



THE CLOUDWATER CHEMISTRY OF IRON AND COPPER AT GREAT DUN FELL, U.K.

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Abstract—The role of iron and copper in the transformation of photooxidants (HO_2/O_2^-) and pollutants in clouds was examined at a rural site (Great Dun Fell, U.K.). The observed concentrations of dissolved iron (60–1600 nM) and copper (4.2–31 nM) were lower than those previously reported at other locations. Measurement of the oxidation state of dissolved iron provided insight into the rates and mechanisms of cloudwater transformation reactions. Whenever the iron-containing aerosols were nucleated for more than several minutes prior to collection, measured iron oxidation states agreed with predictions based upon known rate constants for iron redox reactions. During daytime, the reduction of dissolved Fe(III) by HO_2/O_2^- and Cu(I) or the photoreduction of Fe(III)-oxalato complexes resulted in the establishment of a steady state, with respect to iron oxidation states, in which more than 50% of the dissolved iron was present as Fe(II). At night, Fe(II) was slowly oxidized by H_2O_2 and O_3 . © 1997 Elsevier Science Ltd.

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1. INTRODUCTION

Based upon the results of laboratory studies of aqueous-phase chemical reactions, numerous researchers have hypothesized that transition metals could be important to the transformation of sulfur dioxide, ozone and organic pollutants in cloud droplets (Hoffman and Jacob, 1984; Graedel *et al.*, 1986; Martin *et al.*, 1990; Warneck, 1991; Zuo and Hoigné, 1992; Hoigné *et al.*, 1993; Erel *et al.*, 1993; Sedlak and Hoigné, 1994; Matthijsen *et al.*, 1994). Dissolved iron compounds are probably the most important of the transition metal species, because they are present at concentrations that are at least an order of magnitude higher than those of the other metals and they rapidly react with many of the oxidants and reductants in atmospheric waters. Copper compounds also can be important to transformation reactions, because they react at much faster rates with hydroperoxyl radical (HO_2) and superoxide radical (O_2^-) than the other

species present in cloud droplets (Hoigné *et al.*, 1993; Sedlak and Hoigné, 1993).

The reactivity of dissolved iron compounds towards different photooxidants and pollutants depends upon the oxidation state and speciation of the metal (see Table 1). In its reduced forms (Fe^{2+} and FeOH^+), iron reacts with oxidants such as H_2O_2 , O_3 and HO_2/O_2^- . When present in its uncomplexed, oxidized forms (FeOH^{2+} and Fe^{3+}), iron reacts with reductants such as O_2^- and Cu(I). Complexes of Fe(III) with organic and inorganic ligands are much less reactive with reductants than uncomplexed forms (Sedlak and Hoigné, 1994; Voelker and Sedlak, 1995); however, certain Fe(III) complexes (e.g., Fe(III)-oxalato complexes) are very sensitive to sunlight and can undergo photochemical reactions that result in the reduction of iron and the production of HO_2/O_2^- (Zuo and Hoigné, 1992). In the absence of sunlight, Fe(III) complexes with S(IV) (i.e., HSO_3^- and SO_3^{2-}) dissociate after an electron has been transferred to S(IV) from Fe(III) (Conklin and Hoffmann, 1988; Kraft and van Eldik, 1989; Bal Reddy and van Eldik, 1992). The sulfur radical produced by this reaction then initiates the catalytic oxidation of aqueous SO_2 ($\text{S}[\text{IV}]$). The oxidation state of iron affects the rate of formation of

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Table 1. Important reactions of dissolved iron in cloud droplets

Reaction	Rate constant ^a	Reference
<i>Fe(II) reactions:</i>		
(1) $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH}^\bullet + \text{OH}^-$	$1.9 \times 10^1 \text{ M}^{-1} \text{ s}^{-1}$	Hardwick (1957)
(2) $\text{Fe}^{2+} + \text{O}_3\text{-H}^+ \rightarrow \text{Fe(III)} + \text{OH}^\bullet + \text{O}_2$	$5.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Logager <i>et al.</i> (1992)
(3a) $\text{Fe}^{2+} + \text{HO}_2\text{-H}^+ \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$	$8.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$	Rush and Bielski (1985)
(3b) $\text{Fe}^{2+} + \text{O}_2^- \text{-} 2\text{H}^+ \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$	$7.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Rush and Bielski (1985)
<i>Fe(III) reactions:</i>		
(4) $\text{Fe(III)}^b + \text{O}_2^- \rightarrow \text{Fe(II)} + \text{O}_2$	$1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Rush and Bielski (1985)
(5) $\text{Fe(OH)}^{2+} + \text{Cu(I)} \rightarrow \text{Fe}^{2+} + \text{Cu}^{2+} + \text{OH}^-$	$2.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Sedlak and Hoigné (1993)
(6) $\text{Fe(III)} + n(\text{C}_2\text{O}_4)^{2-} \leftrightarrow \text{Fe(III)}(\text{C}_2\text{O}_4)_n^{(3-2n)}$	See reference	Zuo and Hoigné (1992)
(7) $\text{Fe(III)}(\text{C}_2\text{O}_4)_n^{(3-2n)} - h\nu \rightarrow \text{Fe}^{2+} + 2\text{CO}_2 + n - 1(\text{C}_2\text{O}_4)^{2-} + \text{O}_2^-$	See reference	Zuo and Hoigné (1992)
(8) $\text{Fe(III)}^b + \text{S(IV)}^c - \text{O}_2 \rightarrow \text{Fe(II)} + \text{S(VI)}$	See reference	Sedlak and Hoigné (1994)

Notes:

^a Rate constants corrected to 5°C using measured activation energies where available or an assumed value of 12.5 kJ mol⁻¹.

^b At least two different forms of Fe(III) (i.e., Fe^{3+} , FeOH^{2+}) undergo this reaction. For simplicity, OH^- is not explicitly included in this equation.

^c Two forms of S(IV) (i.e. HSO_3^- and SO_3^{2-}) undergo this reaction. See Conklin and Hoffmann (1988), Kraft and van Eldik (1989), Bal Reddy and van Eldik (1992) and Sedlak and Hoigné (1994) for discussions of the mechanisms and rates of these reactions.

the Fe(III)–S(IV) complex, and the simultaneous reduction of dissolved Fe(III) by photochemical reactions has been demonstrated to inhibit this S(IV) transformation reaction (Sedlak and Hoigné, 1994; Faust and Allen, 1994).

In a cloud droplet that contains a mixture of oxidants, reductants and metal-ion-chelating compounds, the relative concentrations of Fe(II) and Fe(III) are determined by the rates of the simultaneously occurring oxidation, reduction and complexation reactions. Thus, during daytime, when HO_2 concentrations in the interstitial air are high, the rapid reactions of Fe(III) with reductants such as O_2^- (the basic form of HO_2) and Cu(I) (which is formed by the reaction of Cu(II) with O_2^-) and direct photochemical reactions result in more rapid iron reduction, and Fe(II) predominates. At night, when the photochemically-driven Fe(III)-reducing reactions cease, Fe(II) is converted back into Fe(III) by reactions with hydrogen peroxide and ozone. The effect of reactions of uncomplexed S(IV) (i.e., the aqueous S[IV] that is not complexed by aldehydes) and sulfur radicals (e.g., SO_3^\bullet , $\text{SO}_3^{\bullet-}$) on iron redox chemistry is not fully understood, but laboratory experiments performed in the absence of light and photooxidants indicate that, in the presence of S(IV), the ratio of dissolved Fe(II) to Fe(III) reaches a steady state, in which less than half of the iron is present as Fe(II), after several minutes of reaction (Kotronarou and Sigg, 1993; Sedlak and Hoigné, 1994).

