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Speciation and role of iron in cloud droplets at the puy de Dôme station

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Abstract Iron is the most abundant transition metal in the atmosphere and can play a significant role in cloudwater chemistry where its reactivity is closely related to the partitioning between Fe(II) and Fe(III). The objective of this work is to determine the total iron content and the iron speciation in a free tropospheric site, and to understand which factors influence these parameters.

We collected 147 samples of cloudwater during 34 cloud events over a period of four years at the puy de Dôme summit. Besides iron we measured other chemical compounds, solar radiation, physico-chemical and meteorological parameters potentially connected with iron reactivity. The total iron concentrations ranged from 0.1 to 9.1 μM with the major frequency occurring at low levels. The pH and presence of organic complexants seem to be the most significant factors connected with total dissolved iron; while the iron oxidation state seems to be an independent factor. Light intensity, presence of complexants or oxidants (H_2O_2) do not influence the Fe(II)/Fe(Total) ratio, that was quite constant at about 0.75. This could be due to the potential redox that forces the Fe(II)-Fe(III) couple to the reduced form or, more probably to the complexation by Natural Organic Matter, that can stabilize iron in its reduced form and prevent further oxidation.

Our field measurements did not show the diurnal cycle observed in surface water and predicted by models of atmospheric chemistry. This result prompts a more careful review of

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the role of iron and, by analogy, all the transition metals in atmospheric liquid phase, often over-estimated in the literature.

Keywords Reactivity · Cloudwater · Field experiment · Free troposphere · Iron speciation · Natural Organic Matter

1. Introduction

Dissolved trace metals are involved in different chemical processes in liquid atmospheric phase. Because of their capacity to form complexes with water, ammonia, sulphate and organic compounds (e.g. formate, acetate, oxalate or macromolecular compounds) (Feng and Nansheng, 2000; Zuo, 1995), transition metals play a significant role in redox cycles of sulphur (Jacob and Hoffmann, 1983; Hoffmann and Jacob, 1984; Weschler *et al.*, 1986; Graedel *et al.*, 1986; Martin and Hill, 1987; Conklin and Hoffman, 1988; Jacob *et al.*, 1989; Martin and Good, 1991) and organic compounds (Zuo and Hoigné, 1992; Pehkonen *et al.*, 1992; Pehkonen *et al.*, 1993; Erel *et al.*, 1993), in which they react as catalysts. The transition metals also significantly influence the aqueous free radical budget because they are supposed to react efficiently with many of the oxidising and reducing agents in cloudwaters such as $HO_2^\bullet/O_2^{\bullet-}$ or H_2O_2 (Faust and Hoigné, 1990; Zuo and Hoigné, 1992; Zuo and Hoigné, 1994; Sedlak *et al.*, 1997). Moreover, the photochemical dissociation of transition metal complexes may be a source of $OH^\bullet$ radicals and hydrogen peroxide. The reactivity of the transition metals is closely related to their concentration in the aqueous phase; i.e. it has been shown that a twofold increase of dissolved iron concentration could increase the oxidation rate of S(IV) by a factor of 2 (Clarke and Radojevic, 1987).

Iron is the most abundant transition metal in solid and aqueous atmospheric samples: its concentration is at least one order of magnitude larger than other transition metals. The presence of iron in cloudwater depends exclusively on dissolution of aerosol particles through heterogeneous multiphase chemical reaction. It is usually introduced into the atmosphere as soil dust, fly ash from power plants, exhaust from combustion engines, and from industrial operations. The total concentration of dissolved iron in atmospheric aqueous phase is estimated to vary between 0.5 and 4.0%w/w of aerosol iron, for the anthropogenic aerosol (Hoffmann *et al.*, 1997; Germani and Zoller, 1994; Williams *et al.*, 1988), and much less in the crustal aerosol (Desboeufs *et al.*, 2005).

In order to obtain more information on the efficiency of the atmospheric iron redox cycle, it is important to know the partitioning between oxidation states of iron in atmospheric liquid water. Based solely on thermodynamics, the reduced form of iron (Fe(II)) is not expected to be present in natural waters saturated by air, because of the oxidant action of O_2. In fact, in previous studies it has generally been assumed that iron was present predominantly as Fe(III) (Moore *et al.*, 1984; Zhuang *et al.*, 1990). However, more recent works suggest that Fe(II) could be an important constituent in atmospheric liquid water and aerosol particles. In rain samples collected in Germany both Fe(III) and Fe(II) were found in nearly equal amounts (Hoffmann *et al.*, 1991); fog water samples from Switzerland contained 20–90% dissolved Fe(II) of the total amount of iron (Behra and Sigg, 1990). Kotronarou and Sigg (1993) observed that Fe(II) is the predominant form of dissolved iron in fog water at low pH (<5); Deutsch *et al.* (2001) found from 40 to 72% of dissolved iron as Fe(II).

Photochemistry seems to be the first factor regulating the iron oxidation state in surface water: many field studies show clear dependency between the Fe(II)/Fe(III) ratio and light intensity (Warneck, 1988; Erel *et al.*, 1993; Willey *et al.*, 2000; Sigg *et al.*, 2000; Deutsch *et al.*, 2001) Moreover iron speciation is also influenced by the presence of inorganic ($OH^\bullet$, sulphate, sulphite...) and organic (formate, acetate, formaldehyde, oxalate) ligands and by the mineralogy of the parental aerosol.

