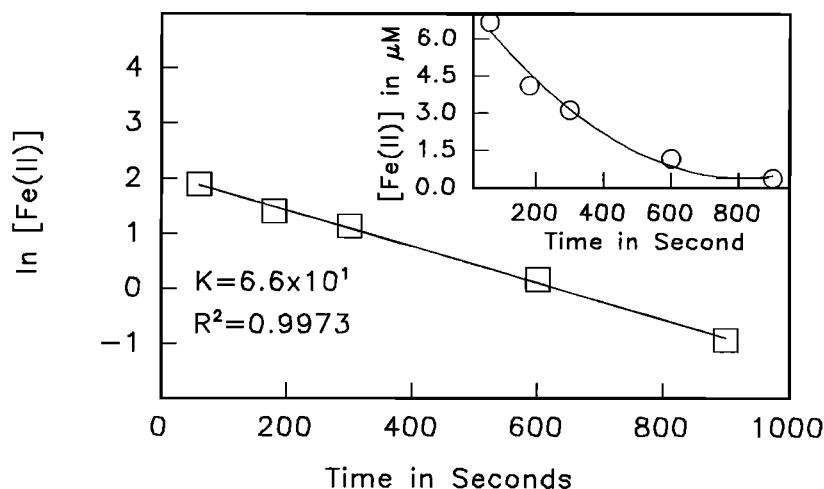


Fig. 5. Plots showing the decay of the Fe(II) concentration in an acidic NaCl solution containing 120 μM $\text{Na}_2\text{C}_2\text{O}_4$ after the solution had been exposed to solar radiation for 30 min and then returned to the darkroom. The slope of the $\ln[\text{Fe(II)}]$ versus time plot yields the rate constant, k . The inset shows the data on a linear scale.

containing various concentrations of organic anions. The α -FeOOH was prepared by hydrolyzing $\text{Fe}(\text{NO}_3)_3$ in KOH at 60°C for 48 hours with an Fe/OH^- ratio of 0.25 and a final pH of about 12 [Atkinson *et al.*, 1967]. The concentrations of $\text{Fe}(\text{II})_s$ and T- Fe_s were measured in both irradiated solutions and dark controls. All of the irradiated solutions were exposed to sunlight during the same period.

The T- Fe_s concentrations in all of the irradiated samples and dark controls are essentially identical to one another (Table 3). This is true even in the solution containing 1000 μM oxalate despite the fact that the $\text{Fe}(\text{II})$ accounted for over 80% of the T- Fe_s in this solution after irradiation compared to only 3-4% in the dark control. The results obtained from solutions with a fixed composition (100 μM oxalate) but exposed to solar radiation for different time periods show a similar constancy in T- Fe_s despite significant reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ (Table 4). The data from both sets of experiments strongly suggest that the photochemical processes affect only the dissolved Fe species. Photochemical reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ appears to have no detectable affect on the solubility of goethite.

DISCUSSION AND CONCLUSIONS

Our results clearly indicate that $\text{Fe}(\text{II})$ can and does exist in aqueous atmospheric aerosol solutions. Because the atmosphere is an oxidizing environment, active reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$ must take place in order to maintain those levels of reduced Fe. The results of our experiments indicate that photochemical processes are very important in this regard. In aqueous solutions, $\text{Fe}(\text{III})$ is hydrated with water molecules or complexed with inorganic and organic ligands if their concentrations are sufficiently high [Weschler *et al.*, 1986]. An important feature of many of these ferric complexes is that they can absorb in the visible region of the solar spectrum as well as in the near-ultraviolet. On the absorption of a photon, the $\text{Fe}(\text{III})$ complexes undergo a charge transfer from the ligand to the metal center. The net result is a concurrent reduction of the metal center and oxidation of coordinated ligand [Graedel *et al.*, 1985].

However, in all of our experiments, a steady state concentration of $\text{Fe}(\text{II})$ was quickly established during exposure of the solutions to solar radiation. This result suggests that subsequent reoxidation limits the amount of $\text{Fe}(\text{II})$ which can exist in the solution. This limit is strongly dependent on both the pH of the solution and on the ligands with which the $\text{Fe}(\text{III})$ is complexed. Moreover, when organic ligands such as oxalate are involved, H_2O_2 produced during irradiation will continue to rapidly oxidize $\text{Fe}(\text{II})$ in the dark.

TABLE 4. The Effect of Photolysis Time (Exposure to Solar Radiation) on the Soluble Iron Concentrations (μmoles) in Acidic NaCl Solutions Containing α -FeOOH and 100 μM $\text{Na}_2\text{C}_2\text{O}_4$

Photolysis Time, hours	Dark Control [T- Fe_s]	After Exposure to Solar Radiation		
		[T- Fe_s]	[$\text{Fe}(\text{II})_s$]	[$\text{Fe}(\text{II})_s$]/[T- Fe_s], %
0.5	148.1	148.9	9.05	6.1
1.0	156.4	158.9	12.14	7.8
2.0	159.8	160.6	15.82	9.9
3.0	160.6	161.4	16.03	9.9
4.0	163.1	164.0	16.47	10.0

Consequently, we might expect that in the ambient environment the $\text{Fe}(\text{II})/\text{T-Fe}_s$ ratio will undergo a substantial diurnal variation with much higher ratios during the day than at night.