Measurements of iron oxidation states in cloud- and fog-water samples have demonstrated that the relative concentrations of Fe(II) and Fe(III) can vary considerably between cloud or fog events and that the presence of sunlight and/or reactive species can only partially explain the distribution of iron between the two oxidation states (Behra and Sigg, 1990;

Kotronarou and Sigg, 1993; Erel *et al.*, 1993). For example, in coastal stratus clouds (Erel *et al.*, 1993), the balance between Fe(II) and Fe(III) should be controlled by sunlight intensity and the concentrations of organic ligands which form photoreactive complexes with Fe(III); however, the percentage of iron present as Fe(II) is not always directly correlated with these two factors, and the oxidation state of iron often appears to be related to the origin of the air masses. One possible explanation for this finding is the influence of meteorological factors on the amount of time that the aerosol was exposed to aqueous-phase reactions prior to sample collection: if the sampled cloud droplets had not been nucleated for a sufficient period of time for the redox reactions to reach a steady state with respect to iron oxidation states, the relative concentrations of Fe(II) and Fe(III) could be more representative of those in dry or deliquescent aerosols than those in aged, sunlit cloud droplets.

In this study, we report our measurements of iron speciation during a series of cloud events at Great Dun Fell, U.K. (GDF). The field campaign (described in detail in other papers in this issue) also included extensive characterization of the meteorology, microphysics and chemistry of the clouds during their passage to and from the sampling site. Consideration of iron speciation data in conjunction with other chemical and meteorological data has allowed us to test kinetic models of the reactions of iron and copper with photooxidants and pollutants in clouds.

2. MATERIALS AND METHODS

Reagents were purchased from Aldrich at the highest grade possible and were used without further purification. The methanol used for elution of the

ferrozine cartridges was reagent grade (Aldrich). Suprapure nitric acid (Merck), used to acidify samples for atomic absorption analysis, was further purified in a quartz distillation apparatus before it was used.

Cloudwater was sampled at the summit of GDF (GDF Summit) (see Colville *et al.* (1997) for a description of the sampling sites) using an activated string collector (Jacob *et al.*, 1985) which was oriented into the prevailing wind direction. This device collects cloud droplets by pulling air with a small fan through a row of Teflon strings oriented at a 45° angle to the ground. The droplets impact on the strings and flow into a collection bottle at a rate of between 50 and 200 ml/h. All parts that came into contact with the cloudwater samples were made of Teflon or were coated with fluorinated ethylene propylene (FEP) (Liosaplast AG, St. Margrethen, Switzerland). Cloudwater was collected in 125 ml or 250 ml polypropylene bottles, which were shielded from sunlight with aluminum foil.

Between events, cloudwater collector parts were cleaned at a nearby laboratory. The parts were first washed with soap and water, and rinsed with tap water followed by three rinses with deionized water. After this initial cleaning procedure, the parts were soaked in 0.1 N HCl for 30 min. The parts were then rinsed three times with deionized water followed by two rinses with Milli-Q water. Finally, the parts were placed in plastic bags and transported to GDF Summit, where they were attached to the collector immediately prior to sampling.

The 10 ml bottles used for the storage of samples to be analyzed by atomic absorption spectroscopy were more rigorously cleaned because the potential for contamination is greater in acidified samples stored for extended periods. The bottles were cleaned using a procedure consisting of a series of washes with soapy water, acetone and different strength solutions of HCl and HNO₃ (Tramontano *et al.*, 1987). The bottles were dried under a filtered air laminar flow hood and sealed in individual plastic bags.

To monitor the effectiveness of the decontamination procedures, wash blank samples were collected before each event. The wash blanks were obtained by passing approximately 100 ml of Milli-Q water (pH adjusted to 4 using HCl) through the collector immediately before it was placed in the field. Total metal concentrations in these samples were always lower than those measured in the cloudwater samples (mean [Fe] = 50 nM, mean [Cu] = 5 nM) and [Fe(II)] was always below detection limits.

Samples were collected at time intervals of 30 or 60 min or whenever at least 75 ml of cloudwater was present. The sample bottles were removed from the collector, gently shaken to suspend any particulate material and split for the different analyses.

Immediately after sample collection, a 50 ml aliquot was analyzed for Fe(II) using a modified version of the solid-phase extraction method developed for seawater by King *et al.* (1991). In our procedure,

the ionic strength of the sample was increased by the addition of 5 ml of 5 M NaCl to the 50 ml samples prior to analysis. The sample was then passed through a Sep Pak C-18 cartridge (Waters) which had been loaded with ferrozine. Dissolved Fe(II) formed complexes with the ferrozine that were retained on the cartridge while Fe(III) and other polar solutes were eluted with the cloudwater. After the sample was passed through the cartridge, the sample bottle and syringe were rinsed with a 5 ml aliquot of 0.1 M NaCl buffered with 5 mM NaHCO₃, and the rinse also was passed through the cartridge. The cartridges were stored in the dark at ambient temperatures (usually 2–5°C) for approximately 1–5 h prior to analysis. Control experiments indicated that the Fe(II)-ferrozine complex was stable for at least 24 h under these conditions. The Fe(II)-ferrozine complex was eluted using 10 ml of methanol and were analyzed at 550 nm in a 2 or 5 cm spectrophotometric cell.

Blank absorption by the cloudwater samples and by the ferrozine reagent were subtracted from the measured absorbance. One or two cloudwater blanks were collected during each event by extracting samples prepared in the manner described above using cartridges which had not been loaded with ferrozine. Ferrozine reagent blanks were prepared by extracting ferrozine-loaded cartridges with methanol to which 50 ml of distilled water had been passed. The detection limit for Fe(II) in the cloudwater samples (5 nM) corresponds to an absorption of approximately 0.003 at $\lambda = 550$ nm in a 5 cm spectrophotometric cell.

Samples also were analyzed for total and filterable iron and copper. A 10 ml aliquot of cloudwater was passed through a 0.45 μ m polysulfone Acrodisc syringe filter (Gelman Scientific). The concentrations of iron and copper measured in the filtrate are referred to as dissolved throughout this paper, despite the fact that this is an operational definition and some colloid-associated Fe or Cu may have passed through the filters. For approximately 10% of the samples, a 5 ml aliquot also was passed through a 0.45 μ m filter followed by a 0.02 μ m Anotop membrane filter (Whatman). Control experiments, using pH 4 solutions containing dissolved Fe(III) and Cu(II) (50 and 20 nM, respectively), indicated that losses of dissolved Fe and Cu during filtration through the 0.45 μ m filters were negligible. Cu also was not retained by the 0.02 μ m filter, but a substantial fraction of the dissolved Fe adsorbed onto the 0.02 μ m filter. Therefore, only Cu was measured in the 0.02 μ m filtered samples.

Filtered and unfiltered samples were acidified with concentrated nitric acid (50 μ l per 10 ml of cloudwater) within 24 h of collection. The samples were analyzed in triplicate at EAWAG for iron and copper using graphite furnace atomic absorption spectroscopy (Varian model AA-875). Iron was quantified by standard addition and copper was quantified using a five-point standard curve. The detection limits for iron and copper were 20 and 1 nM, respectively.

The pH of the bulk cloudwater samples was measured within 4 h of sample collection using a combined pH electrode (Metrohm) calibrated using standard buffers.

Descriptions of the site location, meteorology, microphysics as well as the techniques used to measure liquid water content, concentrations of gaseous SO₂, H₂O₂, and O₃, formaldehyde and aqueous-phase oxalate are described in other papers included in this issue.

3. RESULTS AND DISCUSSION

The concentrations of Fe (total, 0.45 µm filtered and Fe[II]) and Cu (total, 0.45 µm and 0.02 µm filtered) were measured in a total of 92 different samples collected during five different cloud events (Table 2). The concentrations of oxalate in cloudwater sampled at a site approximately 30 m from our collector are reported in Seyffer *et al.* (1997).

3.1. Total Fe and Cu

The measured total concentrations of Fe and Cu in the cloudwater samples varied considerably (range of concentrations: 700–24,000 nM for [Fe]_{tot} and 4–110 nM for [Cu]_{tot}), but the average concentrations of [Fe]_{tot} and [Cu]_{tot} (see Table 3) were not significantly different among events. The relatively large variation in total Fe and total Cu concentrations was attributable to variations in the liquid water content (LWC) of the clouds. When the concentrations of Fe and Cu were expressed in terms of the concentration per volume of air, by multiplying the bulk cloudwater concentration by the LWC (which varied between 96 and 830 mg m⁻³), the variability in the data decreased substantially.