The chemistry of iron is closely connected to various processes that are very important for overall atmospheric chemistry, e.g., oxidation reactions, acidification of rain and aerosol sulphate formation. The goals of the present work are to determine the dissolved iron content in the liquid atmospheric phase in a free tropospheric site, its speciation between Fe(II) and Fe(III) and to understand the sensitivity of iron speciation to external parameters such as cloud chemical composition (especially organics), air mass origin, solar radiation and cloudwater Redox Potential.

2. Experimental

2.1. Study area

Experimental studies were carried out at the puy de Dôme (PDD) Station (48°N, 2°E; 1465 m a.s.l.), in the Central Massif Region (Central France). It is a strategic point from which to observe warm and mixed clouds that are present 50% of the time between November and March. Clouds are frequently formed at the top of the site either during advection of frontal systems or by orographic rise of moist air. During winter/spring time, the station lies in the free troposphere and air masses are usually exempt from the influence of local pollution.

An overall description of measurements performed at the station can be found at www.obs.univ-bpclermont.fr/: meteorological parameters, atmospheric gas concentrations (O_3, NO_X, SO_2, CO), black carbon (BC) and total number of particles (N_{CPC}) are monitored throughout the year.

2.2. Sampling

We characterized iron content and iron speciation on 34 cloud events from February 2001 to January 2005. Although most cloud samples were collected during the winter seasons due to the high cloud frequency, a number of samples are available for every season, including summer. Similarly, equal proportions of day-time and night-time samples were collected. We therefore believe that this set of samples is representative of the conditions prevailing at the station. The cloud events sampled and measurements performed are shown in Table 1.

The cloud droplet sampling was carried out by a one stage cloud impactor (Kruisz, 1993) with a protection screen for the wind; with the air flux used ($86\ m^3\ h^{-1}$) the lower limit of the aerodynamic diameter was about 7 μm, which ensures 80% of collection efficiency. Two different types of impactors were used during this work, one made of Teflon for the iron analysis, and a second one made of stainless steel and aluminium for dissolved organic carbon (DOC) and physico-chemical measurements (ionic chromatography, pH, Redox Potential and Conductivity). The sampling time ranged from 40 to 120 minutes, depending on the liquid water content of the cloud. Measurement of conductivity, redox potential, pH and Iron analyses were carried out in situ directly after sample collection, while a fraction of samples for Dissolved Organic Carbon (DOC) and Ion Chromatography analyses was kept frozen until analysis, performed less than 48 hours after collection.

At every stage, sampling and analyses were carried out with the greatest precaution to minimise all possible external contamination. To check data quality, we analysed at least two field blanks for each cloud event.

Table 1 Cloud events sampled at PDD from February 2001 until January 2005 (Fe: iron measurements (total content and oxidation state); IC: ionic chromatography; DOC: dissolved organic carbon; C: conductivity; E_h: redox potential)

Event	Start	End	Samples number	Air mass origin	Measured parameters
1	08/02/01	09/02/01	6	W/N (marine)	Fe, IC
2	12/02/01	13/02/01	9	E (continental)	Fe, IC
3	17/02/01	18/02/01	11	E (continental)	Fe, IC, pH
4	22/02/01	24/02/01	18	W/N (marine)	Fe, IC, pH
5	28/02/01	01/03/01	12	W/N (marine)	Fe, IC, pH
6	02/03/01	03/03/01	8	W/SW (marine)	Fe, IC, pH
7	08/03/01	08/03/01	2	W (marine)	Fe, IC, pH
8	05/04/01	06/04/01	1	E (continental)	Fe, IC, DOC
9	14/02/02	15/02/02	1	W/N (marine/continental)	Fe, IC, pH, DOC
10	22/02/02	22/02/02	1	W (marine)	Fe, IC, pH
11	27/02/02	27/02/02	1	W (marine)	Fe, IC, pH, DOC
12	28/02/02	28/02/02	1	N/W (marine/continental)	Fe, IC, pH, DOC
13	07/03/02	07/03/02	1	N (continental)	Fe, IC, pH, DOC
14	13/04/02	14/04/02	3	N (continental)	Fe, IC, pH, DOC
15	26/04/02	26/04/02	1	W (marine)	Fe, IC, pH, DOC
16	03/05/02	05/05/02	1	W (marine)	Fe, IC, pH, DOC
17	11/05/02	12/05/02	1	W/N (marine)	Fe, pH, DOC
18	30/04/03	30/04/03	1	W (marine)	Fe, pH
19	06/05/03	06/05/03	1	S (Saharan)	Fe, pH
20	10/05/03	10/05/03	1	S/W (continental)	Fe, pH
21	11/12/03	12/12/03	10	W (marine)	Fe, pH, DOC
22	14/01/04	15/01/04	9	W (marine)	Fe, pH, DOC
23	20/01/04	21/01/04	10	N/W (marine)	Fe, pH, DOC, C, E_h
24	16/02/04	16/02/04	2	N/E (continental)	Fe, pH, DOC, C, E_h
25	17/02/04	18/02/04	4	N/E (continental)	Fe, pH, DOC, C, E_h
26	08/03/04	08/03/04	5	N/E (continental)	Fe, pH, DOC, C, E_h
27	06/04/04	06/04/04	5	W (marine)	Fe, pH, DOC, C, E_h
28	22/04/04	23/04/04	3	N/W (marine)	Fe, pH, DOC, C, E_h
29	24/06/04	25/06/04	2	W (marine)	Fe, pH, DOC, C, E_h
30	08/07/04	09/07/04	1	N/W (marine)	Fe, pH, DOC, C, E_h
31	23/09/04	24/09/04	4	W (marine)	Fe, pH, DOC, C, E_h
32	17/11/04	17/11/04	3	W (marine)	Fe, pH, DOC, C, E_h
33	16/12/04	17/12/04	4	W (marine)	Fe, pH, DOC, C, E_h
34	19/01/05	19/01/05	4	NW (marine)	Fe, pH, DOC, C, E_h

