

## Redox Chemistry of Iron in Fog and Stratus Clouds

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The redox chemistry of Fe in fog and cloudwater has been investigated at coastal and inland locations in the Los Angeles basin, in Bakersfield California, and in Delaware Bay. Samples were collected and analyzed for Fe (Fe(II), Fe(III), total Fe), sulfur (S(IV), S(VI)), organic ligands (formate, acetate, oxalate), total organic carbon (TOC), pH, major cations (sodium, calcium, magnesium, potassium, ammonium), chloride, sulfate, nitrate, peroxides, and aldehydes (HCHO); the amount of sunlight was also measured. The ratio Fe(II)/Fe(total) varied between 0.02 and 0.55. The concentration of Fe(II) varied between 0.1 and 5 micromole, and the concentration of total Fe varied between 2 and 27 micromole. The atmospheric redox cycle of Fe involves both dissolved and aerosol surface species and appears to be related to the presence of organic compounds which act as electron donors for the reduction of Fe(III). Fe(III) reduction is enhanced by light but significant Fe(II) levels were observed in the dark. We suggest that reduction of Fe(III) species by organic electron donors may be an important pathway that affects the speciation of Fe in both urban and rural atmospheres. It is possible that reactions involving Fe and organic compounds might be an important source of carboxylic acids in the troposphere.

### INTRODUCTION

A knowledge of the exact speciation of all oxidation states of transition metals in atmospheric water droplets as a function of variables such as pH, organic ligand content and ionic strength is critical to the computational assessment of in situ reaction pathways involving S(IV), dissolved oxygen, R<sub>2</sub>CO, NO<sub>x</sub>, and peroxides [Jacob and Hoffmann, 1983; Hoffmann and Jacob, 1984; Weschler *et al.*, 1986; Faust and Hoigné, 1990]. Likewise, a knowledge of the speciation of metals such as Fe and Mn in wet and dry atmospheric deposition and the subsequent speciation changes upon introduction to marine waters is important to the assessment of the ability of marine biota to utilize these atmospherically derived elements for nutritional needs [Jackson and Morgan, 1978; Anderson and Morel, 1982; Duce, 1986; Martin *et al.*, 1988, 1989].

Iron is emitted to the troposphere from both natural (e.g., windblown dust) and anthropogenic (e.g., coal combustion) sources [Morales, 1979; Hansen *et al.*, 1984]. It has been proposed that atmospheric Fe participates in a variety of reactions such as the oxidation of S(IV) and organic compounds by Fe(III) via direct electron transfer, and the catalytic autooxidation of S(IV) to S(VI) in the droplet phase [Weschler *et al.*, 1986; Pandis and Seinfeld, 1989; Pandis *et al.*, 1992]. In addition, laboratory experiments have shown that Fe(III) is an important oxidant of S(IV) and organic compounds (e.g., aldehydes to carboxylic acids) [Cunningham *et al.*, 1985; Faust and Hoffmann, 1986;

Martin *et al.*, 1991]. In spite of the known redox chemistry of Fe, most previous investigations of Fe in atmospheric water have been limited to the determination of the total dissolved Fe concentration. Moreover, current models of atmospheric cloud chemistry have assumed that Fe in cloudwater and aerosols is present as mostly Fe(III) in a variety of solid and aqueous phase species [Pandis and Seinfeld, 1989].

Previous measurements of Fe(II) in seawater and in stream water have shown that it is also present at significant levels in oxic surface water [Hong and Kester, 1986; Landing and Westerlund, 1988; McKnight *et al.*, 1988]. In addition, there are a few recent reports of the presence of Fe(II) in atmospheric water and aerosols [Behra and Sigg, 1990; Dedit *et al.*, 1992; Zhuang, 1992; Zhuang *et al.*, 1992; Zhu *et al.*, 1993]. A study of the speciation of Fe in fog collected with the Caltech active strand collector in Zurich [Behra and Sigg, 1990] has shown that a significant fraction of the total Fe (20 to 90%) is present as soluble Fe(II) (up to 200 micromole) over a pH range of 3–7 and that in many samples Fe(II) was the predominant oxidation state in solution (dissolved Fe is operationally defined by filtration with either a 0.45- or 0.05-micrometer membrane filter).

According to Zhuang *et al.* [1992] approximately 50% of the Fe in aerosols collected from the marine environment is Fe(II), while only a few percent of the Fe in aerosols collected over China is Fe(II). Zhuang *et al.* [1992] attributed the large fraction of Fe(II) in marine aerosol to multiple cycles of reductive dissolution of ferric oxides followed by oxidation and precipitation taking place during the long journey of these particles in the atmosphere. They also postulated that the redox cycle of Fe is related to that of S. Zhu *et al.* [1993], on the other hand, reported that Fe(II) makes up only 1% of the total Fe and 7.5% of the soluble Fe in marine aerosols. Zhu *et al.* [1993] conducted photolysis experiments with aerosol extracts and with dissolved Fe(III) in aerated acidic sodium chloride solutions both in the pres-

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ence and in the absence of oxalate (as an electron donor). They observed that within a short time, Fe(II) concentration rose from 0.1 micromole to 1.3 micromole (almost 30% of the total Fe) in aerosol extracts exposed to sunlight. The final concentration was attained within less than an hour and was maintained as long as the samples were irradiated. Once the irradiation ceased, the concentrations of Fe(II) in solution dropped. Based on their experiments with oxalate and dissolved Fe(III), *Zhu et al.* [1993] concluded that oxalate participates in the formation of Fe(II) in irradiated samples via electron transfer within the dissolved Fe-oxalato complexes; however, oxalate oxidation also produces hydrogen peroxide which oxidizes Fe(II) back to Fe(III). The oxidation of Fe(II) by hydrogen peroxide takes over in the dark, leading to the observed decrease in Fe(II) concentrations. *Zhu et al.* [1993] did not observe substantial Fe(II) formation in irradiated goethite suspension in the presence of oxalate.

In light of these considerations we now report on the occurrence of Fe(II) in stratus clouds collected in coastal and inland environments. In addition, we highlight important processes, chemical species, and critical environmental parameters that affect the dynamic redox cycle of Fe in the atmosphere.

#### EXPERIMENTAL METHODS

To reliably analyze the oxidation states of Fe and the partitioning of Fe between particulate matter and solution, we have carried out as many measurements as possible in the field. In addition, the low concentrations of Fe expected in some of the samples required that great care be exercised to minimize and monitor blanks during sample collection and handling.

##### Sample Collection

Fog and cloudwater samples were collected with acid-cleaned Caltech active strand cloudwater collectors (CASCC) [*Daube et al.*, 1987]. Concentrations of Fe and other constituents in blanks were determined before each collection. Of all constituents analyzed, Fe blanks were always the highest relative to Fe concentrations in the samples. Nevertheless, Fe blanks never exceeded 10% of the lowest Fe value measured in a sample. The collectors were placed in two elevated locations within the Los Angeles basin. These sites were (1) a coastal station on the Palos Verdes peninsula and (2) an inland station at Henninger Flats near Mount Wilson [*Munger*, 1989]. In addition, we collected samples in Bakersfield California and on board the RV *Cape Henlopen* (College of Marine Studies, University of Delaware) in Delaware Bay.