The means of the total Fe concentrations, when expressed per volume of air (Table 3), were not significantly different among the five different events. In contrast, the means of the total Cu concentrations, when expressed per unit volume of air, varied considerably among cloud events. The higher concentrations of Cu observed during two of the cloud events appeared to have been related to a source of Cu located south of the site: during the events in which total Cu concentrations were elevated (Events 1 and 3) the air arrived at the site from a southerly direction and during the other three events the air arrived from the northeasterly direction.

One possible source of the elevated concentrations of Cu on the days with southerly air flow was automobile traffic. Traffic-related aerosols are enriched in Cu, relative to continental background aerosols, soil-derived aerosols and other anthropogenic aerosols (Nriagu, 1979; Cass and McRae, 1986; Wiersma and Davidson, 1986). Furthermore, automobile traffic has been estimated to be responsible for approximately 65% of the Cu emissions in the United Kingdom (Berdowski *et al.*, 1994). Nearby sources of the traffic-

related Cu emissions include the M-6 motorway and the local roads near Appleby-in-Westmoreland, which are located approximately 10–15 km southeast of the sampling site. Very few roads are located north-east of the site until the city of Newcastle, which is more than 60 km away, and aerosols arriving at GDF from the northeast can therefore be considered as more representative of background conditions than aerosols arriving from the south. Of course, the locations of other anthropogenic Cu-sources was probably also somewhat correlated with the locations of major roads.

3.2. Dissolved Fe and Cu

Dissolved iron and copper comprised between 1 and 40% and between 20 and 100% of the total metal concentrations, respectively (see Table 2). At these concentrations ([Fe]_{dissolved} = 60–1600 nM and [Cu]_{dissolved} = 4.2–31 nM) reactions with Fe(II/III) and Cu(I/II) greatly enhance the rate at which HO₂/O₂⁻ is transformed into H₂O₂, in cloud droplets (Hoigné *et al.*, 1993; Matthijsen *et al.*, 1994) but only have a relatively small effect on the removal of O₃ in the cloud (Matthijsen *et al.*, 1994). In the pH range of 3 to 5, the Fe-catalyzed oxidation of S(IV) by O₂ could result in the removal of between approximately 0.1 and 5% of the SO₂ in the cloud within an hour (Martin *et al.*, 1992), but at the measured concentrations of dissolved copper, we predict that the reaction is partially inhibited during daytime through the reduction of Fe(III) by Cu(I) (Sedlak and Hoigné, 1994).

The observed solubility of iron decreased slightly with increasing pH. The higher solubility of Fe(III) agreed with solubility data for iron oxides, but the lack of a squared relationship between dissolved iron and [H⁺] (as would be expected for the dissolution of an Fe(III) oxide) suggests the presence of several different forms of solid iron phases (Hansen *et al.*, 1981; Dedik *et al.*, 1992) which each had a different solubility or colloidal iron oxyhydroxides capable of passing through the 0.45 µm filter. A relationship also was not observed between iron solubility and sunlight intensity or the concentration of organic acids. These observations are consistent with previous studies of the photodissolution of iron oxides (Sieffert and Sulzberger, 1991), which indicate that heterogeneous photoreduction is relatively slow at the low concentrations of organic ligands observed at GDF. The slow rates of heterogeneous photodissolution of certain Fe(III)-oxides observed in the laboratory could, however, be important to the dissolution of iron during the long-range transport of aerosols (Zhuang *et al.*, 1990, 1992) or in polluted coastal stratus clouds (Erel *et al.*, 1993).

The variability in the percentage of copper that passed through the 0.45 µm filter was very small (the average and 95% confidence interval for copper solubility was 65 ± 4%) and could not be correlated with any of the data on cloudwater composition. This finding is consistent with theoretical predictions,

Table 2. Concentrations of iron and copper measured at Great Dun Fell

Event	Date	Fe (nanomolar)					Cu (nanomolar)			
		Start	Stop	pH	Fe(II)	0.45 µm filter	Total	0.02 µm filter	0.45 µm filter	Total
1	22/4/93	1335	1400	NA	30	200	3000	NA	33	51
		1400	1430	NA	BDL	NA	2200	NA	NA	39
		1430	1500	NA	BDL	160	3700	20	23	42
		1500	1530	NA	BDL	NA	2700	NA	NA	35
		1530	1600	NA	BDL	90	3500	NA	17	42
		1600	1630	NA	BDL	NA	4400	NA	NA	50
		1630	1700	NA	BDL	110	4600	NA	28	60
		1700	1730	NA	BDL	NA	4000	NA	NA	62
		1730	1800	NA	BDL	160,190	2700	NA	31,30	44
		1800	1830	NA	BDL	NA	2100	NA	NA	42
		1830	1900	NA	BDL	120	2100	33	23	32
		1900	1930	NA	BDL	NA	1600,1600	NA	NA	30,33
		1930	2000	NA	20	170	1600	NA	21	25
		2000	2030	NA	110	NA	3000	NA	NA	34
		2030	2100	NA	80	300	2600	NA	21	28
		2100	2130	NA	130	NA	1600	NA	NA	33
		2130	2200	NA	120	320	1900	NA	25	31
2	5/5/93	1540	1600	NA	120	1600	5700	NA	21	23
		1600	1630	3.7	110	940	3900	19	21	29
		1630	1700	4.0	50	250	NA	NA	13	22
		1700	1730	NA	30	NA	4900	NA	NA	25
		1730	1800	NA	20	320	3900	NA	15	22
		1800	1830	5.3	20	210	7400	NA	5.3	13
		1830	1900	5.8	10	80	3500	3.8	3.1	9
		1900	1930	5.6	20	50	3700,3300	NA	2.3	11,7.4
		1930	2000	5.6	20	50	1600	NA	1.3	3.7
		2000	2030	4.3	30	120,140	2500	3.1	4.6,6.4	6.9
		2030	2100	3.8	60	240	2000	NA	6.6	10
		2100	2130	NA	NA	810	5400	NA	21	27
		2130	2200	NA	70	1200	11000	NA	33	31
		2200	2300	NA	170	1000	13000	NA	22	24
		2300	2400	4.1	110	560	6000	9.5	12	13
	6/5/93	2400	100	4.2	80	230	3500	NA	6.3	8.3
		100	200	4.3	50	180	3200	NA	4.2	7.3
3	8/5/93	1700	1730	3.5	50	NA	1600	NA	NA	98
		2330	25	3.1	540	1200	6300	41	85	110
	9/5/93	25	100	3.3	50	220	3000,2300	NA	19	22,33
		100	130	3.3	80	280	1500	NA	16	26
		130	200	3.1	140	440	4000	29	18	36
		200	230	3.1	170	570	2300	NA	17	38
		230	300	3.3	10	220,330	1300	NA	16	34
		300	330	3.1	50	170	1600	NA	14,12	20
		330	400	3.2	60	240	1800	NA	15	22
		400	430	3.1	60	250	2400	NA	NA	NA
		430	500	3.2	20	230	1300	14	11	16
		500	530	3.3	BDL	180	1800	NA	15	15
		530	600	3.1	70	280	2000	NA	15	23
		600	630	3.3	10	180	1300	NA	13	15
		630	700	3.5	BDL	130	600	NA	9	NA
		700	730	3.7	BDL	90	800	10	8.8	9.4
		730	800	3.9	BDL	90	1100	NA	7.5	9.3
4	9/5/93	2008	2035	4.2	40	100	700	NA	14	20
		2035	2100	4.2	BDL	100	1400	11	8.1	14
		2100	2130	4.2	BDL	100	1700	NA	8.7	15
		2130	2200	4.2	BDL	70	1700	NA	7.7	13
		2200	2230	4.2	BDL	80	1000	NA	7.6	9.2
		2230	2300	4.2	BDL	80	2200	NA	7.3	12,11
		2300	2330	4.1	BDL	440	1100	6	6.6	8.9
		2330	2400	4.2	BDL	60	1000	NA	5.9	7.8
	10/5/93	2400	100	4.2	BDL	90	900	NA	7.5	8.5
		100	200	4.2	BDL	90	1200,1400	NA	4.8	8.7
		200	300	4.2	10	70	1900	6	5.3	10
		300	400	4.2	BDL	110	1500	NA	4.9	11
		400	500	4.2	30	100	2600	NA	4.9	8.4