2.3. Chemical analyses

2.3.1. Iron

To determine iron concentration, a colorimetric complexant (ferrozine) was used, coupled with spectrophotometric detection of complex absorbance ($\lambda_{max} = 562$ nm). Ferrozine (3-(2-pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine) reacts with divalent iron to form a stable magenta complex species which is very soluble in water and can be used for direct determination of iron in water (Stookey, 1970). Fe(II) concentrations were directly determined. After reduction with hydroxylamine chlorhydrate, the total iron content was detected. Fe(III) was calculated by the subtraction of Fe(II) from Fe(Total). The detection limit with a quartz cell with a path length of 10 cm is 0.05 μM for Fe(II) and 0.1 μM for Fe(Total), calculated as three times the standard deviation of field blanks.

Filtration of samples was not used, in order to avoid further contaminations. This analytical technique detects iron dissolved in the liquid phase, both iron free cations and iron complexed by ligands due to the high concentration of ferrozine added for the analysis and the high complexation constant between ferrozine and Fe(II) (3×10^{11} $M^{-1} s^{-1}$, Thompsen and Motola, 1984). Moreover, it was not possible to measure particulate iron, because ferrozine is not able to solubilize solid phase iron, and the time in which acidic reagents and particulate iron were in contact was too short to result in further solubilization of iron. This was confirmed by experiments on filtered (filter porosity at 0.22 μm) and un-filtered samples.

2.3.2. Dissolved organic carbon (DOC)

DOC was measured with a TOC (Total Organic Carbon) analyser, Shimadzu model TOC-5050A. The analyses were carried out on filtered liquid atmospheric phase in order to measure only dissolved organic carbon. The Shimadzu TOC-5050A is capable of performing Total Carbon (TC) analyses by combustion and Inorganic Carbon (IC) analyses by oxidation. TOC measurements were calculated by the difference between TC and IC. The instrument works with a TC combustion tube, which is filled with a TC catalyst and heated to 680°C. When the cloudwater sample is introduced into the TC combustion tube, the carbon in the sample is combusted/oxidized to form CO_2. The carrier gas (purified air) with the combustion product (CO_2) passes through a cell equipped with a Non-Dispersive Infrared Detector (NDIR), where CO_2 is detected. For the IC measurements, the sample is introduced into the IC reaction vessel (containing H_3PO_4 25%), through which the carrier gas flows in the form of tiny bubbles. Only the IC component in the sample is decomposed to form CO_2, which is detected upon reaching the NDIR. Carbon in the form of carbonates and hydrogen carbonates are measured as IC. Calibration curves within the range 0–15 mg L^{-1} were obtained by using potassium hydrogen phthalate for organic carbon and sodium hydrogen carbonate and sodium carbonate for inorganic carbon. Detection limit for DOC was 0.1 mg L^{-1}, calculated as three times the standard deviation of field blanks.

2.3.3. Ion chromatography

Ion chromatographic analyses were performed in a clean room (class 10 000). Cloudwater was injected directly without filtration to avoid further contamination. Working conditions were similar to those detailed by Jaffrezo *et al.* (1998), employing a DIONEX 100 Chromatograph equipped with a CS12 column for the cations, and a DIONEX 500 with AS11 column for the anions. CH_3COO^-, $HCOO^-$, Cl^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} were the ions analysed for the samples from events 1 to 6, for the samples from events 7 to 16 additional mono and di-carboxylic acids were measured: lactic, glycolic, propionic, glyoxylic, glutaric, succinic, maleic, malonic and tartaric acids. Detection limits were calculated from a mean blank plus one standard deviation. The accuracy of ion chromatographic analyses is typically 10% for samples 10 times the detection limit, and approximately 50% for samples twice the detection limit.

2.4. Irradiation experiments

Some samples were irradiated in a laboratory irradiation chamber in order to free photochemical in-situ evidence from the gas phase photochemistry.

The irradiation device was a stainless steel cylinder built on an elliptical basis. It contained three TLAD Philips fluorescent tubes of 15 W, emitting within the wavelength range 300–450 nm with a maximum emission at 365 nm. The reactor was 1L PMP bottle located at one focal point of the elliptical reflecting device maintaining a constant irradiation of the whole sample. Samples were continuously stirred with a magnetic stirrer and a Teflon bar.