##### Sample-Handling Procedures

Fog and cloudwater samples were collected over 15 to 120 min intervals. The samples were weighed immediately after collection to determine their volume in order to calculate liquid water content (LWC) [*Munger*, 1989]. Light intensity was measured with a digital irradiance meter (spectral response from 380 to 750 nm, Biospherical Instruments QSP170B). An aliquot of each sample was removed to determine sample pH. A radiometer PHM80 standard pH meter with a GK2320C semimicrocombination electrode calibrated with pH 4 and 7 buffers was used to measure the pH

in the field. Aliquots of the collected water samples were processed in real time in the field (including filtration through 0.025-micrometer pore size Millipore filters). Fe(II), Fe(III), and other reactive species were determined by spectrophotometric techniques (see below). The complete determination of reactive species in atmospheric waters other than Fe(II) and Fe(III) is beyond the scope of this study. We focused instead on some of the most abundant inorganic and organic compounds in atmospheric water which are likely to exchange electrons with Fe [*Kawamura and Kaplan*, 1991; *Munger*, 1989]. In addition, we determined the total organic carbon (TOC) content as a measure of all the other numerous natural and anthropogenic organic compounds present in atmospheric water. The species that were studied include S(IV)/S(VI), ammonium/nitrate, monocarboxylic acids (e.g. formate, acetate), dicarboxylic acids (oxalate), and formaldehyde. In addition, we monitored changes in the concentration of Fe(II), Fe(III), and pH as a function of time, in samples stored both in darkness and exposed to daylight.

The aliquots of each sample removed for analysis of reactive species were stabilized in the field. Carboxylic acids (oxalate, acetate, formate) and ammonium were preserved by addition of chloroform [*Jacob et al.*, 1986; *Munger*, 1989]. Aliquots for TOC analysis were preserved by addition of mercury chloride solution. HCHO (formaldehyde) was reacted with ammonium-acetylacetone to form 3,5-dihydro-1,4-dihydrolutidine (DDL), which is stable for several weeks [*Smith and Erhardt*, 1975].

A buffered solution of *p*-hydroxyphenylacetic acid (POPA) and peroxidase was used to preserve peroxides by formation of a fluorescent dimer [*Kok et al.*, 1986]. Samples for analyses of total concentrations of Fe and major cations (e.g., sodium, potassium, magnesium, calcium) with a direct current plasma spectrometer (DCP) were acidified (0.1 M HCl) and stored at 4°C until analysis. The particulate matter collected on filters was brought back to the laboratory for analysis and was digested with concentrated HF and HNO<sub>3</sub>. For several samples, Fe<sub>dgs</sub>, the concentration of Fe in filtrate plus filter digest, was compared with Fe concentration in acidified (pH = 1) filtered (Fe<sub>fl</sub>) and unfiltered (Fe<sub>ac</sub>) aliquots (all analyzed by a DCP) and with Fe(II) plus Fe(III) concentration (determined spectrophotometrically) in unfiltered (Fe<sub>reac</sub>) and filtered aliquots.

##### Spectrophotometric Methods of Analyses

Spectrophotometric analyses were performed with (1) Shimadzu UV-1201 portable spectrophotometer with a 5-cm cell, (2) Shimadzu RF-540 recording spectrofluorophotometer, and (3) Shimadzu 500 DOC/TOC analyzer (100 ppb detection limit).

**Iron.** For Fe(II) determination we applied two methods: (1) the ferrozine (3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid, monosodium salt monohydrate) method used originally by *Stookey* [1970] and *Carter* [1971] and which is the most common method for Fe(II) determination in water and blood serum samples; (2) Di-2-pyridyl ketone benzoylhydrazone (DPKBH) was selected as a second chelating agent for Fe, because it is known to complex both Fe(II) and Fe(III) and because of its low solubility in water which enables a preconcentration step [*Garcia-Vargas et al.*, 1986; *Zatar et al.*, 1989; *Pehkonen et al.*, 1992].

Iron chelation by DPKBH both with and without a pre-concentration procedure was carried out in order to cover a wide range of Fe concentrations. A spectrophotometric detection limit of 4 nanomole for both Fe(III) and Fe(II) with a linear response from 4 nanomole up to 0.1 micromole was established for samples extracted with chloroform-water. DPKBH chelation without chloroform extraction showed a linear response from 0.1 micromole to 30 micromole. The molar extinction coefficients of the bis-Fe(II)-DPKBH and bis-Fe(III)-DPKBH complexes are given in Pehkonen *et al.* [1992]. Analytical interference studies on the possible changes in the oxidation state of Fe with S(IV), oxalate, and other potential electron donors have also been carried out [Pehkonen *et al.*, 1992].

*Spectrophotometric measurements of other compounds.* HCHO was measured after addition of iodine (light absorption at 415 nm) [Smith *et al.*, 1975]. S(IV) was analyzed by the "Bunte salt" method (light absorption at 412 nm) [Humphrey *et al.*, 1970]. Peroxide was measured by the fluorescence of the POPA dimer (peroxide excitation at 320 nm and emission at 406 nm) [Kok *et al.*, 1986]. This method is sensitive to both hydrogen peroxide and some organic peroxides.

#### Other Chemical Analyses

*Ion chromatography.* Chloride, nitrate, sulfate, acetate, formate, oxalate, and ammonium were measured in the laboratory using a Dionex BIO LC ion chromatograph with PAX-500 anion column and a NaOH eluent. Gradient elution was employed to enhance the separation of the weakly retained acids and shortening the retention of the unwanted carbonate peaks. One millimole NaOH solution was mixed with 200 millimole NaOH solution at different proportions to gradually increase concentration of NaOH and therefore to improve the elution of ions such as sulfate and oxalate.

*Atomic emission and absorption techniques.* Sodium, potassium, calcium, magnesium, and iron were analyzed with an ARL SpectroSpan VB direct current plasma (DCP) spectrometer. The lower linearity ranges of the instrument used were 2.6, 4.1, 1.3, 0.4, 0.9 micromole, respectively. The coefficients of variance (CV) of cation analysis by the DCP were, at most, 10%. Samples with low iron concentrations were analyzed with a 3030 Perkin Elmer graphite furnace atomic absorption spectrometer (detection limit, 0.02 micromole and a coefficient of variance, 20%).

#### Computational Determination of Chemical Speciation

With the aid of SURFEQL [Morel and Morgan, 1972; Faughnan, 1981; Jacob and Hoffmann, 1983] we used the equilibrium constant approach to solve a complex chemical equilibrium problem, which is defined by a system of mass action equations [Westall, 1987]. The thermodynamic data base consists of equilibrium constants for more than 1500 equilibria. This data base was verified and supplemented for the present calculation.

## RESULTS AND DISCUSSION

A wide range of concentrations of measured constituents were observed in the collected fog and cloudwater samples (Table 1). Inorganic anions (chloride, nitrate, and sulfate) and cations (ammonium, sodium, and proton) were the dominant species in cloudwater with their concentrations

approaching millimole values. The pH varied between 2.2 and 7.1. The concentration of soluble Fe(II) in cloudwater ranged from 0.1 to 5.3 micromole, while the concentration of Fe<sub>ac</sub> varied between 1.8 and 27 micromole (Table 1). The concentrations of peroxides, S(IV), formate, acetate, oxalate, and HCHO were found to be of the same order of magnitude as the Fe<sub>ac</sub> (Table 1).