Table 2. (continued)

Event	Date	Fe (nanomolar)					Cu (nanomolar)			
		Start	Stop	pH	Fe(II)	0.45 μ m filter	Total	0.02 μ m filter	0.45 μ m filter	Total
5	11/5/93	500	530	4.4	10	80	1500	NA	5.3	9
		530	600	4.4	10	70	2600	4.3	5.6	9
		600	630	4.4	BDL	60	1300	NA	4.2	6.6
		630	700	4.4	30	80	2700	NA	6.7	10
		700	730	4.3	20	160	1400	NA	5.6	9
		730	800	4.3	40	130	1900	NA	8	13,12
		800	830	4.3	40	100	2200	NA	7.5	9.4
		830	900	4.2	50	80,80	1600	7.4	6.8	13
		900	930	4.0	100	160	1200	NA	14	17
		930	1000	4.0	100	100	1600	NA	10	16
		1000	1025	4.1	80	120	2000	NA	8.6	8.7
		1025	1055	4.2	BDL	100	2400	NA	4.7	7.5
		1055	1125	4.2	40	90	2000	NA	4.9	8.6
	12/5/93	1905	2000	4.0	370	NA	11000	NA	NA	85
		2000	2130	4.3	290	NA	15000	NA	NA	71
		2130	2220	4.3	250	310	7000	NA	12	63
		2220	2300	4.2	290	NA	7200	NA	NA	33
		2300	2400	4.3	160	520	8500	NA	12	29
		2400	100	4.3	BDL	330	7800	10	7.2	25
		100	200	4.6	BDL	NA	7000	NA	NA	29
		200	300	4.6	90	690,570	17000	NA	12,16	36
		300	400	4.4	BDL	360	12000	24	15	31
		400	500	4.1	40	NA	4500	NA	17	16
		500	530	4.0	60	460	2400	NA	12	20
		530	600	4.0	110	NA	2500	NA	NA	20
		600	645	3.9	600	NA	21000,24000	NA	NA	45
		645	730	4.0	550	NA	4800	NA	NA	37
		730	815	4.3	390	890	5600	NA	23	41
		815	900	4.2	250	330	24000	NA	16	33
		900	945	4.4	90	NA	NA	NA	NA	NA

Notes:

BDL = below detection limit (see Materials and Methods section for detection limits).

NA = not available.

Results of duplicate analyses of samples are separated by commas.

Table 3. Average total Fe and total Cu concentrations at Great Dun Fell

Event	Fe		Cu	
	nM	ng m ^{-3a}	nM	ng m ^{-3a}
1	2800	33	40	0.54 ^b
2	5000	32	17	0.13
3	2000	19	33	0.30 ^b
4	1700	21	11	0.15
5	9900	35	38	0.15
Total	3900	27	26	0.24

Notes:

^aConcentration of metal per unit volume air determined by multiplying aqueous-phase concentration by mean liquid water content during the sampling period.^bMean concentrations were statistically higher than means concentrations for other events, as determined by least significant difference (LSD) analysis ($p = 0.05$). Means for total Fe and total Cu concentrations were not statistically different for other data.

which indicate that most of the copper in atmospheric aerosols should be dissolved in cloudwater, irrespective of pH or other conditions (Weschler *et al.*, 1986). The high solubility of copper also agreed with

previous measurements in atmospheric waters (Hofmann *et al.*, 1991).

3.3. Fe(II)

The percentage of the total dissolved iron present as Fe(II) varied from 0 to 100% during the five cloud events. In most of the samples, Fe(II) accounted for less than half of the dissolved Fe, but during certain periods its concentration increased. To determine the factors that led to the observed changes in the oxidation state of dissolved iron it was important to consider the meteorological and chemical processes that occurred during each cloud event. In particular, it was necessary to compare estimates of the length of time that the aerosol was nucleated in the cloud with estimates of the time required for the iron redox reactions to reach steady state.

During events in which the aerosol had been nucleated for sufficient time for steady state to be achieved, it should be possible to predict the distribution of iron between the Fe(II) and Fe(III) forms using data on pollutant and photooxidant concentrations and published rate constants for iron redox reactions. The results of a simple calculation for the redox

Table 4. Calculated pseudo-first-order rate constants (k') for the oxidation or reduction of iron in cloudwater at Great Dun Fell in the absence of S(IV) or oxalate

Reactant	Assumed conc. ^b (nM)	$k'^a (\times 10^{-3} \text{ s}^{-1})$	
		Fe(II) oxidation	Fe(III) reduction
<i>Daytime only:</i>			
HO ₂ /O ₂ ⁻	2	3.3	33
Cu(I)	0.75		16
hν			0.63
OH•	1.0×10^{-4}	0.033	
<i>Day-or nighttime:</i>			
H ₂ O ₂	3.7×10^4	0.70	
O ₃	1.4	0.80	
O ₂	4.0×10^5	$< 1 \times 10^{-6}$	

Notes:

^aRate constants adjusted to 5°C as described in Table 1. References are included in Table 1 except for Fe(III) reduction by light (h ν): $6.3 \times 10^{-4} \text{ s}^{-1}$ (Faust and Hoigné, 1990); and Fe(II) oxidation by OH[•]: 3.3×10^8 (Christensen and Sehested, 1981) and O₂: $< 1 \times 10^{-8} \text{ m}^{-1} \text{ s}^{-1}$ (Stumm and Morgan, 1981).

^bBased upon typical conditions expected during a morning in the late spring and typical concentrations measured during this sampling campaign (i.e., pH = 4; [Fe]_{dissolved} = 200 nM; [Cu]_{dissolved} = 15 nM). Aqueous-phase concentrations of HO₂/O₂⁻ and OH[•] are based upon calculations of Chameides and Davis (1982) for a zenith angle of 60°. Aqueous-phase concentrations of oxidants are calculated from measured gas-phase concentrations (H₂O₂ = 0.1 ppbv; O₃ = 40 ppbv) and Henry's law coefficients (Jacob, 1986), adjusted to 5°C.

reactions of dissolved iron, under the conditions typically encountered at GDF during morning in the late spring, indicate that, in the absence of oxalate and S(IV), the sums of the pseudo-first-order rate constants (k') for oxidation and reduction of uncomplexed iron equal $4.8 \times 10^{-3} \text{ s}^{-1}$ and $50 \times 10^{-3} \text{ s}^{-1}$, respectively (Table 4). These values can be used to calculate the % Fe(II) after steady state has been achieved:

$$\% \text{Fe(II)} = 100 \frac{[\text{Fe(II)}]}{[\text{Fe(II)}] + [\text{Fe(III)}]}$$

$$= 100 \frac{k'_{\text{Fe(III)reduction}}}{k'_{\text{Fe(III)reduction}} + k'_{\text{Fe(II)oxidation}}} = 91\%. \quad (1)$$

The presence of oxalate results in the formation of photosensitive Fe(III)-oxalate complexes which provide another pathway for Fe(II) formation. Equilibrium calculations for the conditions encountered in the cloud droplets indicate that Fe(III)-oxalato complexes should be the dominant form of dissolved Fe(III) during many of the cloud events; however, it is necessary to consider the fact that Fe(III) can undergo reduction before it forms a complex with a ligand (Sedlak and Hoigné, 1993). When Fe(II) is oxidized in the presence of photooxidants, oxalate and copper, however, it is likely that the reactions of both uncomplexed and oxalate-complexed Fe(III) are important to iron redox chemistry.

The amount of time required for the oxidation state of Fe to reach steady state depends upon the initial distribution of iron between the oxidation states, but it will reach 90% of its steady-state value in approxi-

mately 1 min under the conditions listed in Table 4. At night, the rates of Fe(III) reduction are negligible, and Fe(II) will be oxidized by H₂O₂ and O₃ with pseudo-first-order rate constants of approximately $0.7 \times 10^{-3} \text{ s}^{-1}$ and $0.8 \times 10^{-3} \text{ s}^{-1}$, respectively. Under these conditions, 90% of the Fe(II) will be converted back into Fe(III) in approximately 45 min. (In making this calculation it is necessary to consider that OH[•] formed from the reaction of Fe[II] and H₂O₂ reacts with formaldehyde and formic acid to produce HO₂/O₂⁻, which then reacts with Fe[II/III] and Cu[I/II].) When uncomplexed S(IV) also is present, the formation of Fe(III)-S(IV) complexes result in additional sunlight-independent iron redox reactions.