Our studies show that only a small fraction, a mean of about 7-8%, of the T-Fe in marine mineral aerosols at Barbados is soluble. Also, the $\text{Fe}(\text{II})_s/\text{T-Fe}_s$ ratio is only about 7-12% and the $\text{Fe}(\text{II})_s/\text{T-Fe}$ ratio was less than 1%. Our results would appear to differ substantially from those of Zhuang *et al.* [1992] who reported that $49 \pm 15\%$ of the T-Fe in Barbados aerosol samples was in the form of soluble $\text{Fe}(\text{II})$. However, there was an error in the published text of that paper; their Figure 1 correctly indicates the $\text{Fe}(\text{II})_s/\text{T-Fe}$ ratios in the six Barbados samples: 2.2%; 3.4%; 5.2%; 10.8%; 19.0%; and 49% (G. Zhuang, personal communication). The mean for all six values is 15%. If the highest value is considered to be anomalous, the mean for the other five values is 8.1%. While the latter mean is closer to the percentages that we have measured, it is still markedly higher, and the reason(s) for the apparent discrepancy are still unclear.

The much higher total Fe solubilities obtained by Zhuang *et al.* are attributable to their use much more vigorous dissolution conditions: shaking for at least three hours in a solution with a negative pH [Yi *et al.*, 1992]. Under such conditions, a much larger fraction of the Fe will be leached out. As a check, we used their extraction procedure on some of our Barbados dust samples and, under those conditions, we obtained total Fe solubilities that were comparable to theirs. However, the results from our previous calculations [Zhu *et al.*, 1992] indicate that such extreme pH conditions are unlikely to occur very frequently in aerosol particles under ambient

TABLE 3. Comparison of the Soluble $\text{Fe}(\text{II})$ and Total Soluble Fe Concentrations (μmoles) in Acidic Sodium Chloride Solutions (ASCS, 1 M NaCl + HCl, pH=1) With and Without Exposure to Solar Radiation for 60 Min

Solution Composition	[T- Fe_s]			[$\text{Fe}(\text{II})_s$]			[$\text{Fe}(\text{II})_s$]/[T- Fe_s]	
	Dark	hv	Change, %	Dark	hv	Change, %	Dark, %	hv, %
α -FeOOH + ASCS								
+ Nothing	150.5	152.9	1.55	<0.05	6.25			4.15
+ 10^1 M Oxalate	154.7	154.7	0.00	<0.05	8.75			5.66
+ 10^2 M Oxalate	156.4	158.9	1.61	4.82	12.10	152.00	3.08	7.76
+ 10^3 M Oxalate	160.6	161.4	0.53	6.96	131.40	1787.00	4.34	81.84
+ 10^2 M Citrate	156.4	156.4	0.00	4.64	16.30	250.00	2.97	10.39
+ 10^3 M Citrate	160.6	161.4	0.53	5.89	17.00	188.00	3.67	11.56
+ 10^3 M Glycine	160.6	161.4	0.53	<0.05	6.43			4.00

atmospheric conditions, particularly in the supramicron particle size range that contains the dominant portion of the dust.

Zhuang et al. postulated that photochemical processes are the key reaction producing Fe(II) and that these serve to increase the solubility of marine aerosol Fe. Our goethite solubility/irradiation studies indicate that the higher Fe solubility can not be attributed to photochemical processes on the time scale of our experiment (i.e., 48 hours); the reduction processes appear to affect only the soluble fraction of the Fe. This discrepancy might be explained by the fact that the photo-reduction of Fe(III) to Fe(II) is a very fast reaction, occurring in a matter of minutes, while the dissolution of Fe oxides, on the other hand, is a very slow process. We found that, even immersed in the solution with 1 M NaCl and pH=1 for 48 hours, no more than about 0.5% of either Fe₂O₃ or FeOOH was dissolved. Similar results were obtained by *Brimblecombe and Spedding* [1975]. The dissolution rate for Fe oxides may be limited by surface-controlled processes [*Stumm and Wollast*, 1990].

On the other hand, the higher Fe(II)_s/T-Fe ratios (20-80%) reported for fog water in a suburb of Zurich, Switzerland [*Behra and Sigg*, 1990] may not be unreasonable. The order of magnitude higher absorption cross-sections for Fe(III)-aquo complexes at pH 3 compared to pH 1 suggests that Fe(II) could become the major fraction of T-Fe_s in fog, cloud and rain water. Therefore it is conceivable that mineral particles that are incorporated into cloud droplets could undergo enhanced reduction of Fe(III) and a higher ratio of Fe(II)/Fe(III) [*Zhuang et al.*, 1992]. However, the fact that we observe relatively low ratios in the mineral aerosols collected at Barbados suggests that either the dust has not cycled through cloud or, if it has, that the ensuing in-cloud changes in the Fe(II)/Fe(III) ratio were ephemeral. The same conclusions apply with regard to the low soluble iron fraction that we observe in the Barbados samples.

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