To test the role of light in controlling the reduction of Fe(III), we monitored the production of Fe(II) as function of time both in the light (approximately  $5 \times 10^{16}$  quanta/cm<sup>2</sup> of sunlight) and in the dark immediately after the collection of cloudwater samples which contained appreciable quantities of S(IV) and organic compounds (Table 2). Fe(II) concentrations always increased faster in the presence of light than in the dark. Nevertheless, the observed coexistence of Fe(II) and hydrogen peroxide (which itself is a major oxidant of Fe(II) at the pH range of most of the cloudwater samples [Martin *et al.*, 1991]) in cloudwater samples that were collected in the dark both in California and in Delaware (Table 1) suggests a thermal reduction pathway of Fe(III). In addition, Fe(II) values in cloudwater samples collected during the night in Los Angeles were comparable to those found in samples collected long after sunrise (Figure 1a). It has been shown previously that thermal reduction of Fe(III) by organic compounds that are present in cloudwater (e.g., phenols, aldehydes but not acetate and formate) and by S(IV) is much slower and much less important than photoreduction [Cunningham *et al.*, 1985; Faust and Hoffmann, 1986]. Thus our measurements suggest that either thermal reduction is a viable complementary pathway for the in situ production of Fe(II) in the atmosphere (in contrast to laboratory experiments) or that both reduction and oxidation rates decrease during nighttime to the same extent, leading to unchanged steady state levels of Fe(II).

We found a strong linear correlation between the concentrations of Fe of both oxidation states (Fe(III), Fe(II)) and the concentrations of both oxidation states of S (S(IV), S(VI)) (Figures 1b and 1c). This type of correlation indicates that the relationship between Fe(II) and S(IV) is not determined solely by in situ redox chemistry but that their relationship might also be controlled by a common source of S and Fe. The measured values of S/Cl ratios suggest that most of the S in the cloudwater samples comes from nonmarine (most likely anthropogenic) sources. More study is needed to test the importance of Fe in controlling the oxidation of S(IV) in cloud and fog samples, as well as the possibility that the reversible formation of aldehyde-bisulfite adducts prevent S(IV) from complexing Fe in cloud and fog samples [Conklin and Hoffmann, 1988; Olsson and Hoffmann, 1989].

Among the organic compounds in cloudwater, we studied formaldehyde, formate, acetate, and oxalate as potential electron donors for the reduction of Fe(III) to Fe(II) [Munger, 1989; Kawamura and Kaplan, 1991]. The sum of formaldehyde concentration plus acetate plus formate in the cloudwater samples correlates strongly with TOC ( $R^2 = 0.984$ ) and comprises approximately 20% of the TOC (oxalate values were below detection limit in many of the samples). A plot of [Fe(II)] versus formate in the Los Angeles samples shows two distinctive trends (Figure 2a). The data points that are correlated along the line with a steeper slope (i.e., more Fe(II) per mole of formate) represent cloudwater samples that have higher total Fe (Fe<sub>ac</sub>) concentrations (Figure 2b) and, in general, higher ac-

TABLE 1. The Concentrations of Various Components Measured in Fog and Cloudwater Samples

No.	Site Location	Collection Date	Sample Description	Collection Time	Duration, min	Weight, g	LWC, g/m <sup>3</sup>	pH
1	Henninger	4/25/91	unfiltered	0215	120	NA	NA	3.1
2	Henninger	5/30/91	filtered collector 1	0130	45	100	0.11	NA
3	Henninger	5/30/91	filtered collector 3	0130	45	100	0.11	NA
4	Henninger	5/30/91	unfiltered collector 1	0130	45	100	0.11	NA
5	Henninger	5/30/91	unfiltered collector 3	0130	45	100	0.11	NA
6	Henninger	5/30/91	filter digest collector 3	0130	45	100	0.11	NA
7	Henninger	5/30/91	filtered collector 1	0215	45	100	0.11	2.5
8	Henninger	5/30/91	filtered collector 3	0215	45	100	0.11	2.5
9	Henninger	5/30/91	unfiltered collector 1	0215	45	100	0.11	2.5
10	Henninger	5/30/91	unfiltered collector 3	0215	45	100	0.11	2.5
11	Henninger	5/30/91	filter digest collector 3	0215	45	100	0.11	2.5
12	Henninger	5/30/91	filter digest collector 3	0215	45	100	0.11	2.5
13	Henninger	5/30/91	filtered collector 1	0300	45	100	0.11	2.8
14	Henninger	5/30/91	filtered collector 3	0300	45	100	0.11	2.8
15	Henninger	5/30/91	unfiltered collector 1	0300	45	100	0.11	2.8
16	Henninger	5/30/91	unfiltered collector 3	0300	45	100	0.11	2.8
17	Henninger	5/30/91	filtered collector 1	0345	75	220	0.14	2.8
18	Henninger	5/30/91	filtered collector 3	0345	75	220	0.14	2.8
19	Henninger	5/30/91	unfiltered collector 1	0345	75	220	0.14	2.8
20	Henninger	5/30/91	unfiltered collector 3	0345	75	220	0.14	2.8
21	Henninger	5/30/91	filter digest collector 3	0345	75	220	0.14	2.8
22	San Pedro	6/11/91	unfiltered	0750	20	30	0.07	4.2
23	San Pedro	6/11/91	unfiltered	0825	25	28	0.05	4.0
24	San Pedro	6/11/91	unfiltered	0900	25	61	0.11	3.8
25	San Pedro	6/11/91	unfiltered	0930	25	57	0.11	3.8
26	San Pedro	6/11/91	unfiltered	1000	30	48	0.08	3.5
27	San Pedro	6/11/91	unfiltered	1035	15	21	0.07	NA
28	Henninger	6/27/91	unfiltered	0845	35	65	0.09	3.9
29	Henninger	6/27/91	filtered	0845	35	65	0.09	3.9
30	Henninger	6/27/91	filter digest	0845	35	65	0.09	3.9
31	Henninger	6/27/91	filter digest	0845	35	65	0.09	3.9
32	Henninger	6/27/91	unfiltered	0920	30	25	0.04	3.7
33	San Pedro	7/10/91	unfiltered	1000	35	30	0.04	3.4
34	San Pedro	7/23/91	unfiltered	0855	25	95	0.18	3.2
35	San Pedro	7/23/91	unfiltered	0920	20	90	0.21	2.5
36	San Pedro	7/23/91	unfiltered	0950	15	54	0.17	2.2
37	San Pedro	7/23/91	unfiltered	1020	25	60	0.11	2.4
38	San Pedro	7/23/91	unfiltered	1050	25	30	0.06	2.8
39	San Pedro	7/23/91	unfiltered	1125	45	23	0.02	2.6
40	San Pedro	7/25/91	unfiltered	0830	35	60	0.08	3.2
41	San Pedro	7/25/91	filtered	0830	35	60	0.08	3.2
42	San Pedro	7/25/91	filter digest	0830	35	60	0.08	3.2
43	San Pedro	7/25/91	filter digest	0830	35	60	0.08	3.2
44	San Pedro	7/25/91	unfiltered	0905	50	65	0.06	2.6
45	San Pedro	7/25/91	filtered	0905	50	65	0.06	2.6
46	San Pedro	7/25/91	filter digest	0905	50	65	0.06	2.6
47	San Pedro	7/25/91	unfiltered	0955	40	33	0.04	3.4
48	Delaware	3/5/92	unfiltered	0515	30	15	0.02	NA
49	Delaware	3/5/92	unfiltered	0545	15	31	0.10	2.9
50	Delaware	3/5/92	unfiltered	0605	15	6	0.02	NA
51	Delaware	3/5/92	unfiltered	0705	115	91	0.04	3.8
52	San Pedro	6/5/92	unfiltered	1047	18	48	0.13	4.4
53	San Pedro	6/5/92	unfiltered	1105	30	30	0.05	4.3
54	San Pedro	6/5/92	unfiltered	1135	25	8	0.01	4.2
55	Bakersfield	1/27/93	unfiltered	1125	55	68	0.06	6.4
56	Bakersfield	1/28/93	unfiltered	1225	42	131	0.15	6.7
57	Bakersfield	1/28/93	unfiltered	0107	46	123	0.13	6.8
58	Bakersfield	1/28/93	unfiltered	0153	53	127	0.11	7.1
59	Bakersfield	1/28/93	unfiltered	0246	60	129	0.10	6.8