In the following sections, we utilize chemical and meteorological data from each cloud event to evaluate the factors that controlled the iron oxidation states in the cloud droplets. In some cases (events 1 and 2), the aerosols were not nucleated long enough for iron redox reactions to achieve a steady-state balance between iron oxidation states, and the observed speciation of iron was influenced by the nature of the iron-containing aerosol particles that entered the cloud. However, during several cloud events (events 3–5) the droplets were nucleated for as long as an hour, and the effect of aqueous-phase redox reactions on the oxidation state of iron in cloudwater was observed.

3.4. Event 1: 22 April 1993

During this event, the concentration of Fe(II) was at or near the detection limit until approximately 2000, when Fe(II) increased to approximately 40% of the total dissolved iron (Fig. 1). The event began around

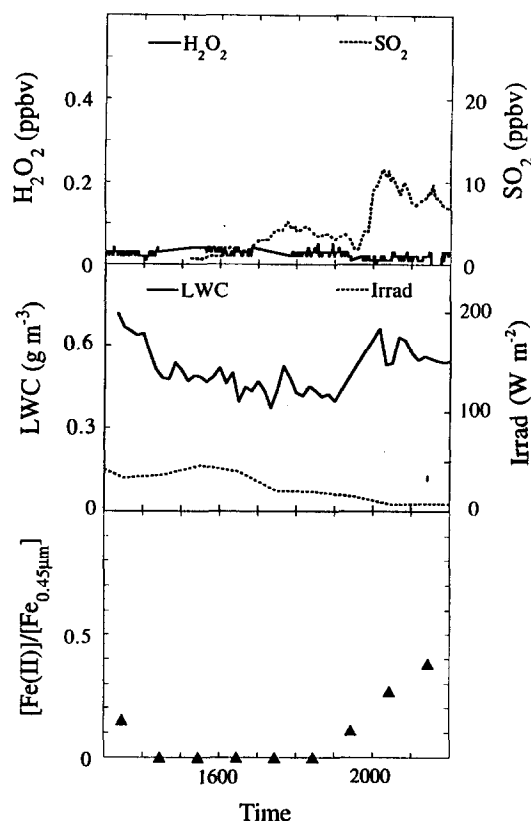


Fig. 1. Concentrations of gaseous-phase H_2O_2 and SO_2 (top), liquid water content (LWC) and solar irradiance (middle) and % Fe(II) ($[\text{Fe(II)}]/[\text{Fe}]_{0.45\mu\text{m}}$) (bottom) measured at Great Dun Fell during event 1.

1300, when air arriving from the southwest formed a small orographic cloud at GDF Summit. An air mass that contained elevated concentrations of SO_2 (up to 12 ppbv) arrived at the site around 2000 and the height of the cloud decreased as the more polluted air mass arrived. Low concentrations of H_2O_2 , (approximately 0.02 ppbv) and moderately low concentrations of O_3 (30 ppbv) were detected in the gaseous phase. The pH of the cloudwater was between 4.0 and 5.5 until 2000, when it decreased to approximately 3.3. Oxalate was observed at $1.6\text{ }\mu\text{M}$ in the only sample collected.

From 1400–2000 the base of the cloud was only approximately 150–200 m below GDF Summit (which corresponds to a linear in-cloud travel distance within the cloud of approximately 1 km from the base of the cloud to the sampling site), and at the measured wind speeds ($10\text{--}15\text{ m s}^{-1}$) the droplet should have been nucleated for 1 to 2 min prior to collection. Under the conditions observed during this time period ($\text{pH} = 5$; $[\text{SO}_2]_{\text{g}} = 3\text{ ppbv}$; temperature = 5°C) the predicted aqueous-phase concentration of S(IV) ($[\text{S(IV)}]_{\text{aq, predicted}}$) is approximately $15\text{ }\mu\text{M}$. (Estimated concentration used throughout this discussion are provided to illustrate trends in the concentrations of solutes in the cloudwater. These estimates ignore disequilibrium between the droplet and the gaseous

phase or differences in composition of droplets of different sizes.) Between 2000 and 2400, when the base of the cloud sunk by an additional 200 m (which corresponds to a linear in-cloud travel distance of approximately 2 km), the amount of time that the aerosols were nucleated increases to approximately 2 to 4 min. In this more acidic cloudwater ($\text{pH} = 3.3$; $[\text{SO}_2]_{\text{g}} = 10\text{ ppbv}$; temperature = 5°C) $[\text{S(IV)}]_{\text{aq, predicted}}$ is approximately $1\text{ }\mu\text{M}$.

Before 2000, when relatively high concentrations of S(IV) were present, the oxidation state of dissolved iron should have been strongly influenced by reactions with uncomplexed S(IV) and sulfur radicals. In laboratory experiments on the Fe-catalyzed oxidation of S(IV) by O_2 , performed at similar S(IV) concentrations and pH values, more than 70% of the added Fe(II) ($[\text{Fe(II)}]_{\text{initial}} = 1\text{ }\mu\text{M}$) was converted into Fe(III) in less than 20 min in the absence of HO_2/O_2^- (Sedlak and Hoigné, 1994). In the presence of HO_2/O_2^- fluxes similar to, or slightly higher than those expected in sunlit cloud droplets, and dissolved copper and S(IV) concentrations in the range of those observed during this event, approximately 40% of the Fe was converted into Fe(II). Although some of the dissolved iron should have been present as Fe(II) during the sunlit period before 2000, it was impossible to detect, because during the time interval between sample collection and analysis (as much as approximately 30 min) the cloudwater was not exposed to HO_2/O_2^- and sulfur radicals would have oxidized any Fe(II).

After 2000, when more acidic cloudwater resulted in significantly lower concentrations of S(IV) in the cloud droplets, the effect of S(IV) reactions on iron oxidation states was less important. Under these conditions, the presence of Fe(II) could have been attributable to photochemical reactions, or reactions with photoproducted HO_2/O_2^- that occurred as the aerosols passed in and out of clouds during the preceding sunlit period. The oxidation of Fe(II) by H_2O_2 ($[\text{H}_2\text{O}_2]_{\text{aq, predicted}} < 1\text{ }\mu\text{M}$) or O_3 ($[\text{O}_3]_{\text{aq, predicted}} = 1\text{ nM}$) would have resulted in the oxidation of less than 10% of the Fe(II) during the period in which the aerosol was in the cloud or, for H_2O_2 , during the period after collection.

3.5. Event 2: 5/6 May 1993

On 5/6 May, Fe(II) accounted for between 5 and 40% of the total dissolved iron (Fig. 2). The air arrived from the northeast during the entire event, and a cap cloud formed at GDF Summit at around 1500. The concentration of gaseous-phase H_2O_2 was below detection limits at all times and SO_2 concentrations were at or near detection limits except during the period between 2000 and 2100, when a maximum concentration of approximately 3 ppbv was observed. O_3 was present at concentrations of approximately 40 ppbv. The pH of the cloudwater ranged from approximately 3.7–5.6. Oxalate concentrations ranged from approximately 1–3 μM .