During irradiation experiments we monitored total iron and iron speciation along a timeline varying from 2 to 5 hours. Laboratory irradiations were performed under laminar flow (class 100). A cooling system inside the reactor with cold water flow stabilised the temperature at around 13°C ± 1°C, in order to limit thermal reactions.

Samples were stored (at the maximum 3 days) in the dark at + 4°C between sampling and irradiation experiments.

3. Results and discussion

3.1. General results

Previous studies at the same site (Sellegri *et al.*, 2003; Marinoni *et al.*, 2004) have shown that the puy de Dôme summit is under the influence of two major air mass fluxes, marine (west and north-west) and continental (north, east), each of them corresponding to a typical chemical signature of aerosol population and cloudwater chemical composition. A further class of anthropogenic events (correspondent to continental flux) can be identified using the chemical signature of the air mass. Occasionally special conditions are observed, like Saharan dust events with a southern flux (event 19) or polluted conditions not explained by air mass back trajectory, but probably due to local conditions like in the case of event 14.

A statistical overview of pH, redox potential (E_h), conductivity and concentrations of DOC measured in cloudwater and classified according to air mass specifications is presented in Table 2. In this Table, averages are weighted by cloud events and not by the total number of samples. Cloudwater pH ranged from 3.1 to 7.6, conductivity values from 4 to 348 μS cm^{-1}; redox potential from 76 to 470 mV and DOC from 1.3 to 18.4 mg L^{-1}. Our observations at the PDD station were within the ranges measured with other atmospheric backgrounds and

Table 2 Average and standard deviation of fundamental parameters measured in 34 cloud events (average of 147 samples) for different air mass origin

Air Mass	Marine	Continental	Anthropogenic	Saharian
Cloud Events	1 4 5 6 7 10 11 12 15 16 17 19 20 21 22 26 27 28 29 30 31 32 33 34	2 3 8 9 13 25	14 23 24	19
pH	5.9 ± 0.6	5.0 ± 0.7	3.7 ± 0.4	7.3
Conductivity (μ S cm^{-1})	29 ± 18	110 ± 69	199 ± 92	n.a
Redox potential (mV)	245 ± 57	338 ± 28	418 ± 46	n.a
DOC (mg L^{-1})	3.3 ± 1.4	8.1 ± 1.8	11.2 ± 5.6	n.a
TIC (mg L^{-1})	13.65 ± 10.31	19.01 ± 86.62	81.63 ± 84.36	n.a.
Iron (μ M)	0.9 ± 0.7	1.6 ± 0.4	5.3 ± 3.2	5.5
Iron(II)/ Iron	77% ± 19%	74% ± 16%	80% ± 12%	7%

anthropogenic cloudwater samples, i.e. Sinner *et al.*, 1994 measured a range of pH from 3.0 to 6.5 and E_h from 200 mV to 500 mV.

It is clear from Table 2 that most factors varied with the air mass type, especially pH and conductivity.

Considering averaged events, marine air masses were characterised by the highest pH values (ranging from 4.8 to 7.0 pH unity) and by the lowest values for conductivity (from 8 to 59 μS cm^{-1}) and redox potential (from 134 to 320 mV, measured by a calomel electrode). In agreement with the conductivity range, both organic and inorganic contents were low: DOC varies from 1.3 to 8.9 mg L^{-1}) and TIC (Total Ionic Content) from 3.3 to 36.3 mg L^{-1}.

On the contrary anthropogenic air masses had typically low pH values (within a range of 3.1 to 4.6) and high conductivity (ranging from 105 to 348 μS cm^{-1}) and redox potential (ranging from 357 to 470 mV). In fact low pH values can be due to both higher concentrations of anthropogenic gas (such as SO_2 and NO_x) and to the high load and more acidic aerosol in the anthropogenic air masses. The gas and aerosols solubilized in cloud droplets can be an important source of ionic species (SO_4^{2-}, NO_3^-, H_3O^+) that increase cloudwater conductivity. The considerable aerosol load leads to a significant number of smaller droplets than marine events and consequently larger concentrations of solubilized species, both from gas and aerosol scavenging (Marinoni *et al.*, 2004). Moreover, low pH values could be a factor enhancing the solubility of some species from aerosol particles, especially for metals, like iron.

The cloudwater from continental air masses has intermediate characteristics: pH varies from 4.1 to 5.5, conductivity from 38 to 175 μS cm^{-1} and redox potential from 318 to 370 mV.

3.2. Total dissolved iron

The statistics per event that describe the total dissolved iron concentration and its speciation monitored throughout four years are shown in Table 3.