TABLE 1. (continued)

No.	Light q/(s cm <sup>2</sup> )	Temp. c	Fe(II)* (DPKBH)	Fe(III)* (DPKBH)	Fe(II)* (Ferrozine)	Fe (DCP)	Peroxide	Oxalate	HCHO	Formate	Acetate
1	dark	NA	13.1	5.0	NA	NA	12.0	BDL	3.6	55.4	BDL
2	dark	NA	NA	NA	NA	NA	4.2	BDL	41	56.3	19.3
3	dark	NA	NA	NA	NA	9.1	4.2	BDL	41	56.3	19.3
4	dark	NA	NA	NA	NA	16.9	4.2	BDL	41	56.3	19.3
5	dark	NA	NA	NA	NA	25.5	4.2	BDL	41	56.3	19.3
6	dark	11.0	NA	NA	NA	25.9	NA	NA	NA	NA	NA
7	dark	11.0	NA	NA	NA	NA	4.6	BDL	35	56.9	26.3
8	dark	11.0	NA	NA	NA	4.0	4.6	BDL	35	56.9	26.3
9	dark	11.0	4.9	6.7	NA	26.5	4.6	BDL	35	56.9	26.3
10	dark	11.0	2.9	6.1	NA	20.7	4.6	BDL	35	56.9	26.3
11	dark	11.0	NA	NA	NA	19.0	NA	NA	NA	NA	NA
12	dark	11.0	NA	NA	NA	17.6	NA	NA	NA	NA	NA
13	dark	10.5	NA	NA	NA	NA	5.2	BDL	48	46.2	BDL
14	dark	10.5	NA	NA	NA	NA	5.2	BDL	48	46.2	BDL
15	dark	10.5	4.1	3.3	NA	13.2	5.2	BDL	48	46.2	BDL
16	dark	10.5	3.8	4.1	NA	10.9	5.2	BDL	48	46.2	BDL
17	dark	10.5	NA	NA	NA	NA	3.5	BDL	47	54.6	11.4
18	dark	10.5	0.0	2.3	NA	2.2	3.5	BDL	47	54.6	11.4
19	dark	10.5	1.2	2.0	NA	4.3	3.5	BDL	47	54.6	11.4
20	dark	10.5	0.9	2.5	NA	6.7	3.5	BDL	47	54.6	11.4
21	dark	10.5	NA	NA	NA	23.7	NA	NA	NA	NA	NA
22	3.3E+16	NA	NA	NA	NA	NA	33.7	BDL	19.4	29.9	BDL
23	5.2E+16	NA	3.9	4.2	NA	4.5	48.1	BDL	16.8	43.4	BDL
24	5.4E+16	NA	1.4	1.2	NA	2.6	29.4	BDL	17.8	26.2	BDL
25	6.3E+16	NA	1.5	1.1	NA	2.3	53.4	BDL	17.9	30.1	BDL
26	7.6E+16	NA	2.0	1.5	NA	2.9	64.2	BDL	17.4	47.5	BDL
27	9.0E+16	NA	4.3	3.2	NA	3.3	78.6	BDL	19.7	51.3	BDL
28	1.0E+16	16.0	7.6	3.4	4.2	8.2	2.1	BDL	23	26.5	BDL
29	1.0E+16	16.0	NA	NA	NA	7.0	2.1	BDL	23	26.5	BDL
30	1.0E+16	16.0	NA	NA	NA	1.5	NA	NA	NA	NA	NA
31	1.0E+16	16.0	NA	NA	NA	1.5	NA	NA	NA	NA	NA
32	7.5E+16	16.0	7.7	2.4	5.3	9.7	1.5	BDL	25.6	28.6	BDL
33	6.0E+16	18.0	1.1	0.0	1.1	3.9	7.0	BDL	32.1	23.6	36.6
34	3.2E+16	15.0	7.9	4.1	3.8	9.5	3.6	BDL	12	28.1	24.9
35	3.7E+16	15.0	8.0	3.3	4.7	10.2	4.8	BDL	12.2	27.2	26.6
36	4.0E+16	15.0	9.9	NA	NA	9.0	4.8	BDL	11.7	29.6	32.0
37	5.0E+16	15.5	9.3	NA	NA	8.8	8.3	BDL	11.5	34.3	36.9
38	6.4E+16	16.2	11.1	NA	NA	12.2	9.6	5.7	12.3	42.6	47.6
39	9.5E+16	19.0	18.7	NA	NA	20.6	6.2	9.1	15.7	75.6	88.2
40	1.7E+16	14.5	1.7	1.2	0.5	2.0	24.3	7.7	8.62	22.7	17.4
41	1.7E+16	14.5	0.7	0.3	NA	1.4	24.3	7.7	8.62	22.7	17.4
42	1.7E+16	14.5	NA	NA	NA	4.4	NA	NA	NA	NA	NA
43	1.7E+16	14.5	NA	NA	NA	4.2	NA	NA	NA	NA	NA
44	3.0E+16	14.5	1.1	0.8	0.3	1.8	32.6	8.3	8.35	27.7	21.7
45	3.0E+16	14.5	0.4	0.1	NA	BDL	32.6	8.3	8.35	27.7	21.7
46	3.0E+16	14.5	NA	NA	NA	4.3	NA	NA	NA	NA	NA
47	4.0E+16	14.5	1.8	1.2	0.7	2.7	40.5	13.2	10.1	39.8	36.8
48	1.1E+15	NA	NA	NA	NA	4.2	NA	NA	NA	NA	NA
49	4.2E+14	NA	NA	NA	0.7	3.0	NA	16.8	NA	21.2	49.0
50	7.0E+13	NA	NA	NA	NA	NA	NA	13.5	NA	13.4	25.6
51	2.0E+13	NA	NA	NA	0.4	1.0	NA	8.6	NA	16.9	19.4
52	7.4E+16	14.0	0.6	0.6	0.6	0.9	NA	13.5	1.52	31.7	30.5
53	8.5E+16	14.0	1.5	1.2	1.1	2.0	NA	1.5	NA	14.3	10.7
54	1.0E+17	14.0	2.0	1.6	NA	NA	NA	5.3	NA	19.5	18.2
55	dark	10.0	NA	NA	0.1	5.9	0.0	8.5	NA	66.0	153.0
56	dark	10.0	NA	NA	0.3	5.4	1.1	4.0	NA	40.0	92.0
57	dark	10.0	NA	NA	0.2	2.7	1.4	5.0	NA	45.0	109.0
58	dark	10.0	NA	NA	0.3	4.9	2.4	4.0	NA	38.0	119.0
59	dark	10.0	NA	NA	0.2	2.8	5.4	4.0	NA	61.0	123.0