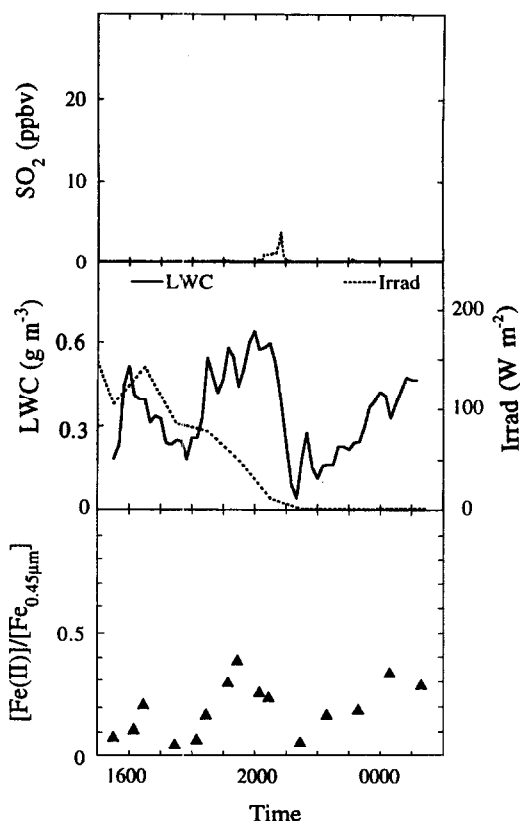


Fig. 2. Concentrations of gaseous-phase SO_2 (top), liquid water content (LWC) and solar irradiance (middle) and % Fe(II) ($[\text{Fe(II)}]/[\text{Fe}]_{0.45\mu\text{m}}$) (bottom) measured at Great Dun Fell during event 2. Gaseous-phase H_2O was below the detection limit at all times.

Meteorological conditions varied considerably during this event, and the amount of time that the droplets were nucleated prior to collection was influenced by the air flow patterns. During periods in which entrainment of aerosols into the cloud did not occur, the droplet lifetime was estimated to range from 20 to 60 min. Considering this relatively long period and the low concentrations of SO_2 and H_2O_2 in the gaseous phase, Fe(III) should have been reduced through reactions with HO_2/O_2^- and Cu(I) or the photolysis of Fe(III)-oxalato complexes. After sunset, Fe(II) should have been oxidized by O_3 (Sedlak and Hoigné, 1993). These reactions should have resulted in the conversion of approximately 90% of the dissolved Fe into the Fe(II) form during daytime, and, during nighttime, the oxidation of Fe(II) by O_3 should have lowered the percentage of Fe(II) to between approximately 20–50% by the time the sample was collected. The data do not always agree with these predictions, because the unstable meteorological conditions resulted in a great deal of variability in the amount of time the droplets were nucleated prior to collection.

3.6. Event 3: 8/9 May 1993

Fe(II) accounted for approximately 30% of the total dissolved iron in approximately half of the sam-

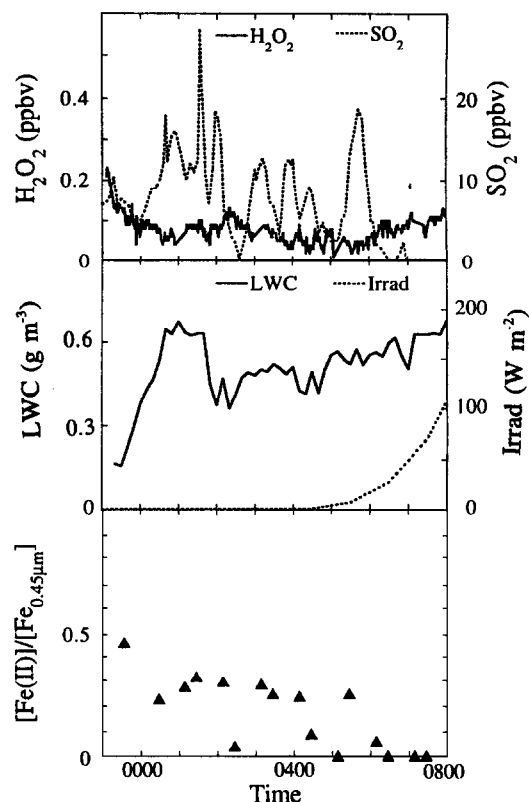


Fig. 3. Concentrations of gaseous-phase H_2O_2 and SO_2 (top), liquid water content (LWC) and solar irradiance (middle) and % Fe(II) ($[\text{Fe(II)}]/[\text{Fe}]_{0.45\mu\text{m}}$) (bottom) measured at Great Dun Fell during event 3.

ples, and less than 10% of the dissolved iron in the remaining samples collected during event 3 (Fig. 3). This event began when air arriving from the southwest formed a small cap cloud at GDF Summit at approximately 2330. During the night, the wind shifted towards the north or northeast, but the LWC and wind speed remained approximately constant during the entire event. The air mass contained between approximately 0.05 and 0.10 ppbv of H_2O_2 , 0 and 25 ppbv of SO_2 and approximately 40 ppbv of O_3 . The cloudwater pH ranged from approximately 3.1–4.0. Oxalate concentrations ranged from approximately 2–4 μM .

Based upon the observed extent of cloud cover in the area northeast of the site, we estimate that the droplet should have been nucleated for between approximately 20 to 60 min prior to collection. Under these conditions ($\text{pH} = 3.3$; temperature = 3°C ; $[\text{SO}_2]_{\text{g}} = 10\text{--}20$ ppbv; $[\text{H}_2\text{O}_2]_{\text{g}} = 0.05\text{--}0.10$ ppbv) $[\text{S(IV)}]_{\text{aq, predicted}} = 1\text{--}2\text{ }\mu\text{M}$ and $[\text{H}_2\text{O}_2]_{\text{aq, predicted}} = 20\text{--}40\text{ }\mu\text{M}$. (For a discussion of S(IV) oxidation reactions during this event see Fuzzi *et al.*, this issue.) At these low S(IV) concentrations, Fe(II) should have been oxidized by H_2O_2 and O_3 . Considering both the period in which the droplets were nucleated and the time interval between sample collection and analysis for H_2O_2 , and only the in-cloud period for O_3 (which,

unlike H_2O_2 , is rapidly depleted by aqueous-phase reactions), we predict that at least 50% of the Fe(II) initially present on the aerosol should have been oxidized during its passage through the cloud and during the time between sample collection and analysis. The presence of Fe(II) in these samples suggests that most of the soluble iron in the nucleated aerosols was originally Fe(II) .

3.7. Event 4: 9/10 May 1993

During this event, Fe(II) was below detection limits in almost all of the samples collected at night and increased to approximately 65% of the dissolved iron after sunrise (Fig. 4). The cloud formed when air arriving from the northeast nucleated near the upwind Moor House site. The cloud extended to GDF Summit (resulting in an in-cloud travel distance of at least 5 km between the base of the cloud and the sampling site) during most of the event. The air mass contained between approximately 0.05 and 0.10 ppbv of H_2O_2 , SO_2 was at or near the detection limit at all times and O_3 was present at a concentration of approximately 40 ppbv. The pH of the cloudwater samples ranged from 4.0 to 4.5. Oxalate concentrations ranged from approximately 2–5 μM .

Under the stable meteorological conditions that persisted during this event, the sampled cloud droplets were nucleated for between approximately 10–60 min, except for the period beginning at approximately 1000 on 10 May, when the cloud base quickly rose above the GDF Summit. Accounting for reactions that occurred before and after sample collection, we predict that the reaction of Fe(II) with H_2O_2 ($[\text{H}_2\text{O}_2]_{\text{aq, predicted}} = 20\text{--}40\text{ }\mu\text{M}$) or O_3 should have resulted in the oxidation of more than 90% of the Fe(II) that entered the cloud at night. At sunrise, the reactions of iron with HO_2/O_2^- and/or Cu(I) and the photolysis of Fe(III) -oxalato complexes should have resulted in the conversion of most (i.e., 90%) of the Fe into the Fe(II) form.

The measured speciation of iron agreed well with predictions based upon the kinetics of iron redox reactions. At night, the concentrations of Fe(II) were consistent with the in-cloud oxidation of Fe(II) by H_2O_2 and O_3 . The observed increase in the percentage of Fe(II) at sunrise was attributable to the gradual increase in HO_2 and the increase in sunlight intensity.