The total dissolved iron concentrations in cloudwater at the puy de Dôme ranged from 0.1 to 9.1 μM, with the major frequency occurring at low levels, as is also suggested by the comparison between the average (1.8 μM) and the median value (1.1 μM). The most frequent concentrations representing the tropospheric background ranged from 0.2 to 1.6 μM corresponding to 11 to 90 μg L^{-1}. With a liquid water content (LWC) of 0.3 g m^{-3} (average value at the puy de Dôme for marine events) the concentrations of iron corresponded approxi-

Table 3 Statistics of dissolved iron distribution (total iron and its speciation) in 34 cloud events sampled throughout four years of sampling campaigns

Iron concentration (μM)	[Fe(II)]	[Fe(Total)]	[Fe(III)]	[Fe(II)]/[Fe(Total)]
MIN	0.1	0.1	0.0	7.3%
10° centile	0.2	0.3	0.0	54.9%
25° centile	0.3	0.6	0.1	63.2%
Average	1.2	1.8	0.6	74.5%
Median	0.7	1.1	0.3	73.6%
75° centile	1.1	1.8	0.6	88.9%
90° centile	3.0	3.9	2.0	98.3%
MAX	6.8	9.1	5.1	109.4%
Standard deviation	1.5	2.1	1.0	20.6%

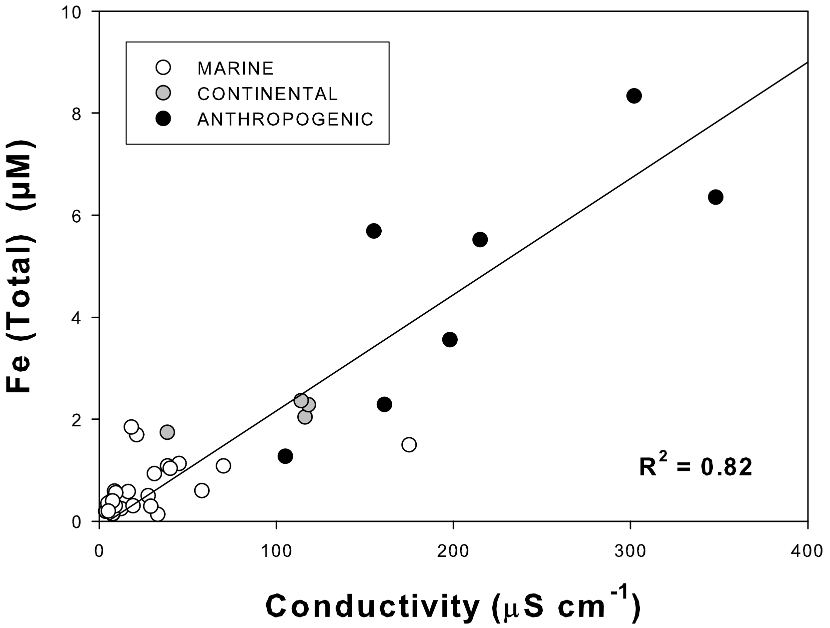

Fig. 1 Correlation between total dissolved iron concentration and conductivity in 45 samples collected during winter 2003/2004

mately to 3 to 30 ng m^{-3} of air during the marine events. However, in different meteorological conditions (continental flux) a subsequent continental or anthropogenic component can be superposed and iron concentration could reach several hundreds of ng m^{-3}.

The range of concentrations measured at the puy de Dôme was generally quite low in comparison with measurements at other free tropospheric and marine sites: Sedlack *et al.* (1997) found values ranging from 2 to 27 μM at Great Dun Fell (England, continental free troposphere site), and from 2 to 10 μM at Palos Verdes Peninsula (marine site, Erel *et al.*, 1993). The PDD iron concentrations are in the same range as the Cleopatra field experiment carried out in South Germany (Sinner *et al.*, 1994) and samples from Whiteface Mountain (Arakaki and Faust, 1998).

The concentration of dissolved iron is linked to the air mass origin as suggested by Table 2 and by the good correlation ($R^2 = 0.82$) between conductivity and Fe(Total) concentration (Figure 1). It should be noted that iron always represented less than 0.1% of total conductivity. During polluted events, concentrations of dissolved iron could reach nearly 10 μM. In any case these concentrations were far lower than those measured at different urban sites, like Dubendorf-Zurig (2–70 μM, Sigg *et al.*, 1987), San Joaquin Valley in California (2–115 μM), Po Valley in Italy (1–30 μM, Fuzzi *et al.*, 1988). The relatively low concentration (5.5 μM) of dissolved iron during Saharan dust events as compared to dissolved iron during the special polluted event and the iron content of Saharan aerosol at the same site (Sellegri *et al.*, 2003) reflects the fact that a small fraction of Fe in desert dust can dissolve in water (Desboeufs *et al.*, 2005).

Both pH and organic complexants influence the dissolution of iron in the liquid atmospheric phase by increasing its solubility. This was confirmed in our samples, as shown in Figure 2. The highest concentrations of total dissolved iron (>4 μM) occur at low pH (<4),