TABLE 1. (continued)

No.	TOC, mg/l	S(TV)	Sulfate	Cl	Nitrate	Ammonium	Na	K	Ca	Mg
1	NA	NA	376	2299	2563	1400	960	49	38	NA
2	NA	NA	631	947	3342	1500	NA	NA	NA	NA
3	NA	NA	631	947	3342	1500	481	20	65	60
4	NA	NA	631	947	3342	1500	343	17	45	45
5	NA	NA	631	947	3342	1500	493	25	63	64
6	NA	NA	NA	NA	NA	NA	19	16	5	14
7	NA	NA	320	589	1639	1300	NA	NA	NA	NA
8	NA	NA	320	589	1639	1300	552	20	58	65
9	NA	NA	320	589	1639	1300	627	32	64	78
10	NA	NA	320	589	1639	1300	567	25	54	69
11	NA	NA	NA	NA	NA	NA	BDL	11	6	8
12	NA	NA	NA	NA	NA	NA	BDL	12	5	6
13	NA	NA	382	595	1989	1400	NA	NA	NA	NA
14	NA	NA	382	595	1989	1400	NA	NA	NA	NA
15	NA	NA	382	595	1989	1400	345	16	27	42
16	NA	NA	382	595	1989	1400	307	14	26	41
17	NA	NA	313	539	1777	1100	NA	NA	NA	NA
18	NA	NA	313	539	1777	1100	213	9	16	26
19	NA	NA	313	539	1777	1100	224	10	18	28
20	NA	NA	313	539	1777	1100	222	9	17	30
21	NA	NA	NA	NA	NA	NA	19	16	6	15
22	19.5	17.8	397	444	757	NA	NA	NA	NA	NA
23	11.3	2.4	185	206	426	NA	16	4	5	6
24	11.4	0.0	206	636	323	NA	22	4	7	7
25	8.4	0.0	193	702	359	NA	31	4	7	7
26	11.1	1.9	239	729	461	NA	60	7	17	12
27	16.1	0.9	318	931	602	NA	106	10	30	19
28	14.0	1.9	64	2320	392	630	199	10	24	27
29	NA	1.9	64	2320	392	630	193	9	22	26
30	NA	NA	NA	NA	NA	NA	BDL	1	2	BDL
31	NA	NA	NA	NA	NA	NA	BDL	1	2	BDL
32	NA	2.4	61	2700	679	700	352	17	41	46
33	15.0	7.7	364	118	572	880	31	8	29	8
34	10.4	17.0	411	163	839	730	232	12	46	35
35	10.8	15.0	394	168	869	690	223	13	59	38
36	13.5	13.0	503	179	1040	790	250	12	69	43
37	14.8	12.7	644	238	1180	1000	337	16	85	55
38	NA	15.3	903	315	1550	1200	441	16	160	74
39	NA	22.1	1400	470	2480	NA	721	39	260	133
40	7.1	7.1	147	56	284	440	29	6	13	6
41	7.1	7.1	147	56	284	440	28	6	13	5
42	NA	NA	NA	NA	NA	NA	BDL	4	5	BDL
43	NA	NA	NA	NA	NA	NA	BDL	4	5	BDL
44	7.4	5.8	167	62	304	560	20	6	BDL	4
45	7.4	5.8	167	62	304	560	18	5	BDL	4
46	NA	NA	NA	NA	NA	NA	BDL	4	5	BDL
47	12.3	4.2	264	95	515	1500	26	9	22	9
48	NA	NA	NA	NA	NA	NA	91	25	79	70
49	NA	NA	527	299	552	NA	43	15	43	41
50	NA	NA	526	239	514	NA	NA	NA	NA	NA
51	NA	NA	319	115	310	NA	13	8	29	17
52	NA	2.5	72	106	84	NA	12	3	4	9
53	NA	NA	111	175	134	NA	31	9	14	25
54	NA	NA	236	345	299	NA	NA	NA	NA	NA
55	NA	NA	318	27	1840	NA	12	4	34	7
56	NA	NA	145	17	987	NA	6	6	19	5
57	NA	NA	131	18	793	NA	3	4	10	2
58	NA	NA	118	13	638	NA	4	4	13	4
59	NA	NA	198	18	1190	NA	4	4	10	2

Concentrations of all components are in micromolar units, except where indicated. Charge is omitted from all components except for Fe and S. LWC, liquid water content. DCP, direct current plasma. BDL, below detection limit. NA, not measured or not applicable. Read 3.3E+16 as  $3.3 \times 10^{16}$ .

\* Fe for DPKBH analysis was fixed in the field [Garcia-Vargas *et al.*, 1986; Zatar *et al.*, 1989], and the measurements were carried out in the laboratory. All the Fe-ferrozine measurements were carried out in the field.

Table 2: Changes of Fe(II) Concentrations in Cloudwater Samples Stored in Daylight and in the Dark as a Function of Time

Sample	Fe(II), $\mu\text{M}$	Time Lapsed, min	Dark/light	$\Delta\text{Fe(II)}/\Delta t$ , $\text{nM/s}^*$
San Pedro1	1.43	0	light	-
San Pedro1	3.04	30	light	0.90
San Pedro1	4.18	105	dark	0.25
San Pedro1	5.14	165	dark	0.27
San Pedro2	9.80	0	light	-
San Pedro2	12.05	~10	light	-
San Pedro2	12.34	~20	dark	-
San Pedro2	12.23	~30	dark	-
San Pedro3	13.05	0	light	-
San Pedro3	14.81	~10	light	-
San Pedro3	14.66	~20	dark	-

\* Change in [Fe(II)] and time lapsed since the last measurement.

etate/formate ratios (~ 1:1) than the data obtained from samples falling on the line with a lower slope (acetate/formate ~ 0.5). Anthropogenic continental air masses appear to have higher acetate/formate ratios than air masses originating in remote environments [Keene and Galloway, 1984; Talbot et al., 1988; Gunz and Hoffmann, 1990]. Therefore the relationship between Fe and formate appears to be determined primarily by their common source region, although redox reactions cannot be ruled out. Samples correlated along the line with a steeper slope in Figure 2a are indicative of air masses of anthropogenic origin, while those correlated along the line with a lower slope appear to be cleaner air masses. In contrast, it seems that redox reactions, rather than a common source, control the relationship between Fe and acetate. This is suggested by the fact that in the Los Angeles samples the correlation between acetate and Fe(II) (Figure 2c) is much better than the correlation between acetate and  $\text{Fe}_{\text{ac}}$  (Figure 2d) and between Fe(II) and formate. Acetate is formed either by the oxidation of aldehydes as catalyzed by Fe(III)/Fe(II) or it is depleted by direct electron transfer to Fe(III) species; or both processes may take place simultaneously. The Fe-catalyzed oxidation of aldehydes to produce carboxylic acids might provide an important source of these acids to the troposphere [Keene and Galloway, 1986].