3.8. Event 5: 11/12 May 1993

Fe(II) comprised less than 30% of the dissolved iron in samples collected at night and approximately 80% of the dissolved iron in samples collected shortly after sunrise and sunset (Fig. 5). The cloud formed as air arriving from the northeast nucleated at the GDF Summit Site. The cloud thinned several times during the night and finally dissipated at GDF Summit at approximately 1000 on 12 May. The air mass contained approximately 0.20 ppbv of H_2O_2 , SO_2 at or near the detection limit at all times and O_3 at approximately 40 ppbv. The cloudwater pH ranged from

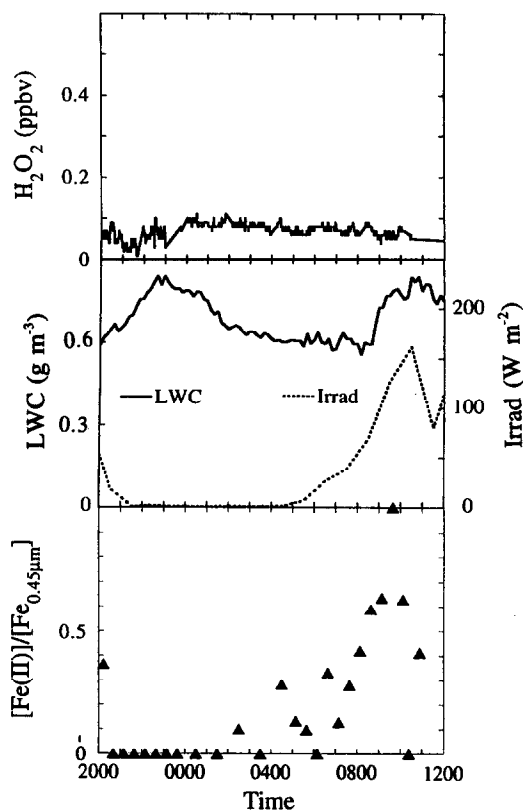


Fig. 4. Concentrations of gaseous-phase H_2O_2 (top), liquid water content (LWC) and solar irradiance (middle) and % Fe(II) ($[\text{Fe(II)}]/[\text{Fe}]_{0.45\text{ }\mu\text{m}}$) (bottom) measured at Great Dun Fell during event 4. Gaseous-phase SO_2 was below the detection limit at all times.

approximately 4.0–4.7 and oxalate concentrations ranged from approximately 5–10 μM .

The sampled droplets were nucleated for as long as approximately an hour as the air flowed to GDF Summit from the fog-covered valley, but, at times, entrainment of air upwind of the site was considerable. Overall, the conditions during this event were similar to those observed during event 4, except the LWC was generally lower and the aqueous-phase concentrations of Fe , Cu and oxalate in the droplets were therefore higher. At night, we predict that more than 90% of the Fe(II) in the droplets should have been oxidized by H_2O_2 ($[\text{H}_2\text{O}_2]_{\text{aq, predicted}} = 80\text{ }\mu\text{M}$) and O_3 ($[\text{O}_3]_{\text{aq, predicted}} = 1.4\text{ nM}$) within 1 h. As was the case during the other events, photochemical reactions should have resulted in the formation of Fe(II) during daytime. In this case the reduction of Fe(III) was attributable to the direct photoreduction of Fe -oxalato complexes (see Zuo and Hoigné (1992) for details of the speciation of Fe(III) in the presence of oxalate).

The observed oxidation states of iron during this event agreed well with predictions based upon known iron redox reactions. After sunset, Fe(II) was rapidly oxidized by H_2O_2 and O_3 . After sunrise, the photoreduction of Fe(III) -oxalato complexes resulted in the

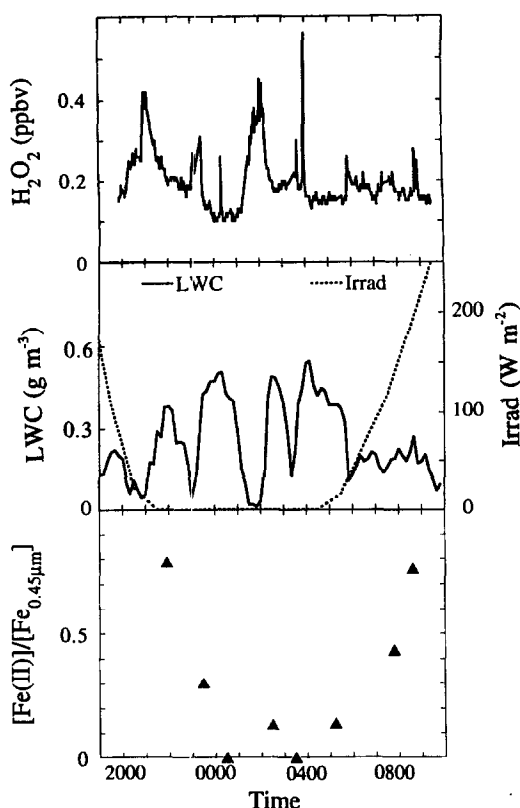


Fig. 5. Concentrations of gaseous-phase H_2O_2 (top), liquid water content (LWC) and solar irradiance (middle) and % Fe(II) ($[\text{Fe(II)}]/[\text{Fe}]_{0.45\mu\text{m}}$) measured at Great Dun Fell during event 5. Gaseous-phase SO_2 was below the detection limit at all times.

conversion of approximately 60% of the dissolved iron into the Fe(II) form.

4. COMPARISON WITH PUBLISHED DATA FROM OTHER REGIONS

Previous measurements of the concentrations of iron and copper in atmospheric waters have been limited to radiation fogs (Behra and Sigg, 1990; Kontronarou and Sigg, 1993; Xue *et al.*, 1991; Joos and Baltensperger, 1991) and clouds in urbanized regions (Munger *et al.*, 1986; Erel *et al.*, 1993). Not surprisingly, the concentrations of iron and copper measured in air masses that arrived at GDF were lower than those previously reported in more-polluted air masses.

The observation that a significant percentage of dissolved iron is present as Fe(II) in atmospheric waters also has been reported in several other regions. For example, between approximately 20 and 90% of the dissolved Fe has been observed in the Fe(II) form in fogwater collected in Dbendorf, Switzerland (Behra and Sigg, 1990; Kontronarou and Sigg, 1993). As discussed by Kontronarou and Sigg (1993), the oxidation state of iron in polluted fogwater is prob-

ably controlled by the presence of relatively high concentrations of S(IV) and/or reactions involving uncharacterized organic compounds. In less-polluted fogwater and in coastal stratus clouds (Erel *et al.*, 1993), between 2 and 55% of the total iron was present as Fe(II). The oxidation state of iron in these cloud droplets was not always correlated with sunlight intensity, but overall a positive relationship was observed between sunlight intensity and the percentage of Fe(II) detected. Conceivably, the discrepancies in this relationship could be explained by some of the same types of meteorological factors described in this study. The presence of a significant fraction of the iron as Fe(II) in aerosol particles collected over the Pacific and Caribbean Oceans (Zhuang *et al.*, 1990, 1992) suggests that the photoreduction of Fe(III) also occurs in maritime air masses.

5. CONCLUSIONS

The concentrations of dissolved iron and copper in cloudwater (60–1600 nM and 4.2–31 nM, respectively) collected at Great Dun Fell are high enough to affect the production and destruction of certain photooxidants and pollutants. By analyzing data on iron and copper concentrations in cloudwater in conjunction with chemical and meteorological data, we have demonstrated how the oxidation state of dissolved iron can be used as an indicator of the relative rates of reactions between dissolved Fe or Cu and H_2O_2 , O_3 and HO_2/O_2^- or the direct photochemical reactions of Fe(III)-oxalato complexes. Despite the complicated conditions encountered in this field project, it was possible to predict the rates of several important aqueous phase chemical reactions. Hopefully, this approach can be used at other sites to gain insight into the reaction mechanism of photooxidants and pollutants in clouds.

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REFERENCES

- Bal Reddy K. and van Eldik R. (1992) Kinetics and mechanisms of the sulfite-induced autoxidation of Fe(II) in acidic aqueous solution. *Atmospheric Environment* **26A**, 661–665.
- Behra P. and Sigg L. (1990) Evidence for redox cycling of iron in atmospheric droplets. *Nature* **344**, 419–421.