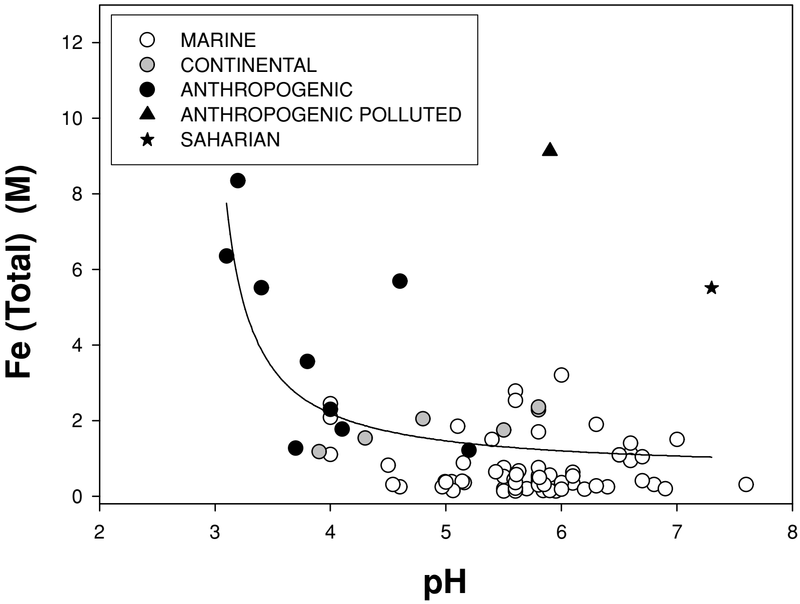

Fig. 2 Influence of pH on the solubility of total iron in 86 samples of cloud water

while in more neutral conditions the dissolved iron concentrations are much lower and do not exceed 3 μM). This confirms aerosol leaching studies (Desboeufs *et al.*, 2005) and field data on cloudwater (Sedlack *et al.*, 1997) showing that the solubility of iron decreased with increasing pH. However, because we did not measure the soluble fraction of Fe, we cannot conclude on whether the relationship with pH originates from increased dissolution or from higher loading of soluble Fe in anthropogenic air masses.

The concentration of dissolved Fe during the Saharan dust event sampled on 6 May 2003 showed a higher level of total iron dissolved with regard to pH value, as compared to other samples. We can suggest that the very high aerosol load from Saharan flux (Sellegri *et al.*, 2003) and the crustal origin (reach in iron content) of Saharan dust could strongly impact the dissolved iron concentration.

In the case of the anthropogenic very polluted event (14), the high concentration of dissolved Fe was linked to elevated ionic content (180 mg L^{-1}) and dissolved organic compounds (DOC = 15.4 mg L^{-1}). We can hypothesise that, in the case of this polluted event, the role of complexants was quantitatively more important to initiate iron dissolution than the pH value. However, although conductivity was well-connected with total dissolved iron concentration (Figure 1), no clear correlation existed between concentrations of Fe and of any of the major ionic species measured by ion chromatography (listed in 2.3.3). In particular, no relationship was found between dissolved Fe and concentrations of organic acids (acetic, formic, oxalic, lactic, glycolic, propionic, glyoxylic, glutaric, succinic, maleic, malonic and tartaric acids) or inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) that can complex iron.

Instead, the concentration of dissolved iron appeared to be linked to the Dissolved Organic Carbon content of clouds as shown in Figure 3, in particular for continental and anthropogenic samples. Both the lack of correlation with major ions and the relationship with DOC suggest that the concentration of dissolved Fe in cloudwater was linked first to the total aerosol loading and second to the presence of Fe-complexing organic substances that can prime subsequent

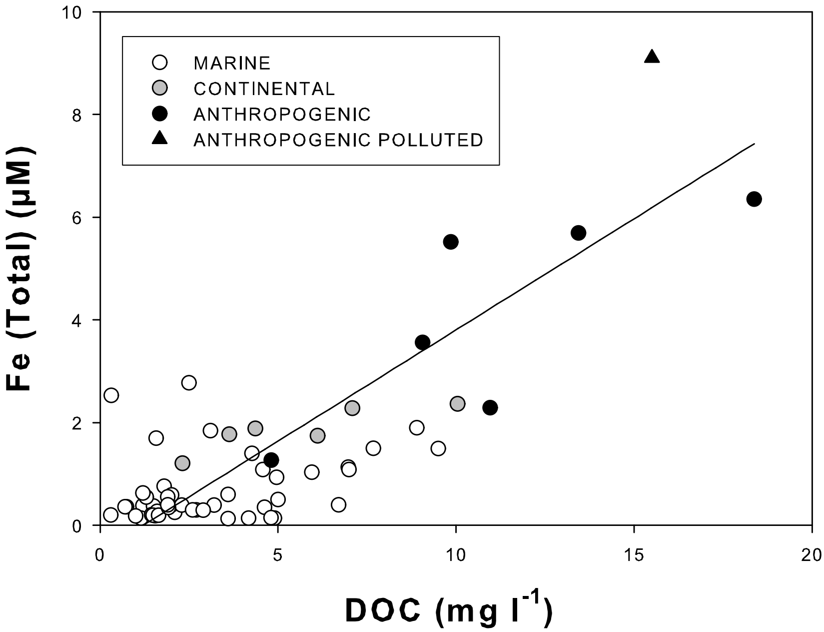

Fig. 3 Correlation between dissolved organic carbon and total dissolved iron measured simultaneously in 74 samples of cloudwater

iron dissolution from particles and that can also provide a source of dissolved iron. In fact, the presence of dissolved organic matter may affect the iron chemistry by sequestration or complex formation and hence regulate, in part, solubility and redox potential (Mill, 1980). On the contrary, in the marine events (represented by open circles in Figure 3), characterised by low concentrations for all organic and inorganic species, the iron concentration was less correlated with DOC and seemed predominantly linked to primary dust particles. In the anthropogenic polluted event (14), where the very high inorganic anions content largely exceeded the organic species, the action of inorganic complexants could prevail over that of organic ones.