The relationship between Fe and oxalate is different from the observed linear relationships between Fe(II) and both formate and acetate (Figure 3a). Although we have analyzed relatively few cloudwater samples with measurable Fe(II) and oxalate concentrations, it appears that there is no correlation between their concentrations (Table 1, Figure 3a). Therefore it is suggested that Fe and oxalate do not have common sources and that oxalate has no net effect on the formation of Fe(II). On the other hand, the oxalate (but neither formate nor acetate) concentrations in cloudwater samples show a positive correlation with peroxide (Figure 3a). These observations suggests that Fe may have had a primary source of emission to the atmosphere, while oxalate had a secondary source (photochemical production with peroxide) in the atmosphere [Zuo and Hoigné, 1992].

Results from our ongoing laboratory investigation on the photoreduction of aerated suspensions of goethite, hematite, amorphous Fe hydroxide, and ambient aerosol particles are

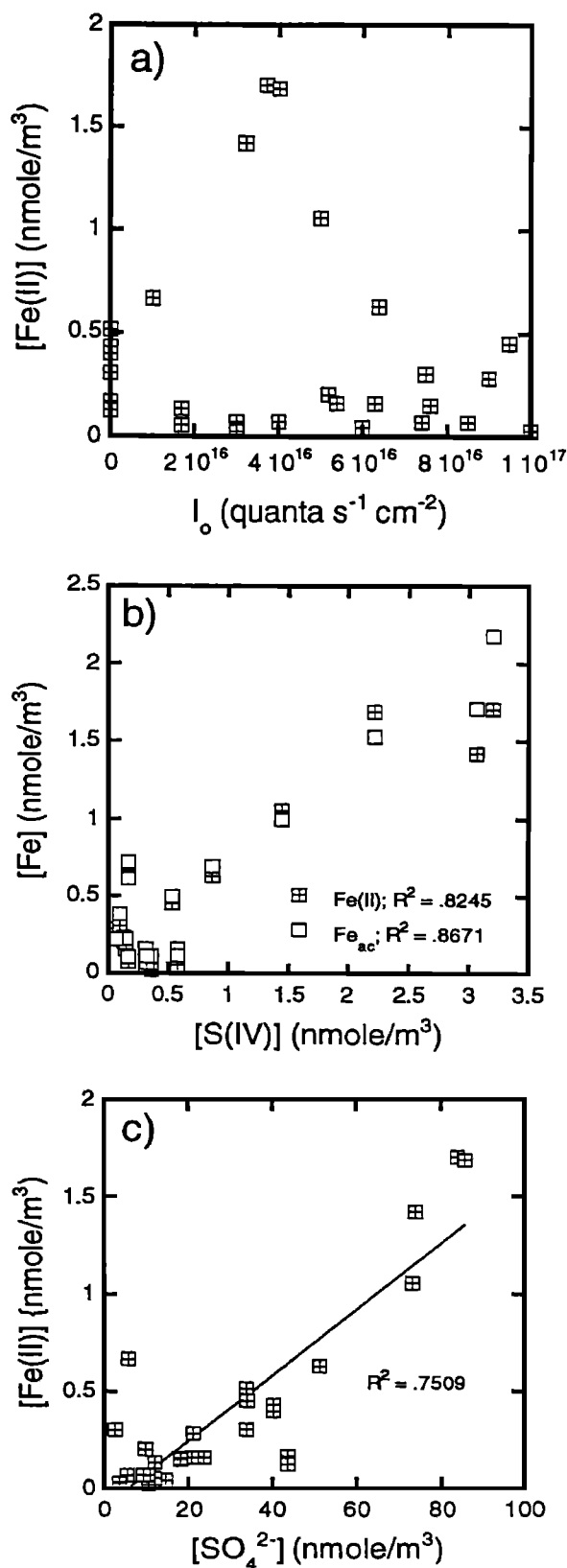


Fig. 1. Correlation between different parameters in cloudwater samples collected in Los Angeles. Concentrations were obtained by multiplying the measured concentration in a sample with the liquid water content of the cloud in order to obtain concentration per unit volume of air: (a) Fe(II) versus light, (b) S(IV) versus both Fe(II) and  $\text{Fe}_{\text{ac}}$  ( $\text{Fe(II)} + \text{Fe(III)}$ ) concentration in unfiltered acidified sample, and (c) Fe(II) versus sulfate.