- Berdowski J. J. M., Pacyna J. M. and Veldt C. Emissions of non-acidifying pollutants over Europe. In *The Impact of Atmospheric Deposition of Non-acidifying Pollutants on the Quality of European Forest Soils and the North Sea* (edited by van den Hout K. D.), pp. 19–32. Institute of Environmental Sciences IMW-TNO, Delft, The Netherlands.
- Cass G. R. and McRae G. R. (1986) Emissions and air quality relationships for atmospheric trace metals. In *Toxic Metals in the Atmosphere* (edited by Nriagu J. O.), pp. 145–172. Wiley-Interscience, New York.
- Chameides W. L. and Davis D. D. (1982) The free radical chemistry of cloud droplets and its impact upon the composition of rain. *J. geophys. Res.* **87**, 4863–4877.
- Christensen H. and Sehested K. (1981) Pulse radiolysis at high temperatures and high pressures. *Radiat. Phys. Chem.* **18**, 723–731.
- Colville R. N., Bower K. N., Choularton T. W., Gallagher M. W., Beswick K. M., Arends B. G., Kos G. P. A., Wobrock W., Schell D., Hargreaves K. J., Storeton-West R. L., Cape J. N., Jones B. M. R., Wiederschler A., Hansson H.-C. and Wendisch M. (1997) Meteorology of the Great Dun Fell cloud experiment 1993. *Atmospheric Environment* **31**, 2407–2420.
- Conklin M. H. and Hoffmann M. R. (1988) Metal ion sulfur (IV) chemistry. 3. Thermodynamics and kinetics of transient iron(III)-sulfur(IV) complexes. *Envir. Sci. Technol.* **22**, 1115–1123.
- Dedik A. N., Hoffmann P. and Ensling J. (1992) Chemical characterization of iron in atmospheric aerosols. *Atmospheric Environment* **26A**, 2545–2548.
- Erel Y., Pehkonen S. O. and Hoffmann M. R. (1993) Redox chemistry of iron in fog and stratus clouds. *J. geophys. Res.* **98**, 18,423–18,434.
- Faust B. C. and Hoigné J. (1990) Photolysis of Fe(III)-hydroxy complexes as sources of OH radicals in clouds, fog and rain. *Atmospheric Environment* **24A**, 79–89.
- Faust B. C. and Allen J. M. (1994) Sunlight-initiated partial inhibition of the dissolved iron(III)-catalysed oxidation of S(IV) species by molecular oxygen in aqueous solution. *Atmospheric Environment* **28**, 745–748.
- Graedel T. E., Mandich M. L. and Weschler C. J. (1986) Kinetic studies of atmospheric droplet chemistry 2. Homogeneous transition metal chemistry in raindrops. *J. geophys. Res.* **91**, 5205–5221.
- Hansen L. D., Silberman, D. and Fisher G. L. (1981) Crystalline components of stack-collected, size-fractionated fly ash. *Envir. Sci. Technol.* **15**, 1057–1061.
- Hardwick T. J. (1957) The rate constant of the reaction between ferrous ions and hydrogen peroxide in acid solution. *Can. J. Chem.* **35**, 428–436.
- Hoffmann M. R. and Jacob D. J. (1984) Kinetics and mechanisms of the catalytic oxidation of dissolved sulfur dioxide in aqueous solution: an application to nighttime fog water chemistry. In *SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations* (edited by Calvert J. G.), pp. 101–172. Butterworths, London.
- Hofmann H., Hoffmann P. and Lieser, K. H. (1991) Transition metals in atmospheric samples, analytical determination and speciation. *Fres. J. Anal. Chem.* **340**, 591–597.
- Hoigné J., Zuo Y. and Nowell L. (1993) Photochemical reactions in atmospheric waters; role of dissolved iron species. In *Aquatic and Surface Photochemistry* (edited by Helz G., Zepp R. and Crosby D.), Lewis Publishers, Chelsea, Michigan.
- Jacob D. J., Munger J. W., Haghi M., Hoffmann M. R., Flagan R. C. (1985) Instrument to collect fogwater for chemical analysis. *Rev. Scient. Instrum.* **56**, 1291–1293.
- Jacob D. J. (1986) Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. *J. geophys. Res.* **91**, 9807–9826.
- Joos F. and Baltensperger U. (1991) A field study on chemistry, S(IV) oxidation rates and vertical transport during fog conditions. *Atmospheric Environment* **25A**, 217–230.
- King D. W., Lin J. and Kester D. R. (1991) Determination of Fe(II) in seawater at nanomolar concentrations. *Anal. Chim. Acta* **247**, 125–132.
- Kotronarou A. and Sigg L. (1993) SO₂ oxidation in atmospheric water: Role of Fe(II) and effect of ligands. *Envir. Sci. Technol.* **27**, 2725–2735.
- Kraft J. and van Eldik R. (1989) The possible role of iron(III)-sulfur(IV) complexes in the catalyzed autoxidation of sulfur(IV)-oxides. A mechanistic investigation. *Atmospheric Environment* **23**, 2709–2713.
- Logager T., Holcman J., Sehested K. and Pedersen T. (1992) Oxidation of ferrous ions by ozone in acidic solutions. *Inorg. Chem.* **31**, 3523–3529.
- Martin L. R., Hill M. W., Tai A. F. and Good T. W. (1991) The iron catalyzed oxidation of sulfur(IV) in aqueous solution: Differing effects of organics at high and low pH. *J. geophys. Res.* **96**, 3085–3097.
- Matthijsen J., Bultjes P. J. H. and Sedlak D. L. (1994) Cloud model experiments of the effect of iron and copper on tropospheric ozone under marine and continental conditions. *Met. Atmos. Phys.* **57**, 43–60.
- Munger J. W., Jacob D. J., Waldman J. M. and Hoffmann M. R. (1983) Fogwater chemistry in an urban atmosphere. *J. geophys. Res.* **88**, 5109–5121.
- Nriagu J. O. (1979) Copper in the atmosphere and precipitation. In *Copper in the Environment, Part 1: Ecological Cycling* (edited by Nriagu J. O.), pp. 43–121. Wiley Interscience, New York.
- Rush J. D. and Bielski B. H. J. (1985) Pulse radiolysis studies of the reactions of HO₂/O₂⁻ with ferric ions and its implication on the occurrence of the Haber–Weiss reaction. *J. phys. Chem.* **89**, 5062–5066.
- Sedlak D. L. and Hoigné J. (1993) The role of copper and oxalate in the redox cycling of iron in atmospheric waters. *Atmospheric Environment* **27A**, 2173–2185.
- Sedlak D. L. and Hoigné J. (1994) The oxidation of S(IV) in atmospheric water by photooxidants and iron in the presence of copper. *Envir. Sci. Technol.* **28**, 1898–1906.
- Sieffert C. and Sulzberger B. (1991) Light-induced dissolution of hematite in the presence of oxalate: a case study. *Langmuir* **7**, 1627–1634.
- Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry*, 2nd Edn., p. 465. Wiley and Sons, New York.
- Tramontano J. M., Scudlark J. R. and Church T. M. (1987) A method for the collection, handling, and analysis of trace metals in precipitation. *Envir. Sci. Technol.* **21**, 749–753.
- Voelker B. M. and Sedlak D. L. (1995) Iron reduction by photoproduced superoxide in seawater. *Marine Chem.* **50**, 93–102.
- Warneck P. (1991) Chemical reactions in clouds. *Fres. J. Anal. Chem.* **340**, 587–593.
- Weschler C. J., Mandich M. L. and Graedel T. E. (1986) Speciation, photosensitivity and reactions of metal ions in atmospheric droplets. *J. geophys. Res.* **91**, 5189–5204.
- Wiersma G. B. and Davidson C. I. (1986) Trace metals in the atmosphere of rural and remote areas. In *Toxic Metals in the Atmosphere* (edited by J. O. Nriagu), pp. 201–266. Wiley-Interscience, New York.
- Xue H., Gonçalves M. D. S., Reutlinger M., Sigg L. and Stumm W. (1991) Copper(I) in fogwater: determination and interactions with sulfite. *Envir. Sci. Technol.* **25**, 1716–1722.
- Zhuang G., Duce R. A. and Kester D. R. (1990) The dissolution of atmospheric iron in surface seawater of the open ocean. *J. geophys. Res.* **95**, 16,207–16,216.
- Zhuang G., Yi Z., Duce R. A. and Brown P. R. (1992) Link between iron and sulfur suggested by detection of Fe(II) in remote marine aerosols. *Nature* **355**, 537–539.
- Zuo Y. and Hoigné J. (1992) Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes. *Envir. Sci. Technol.* **26**, 1014–1022.