3.3. Iron speciation

The speciation between Fe(II) and Fe(III) was measured in cloud samples in order to provide constraints on iron reactivity. A high percentage of Fe(II) relative to Fe(III) was detected in the majority of samples. The Fe(II)/Fe(Total) ratio ranged from 0.07 to 1.09 (uncertainty with the measurements gave some values larger than 1), with an average of 0.75 ± 0.24 (calculated on the averages of 34 cloud events). The very similar values of median and average showed a quite symmetrical distribution, with 25° and 75° percentiles close to the median value (Table 3). The low level of dispersion of Fe(II)/Fe(Total) in samples is also clear from Figure 4. Cloud water showed a very stable ratio between Fe(II) and Fe(Total) especially during anthropogenic and very polluted events (0.77 ± 0.14; $R^2 = 0.95$), while a somewhat higher fraction of Fe(III) was found for some background events: under these background conditions, a few samples even showed a proportion of Fe(III) higher than 30%. The sample collected during the Saharan dust episode showed a very high fraction of Fe(III)

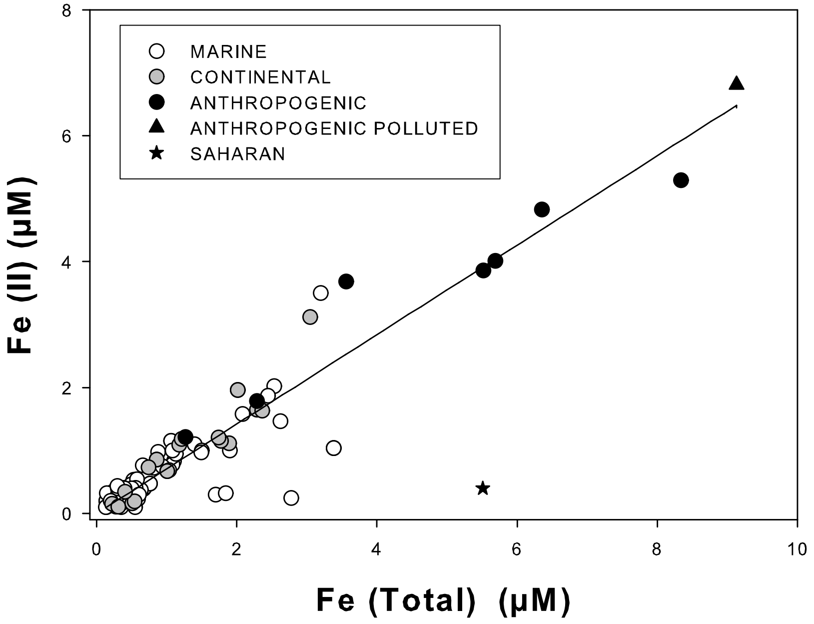

Fig. 4 Fe(II) concentration as a function of Fe(Total) concentration in 146 samples of cloudwater

(93%) probably due to the dust mineralogy as Fe(III) is the most frequent form of iron in the crystalline phase of the most frequent minerals in the earth's crust (Wedepohl, 1995).

The stability of the Fe(II)/Fe(Total) ratio is confirmed by the lack of correlation between the oxidation state of iron and solar radiation (as measured by pyranometers at the station) or oxidation parameters (redox potential or H_2O_2 were measured in about 50 samples). In fact, no significant difference in Fe(II)/Fe(Total) was found between day-time and night-time samples. In contrast with some experimental studies (Erel *et al.*, 1993; Willey *et al.*, 2000; Sigg *et al.*, 2000; Deutsch *et al.*, 2001), daylight did not appear to favour Fe(II) production in cloudwater at the puy de Dôme summit.

In order to understand the influence of light on the oxidation state of iron in puy de Dôme cloudwater, experiments were conducted to irradiate natural samples of puy de Dôme cloudwater in the laboratory. During 10 cloud events, sufficient volume (500 mL) of cloudwater was collected to perform additional irradiation experiments. Samples were irradiated in a reactor at wavelengths between 300 nm and 450 nm (well-representative UV-visible wavelengths of the tropospheric solar spectrum) in order to monitor the behaviour of iron. In Table 4 we reported the averaged value of normalised variations of Fe(II)/Fe(Total) ratio during irradiation. The averaged results of these 10 experiments showed no clear evolution of iron speciation with irradiation. The ratio between the two oxidation states varied very little, and did not show any tendency to evolve during irradiation. The same kind of experiments carried out with Milli-Q water spiked with Fe(II), Fe(III) and a source of organic carbon showed a very quick increase of Fe(II) concentration under irradiation. The photostationary equilibrium between Fe(II) and Fe(Total) was close to 1 after 15 minutes of irradiation (Mailhot *et al.*, 2002). The fraction of Fe(II) in cloudwater appeared to be much more stable than theoretically expected.