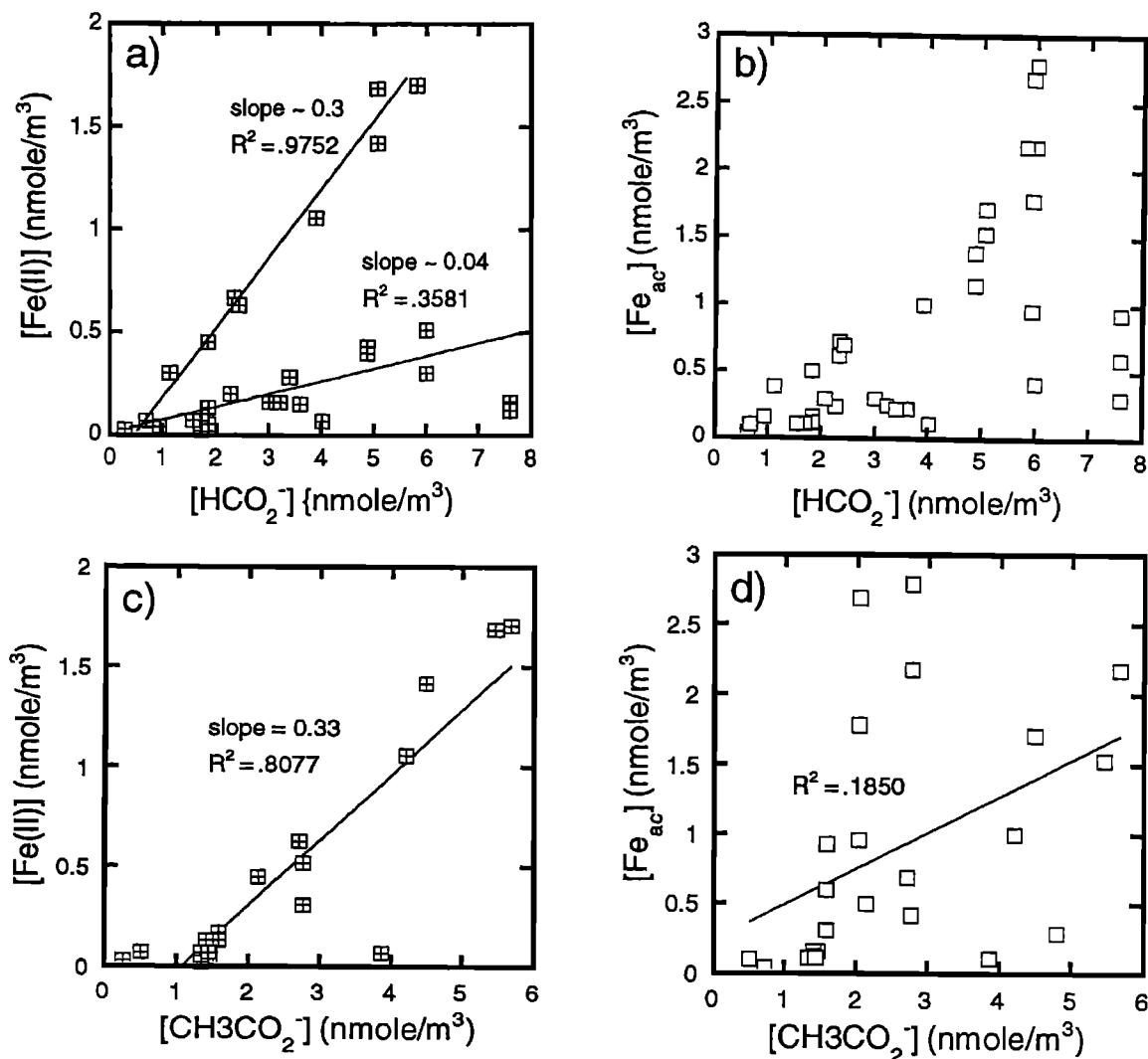


Fig. 2. The correlation between Fe and monocarboxylic acids in cloudwater samples collected in Los Angeles: (a) formate versus Fe(II), (b) formate versus Fe<sub>ac</sub>, (c) acetate versus Fe(II), and (d) acetate versus Fe<sub>ac</sub>.

consistent with the results obtained in the field. In these laboratory experiments, no Fe(II) was detected in irradiated particle suspensions in the presence of oxalate, while at the same time large amounts of hydrogen peroxide were produced [Pehkonen *et al.*, 1993]. When the same experiments were performed in the presence of formate and acetate, a significant fraction of Fe(III) was reduced to Fe(II) without the concomitant production of hydrogen peroxide. Our observations are consistent with those of Wehrli *et al.* [1989] and Siffert and Sultzberger [1991]; they noted that Fe(II) is not produced in irradiated hematite suspensions in the presence of oxalate under oxic conditions. In these cases, adsorbed oxalate appears to be oxidized by dioxygen adsorbed on the surface of the Fe(III) oxyhydroxides to form hydrogen peroxide and carbon dioxide. The hydrogen peroxide in turn oxidizes Fe(II) released from the particle surface before it diffuses to the bulk solution. However, under anoxic conditions appreciable concentrations of Fe(II) were detected [Wehrli *et al.*, 1989; Siffert and Sultzberger, 1991]. Based on these observations, there appears to be a unique photochemical behavior for oxalate in the presence of Fe(III) oxyhydroxide surfaces.

To assist in the interpretation of the aqueous phase speciation of Fe, we have predicted, via thermodynamic calculation, the soluble Fe-containing species in the cloudwater samples. For these calculations we used the measured concentrations of components (including Fe(III) and Fe(II)) observed in an 1/2-hour period in a stratus cloud event that was 5 hours in duration (sample 47, Table 1; similar results were obtained with all the samples which contained appreciable concentrations of oxalate). The major Fe species were as follows: Fe(H<sub>2</sub>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>-</sup>, Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3-</sup>, Fe(H<sub>2</sub>O)<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>+</sup>, and Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> (Figures 3b and 3c). Under the above assumptions (not considering any other organic ligands that might be present in solution) the three ferric iron species constitute more than 95% of the total dissolved Fe(III). This computation demonstrates the strong chemical interaction between oxalate and Fe(III). However, most of the cloudwater samples contained low levels of oxalate (<1-2 micromole). Similar calculations done on these samples show that hydrolysis is the main reaction which controls the speciation of Fe(III). Among the Fe(III)-oxalate species, Fe(H<sub>2</sub>O)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>-</sup> which is photochemically very reactive [Vincze and Papp, 1987] makes up



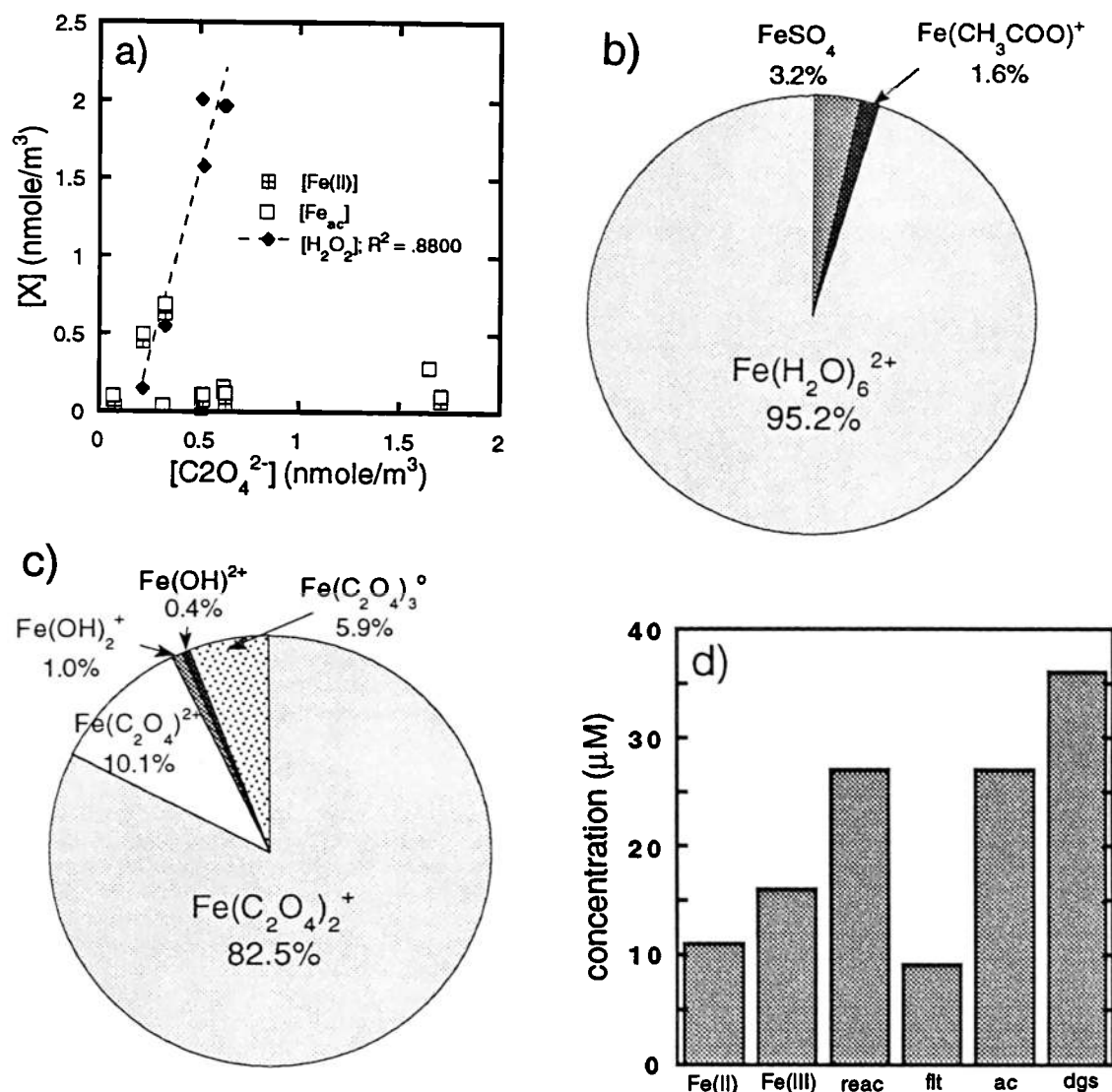
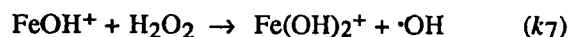
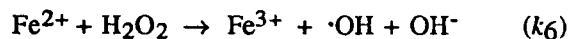
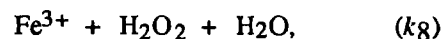
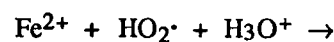


Fig. 3. (a) oxalate vs. Fe(II), Fe<sub>ac</sub>, and peroxides, (b) speciation calculation of Fe(II), and (c) speciation calculation of Fe(III). Both (a) and (b) were done on sample 47, Table 1. The measured concentrations are (micromole): [Fe(III)] = 1.2; [Fe(II)] = 1.8; [sulfate] = 260; [(acetate+formate)] = 77; [oxalate] = 13; [hydrogen peroxide] = 41; [formaldehyde] = 10; pH = 3.4; (d) measured "dissolved" and particulate Fe in cloudwater sample. Fe(II), Fe(III) were measured spectrophotometrically in unfiltered sample aliquot, reac = Fe<sub>reac</sub> the sum of the previous columns, flt = Fe<sub>flt</sub>, (both oxidation states) measured by direct current plasma (DCP) in a filtered aliquot of the sample (0.025 micrometer Millipore filter); ac = Fe<sub>ac</sub>, (both oxidation states) measured by DCP in an aliquot of the sample that was acidified to pH = 1 and then filtered; dgs = Fe<sub>dgs</sub>, sum of Fe<sub>flt</sub> and Fe (both oxidation states) measured by DCP in particles collected on the filter after they were digested with concentrated HF and HNO<sub>3</sub>.

85% of the Fe(III) concentration. Oxalate reacts with hexaquo Fe(III) to form an inner-sphere complex which then undergoes a ligand-to-metal electron transfer (i.e., to produce Fe(II)C<sub>2</sub>O<sub>4</sub><sup>-</sup> [Zuo and Hoigné, 1992]). Fe(II), which is present mostly as Fe(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>, is likely to be oxidized via one of the following pathways: (1) oxidation by dissolved oxygen (reasonably fast at pH above 5 [Stumm and Morgan, 1981; Millero et al., 1987]), (2) peroxides, and (3) ozone [Hoigné et al., 1985]. Of the three pathways it seems that in cloudwater samples of pH below 4.5 (i.e., all the samples except those collected in Bakersfield) Fe(II) reaction with peroxides to form OH radicals is the predominant pathway:



The species-dependent reactivity of Fe(II) toward hydrogen peroxide is seen clearly by comparison of  $k_6$  (76 M<sup>-1</sup> s<sup>-1</sup>) [Walling, 1975] and  $k_7$  (1.9 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>) [Moffett and Zika, 1987]. Fe(II) also reacts with hydroperoxyl radical to form hydrogen peroxide,



and with peroxymonosulfate [Sato *et al.*, 1984] to yield Fe(III) and S(V) as  $\text{SO}_4^{2-}$ :



The samples collected in Bakersfield have the lowest content of Fe(II) although their  $\text{Fe}_{\text{ac}}$  content is similar to other samples and they have relatively high concentrations of formate and acetate (Table 1). It is interesting to note that the Bakersfield samples have pH values above 6.4. At this pH range, oxidation of Fe(II) by oxygen (Haber-Weiss mechanism) is a rapid process operating in addition to the oxidation of Fe(II) by peroxides (which itself is faster at high pH) to suppress the concentration of Fe(II) in solution. Another explanation for the low Fe(II) content of the Bakersfield samples is discussed in the next paragraph.

The similarity between the field results and the laboratory experiments on particle suspensions implies that photoassisted heterogeneous reactions are taking place within cloudwater droplets. The presence of surface-bound Fe is indicated by the results shown in Figure 3d. In this case, the concentration of reactive Fe ( $\text{Fe}_{\text{reac}} = [\text{Fe(II)}] + [\text{Fe(III)}]$ ) was always found to be larger than filtered Fe,  $\text{Fe}_{\text{flt}}$  (i.e.,  $[\text{Fe(II)} + \text{Fe(III)}] < 0.025$  micrometer), and was either smaller or equal to  $[\text{Fe}_{\text{ac}}]$ .  $[\text{Fe}_{\text{ac}}]$  is the sum of  $[\text{Fe(II)}]$  and  $[\text{Fe(III)}]$  measured as total Fe in an unfiltered sample at pH = 1. This latter value includes Fe that is dissolved, Fe released to solution from particle surfaces and Fe released to solution from the dissolution of oxyhydroxides at pH 1.  $\text{Fe}_{\text{ac}}$  values in the samples were always lower than total Fe values ( $\text{Fe}_{\text{dgs}}$ , the concentration of Fe in filtrate plus filter digest; i.e., digested with concentrated HF and  $\text{HNO}_3$ ), suggesting that only a fraction of the total Fe in aerosols is likely to be released to cloudwater either by proton promoted or by reductive dissolution.  $\text{Fe}_{\text{ac}}/\text{Fe}_{\text{dgs}}$  ratios varied largely from one sample to another, suggesting that the fraction of reactive Fe in aerosol samples was sensitive to the nature of the Fe-containing phases, which in turn were determined by the sources of Fe to the atmosphere. Such observations might explain the discrepancies between different authors regarding the fraction of reactive Fe in atmospheric aerosols [Zhuang *et al.*, 1992; Zhu *et al.*, 1993]. Based on selective leaching experiments (R. Siefert, California Institute of Technology, personal communication, 1992) it appears that approximately 5-10% of the total Fe in aerosols collected in Los Angeles was associated with natural and anthropogenic organic compounds via surface coatings and intergrowth. These organic compounds could serve as electron donors to reduce particulate Fe(III). Furthermore, the low Fe(II) content of the high pH samples from Bakersfield in spite of high formate and acetate concentrations is in accordance with the well-documented observations that both organic ligands and bisulfite are not likely to be adsorbed to Fe-rich phases at high pH, and therefore heterogeneous electron transfer reactions are less likely to take place [Stumm and Morgan, 1981; Faust *et al.*, 1989].

#### CONCLUSIONS

We suggest that the redox cycle of Fe in the near-shore continental troposphere involves both dissolved and aerosol surface species. Only a fraction of the total Fe measured in

atmospheric aerosols is likely to participate in these redox reactions, and this fraction varies greatly from one sample to another. Photoreduction of Fe(III) in fog and cloudwater samples appears to be more significant than thermal reduction, although Fe(II) was also detected in the dark. Fe(III) reduction is determined primarily by oxidizable organic compounds, which undergo thermal and photoassisted oxidation by Fe(III) to yield carboxylic acids. The strong correlation observed between Fe(II) and organic matter, in the face of much weaker correlation between total Fe and organic matter, suggests chemical interdependency between Fe and some organic compounds (e.g., acetate) in fog and cloudwater samples. In addition, Fe(III)-organic compound reactions may provide an important source of carboxylic acids in the troposphere.

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