Table 4 Averaged result of Fe(II)/Fe(Total) variation from 10 irradiation experiments showing no evolution in iron speciation varying light intensity

Irradiation time (h)	[Fe(II)]/[Fe(Total)]	Standard deviation
t_0	0.68	0.07
1	0.78	0.25
2	0.71	0.15
3	0.65	0.24
4	0.71	0.12

This lack of dependency of iron speciation on light intensity could be due to factors limiting the presence of the oxidized form of iron and stabilising it.

In the range of pH, E_h and Fe concentrations measured, the expected fraction of soluble iron was much lower than that measured in our cloudwater samples (a factor about 10–10^5), especially in the case of marine events. This is clearly shown in the Pourbaix iron speciation diagram in pure water (Figure 5) where only a few acidic samples dissolved iron at the expected concentration.

This enhanced solubility was likely due to the presence in the water of other forms of iron than iron free cation. In particular, iron in cloudwater could be rapidly adsorbed onto Natural Organic Matter (NOM) (Rose *et al.*, 1997). The major fraction of freshly solubilized iron from aerosol particles should be in its reduced form (Fe(II)), according to the Pourbaix diagram (i.e. E_h lower than 770 mV) and due to daytime photo-reduction.

Iron in both Fe(II) and Fe(III) oxidation state may be stabilised in aqueous aerobic conditions by organic acids. Fe(II) organic complexes analogous to those of humic acids are resistant to oxidation for considerable periods of time (Mill, 1980). Moreover the NOM can

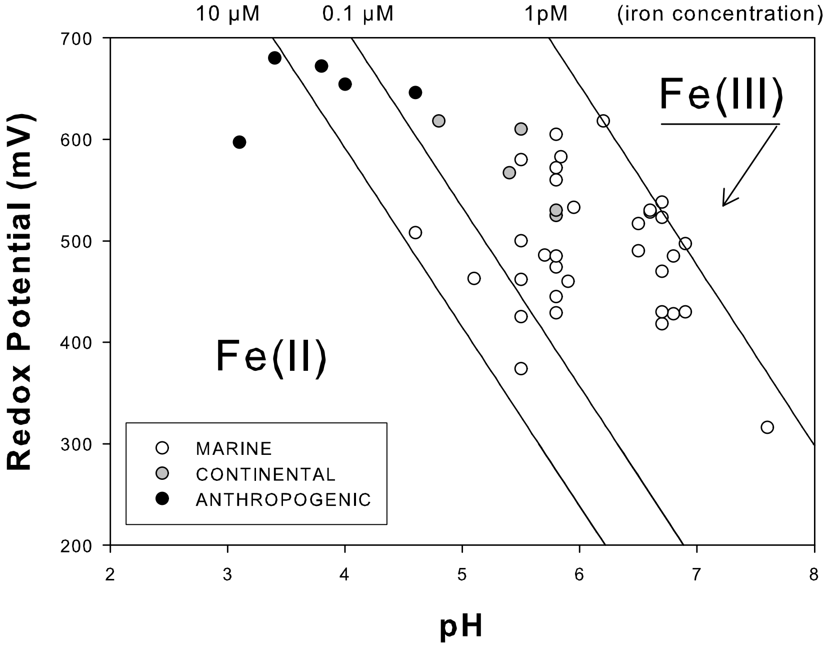

Fig. 5 Pourbaix diagram for an iron solution in absence of other chemicals. The Redox values are corrected with reference to the hydrogen electrode (E_h hydrogen = E_h calomel + 240 mV)

lead to the reduction from Fe(III) to Fe(II). Both oxidation states are able to form stable complexes with NOM (especially with humic substances), especially Fe(III), but also Fe(II) by adsorption of the $Fe(OH)_2$ species on colloidal organic mater. This fraction of colloidal iron was included in our iron measurements because of the very small size of this kind of colloid (i.e. diameter lower than 0.22 μm which is the size of the pores of filters used to determine if we also measured some particulate iron). This small Fe(II)-NOM colloid may have stabilized iron in this oxidation state and prevented further re-oxidation. This hypothesis is consistent with previous studies at the same site found that hydrophobic macromolecular compounds could constitute around 40% of the total DOC in cloudwater (Zappoli S., personal communication).

The difference between the photo-oxido-reduction cycles of iron observed in natural surface waters and our observations in cloudwater may be explained by the presence of these Fe-NOM colloids and by the higher redox potential in atmospheric aqueous aerosols, relatively to the surface waters. In fact at the same pH values, lower E_h allowed higher concentration of free soluble iron which might be more reactive and photo-reactive than iron adsorbed on humic substances (Faust, 1994).

The distribution of iron between its two main oxidation states (+II and +III) is considered in scientific literature to be a good indicator of oxido-reduction potential and the reactivity in cloud droplets (especially in radical production and oxidation reactions). The sensitive parameters that impact iron speciation are identified in i) solar radiation, ii) presence of oxidants (especially H_2O_2) and iii) oxalate concentrations.

Field measurements shown in this study did not show the diurnal cycle observed in surface water (Willey *et al.*, 2001) and predicted (expected) by atmospheric chemistry model (Deguillaume *et al.*, 2004). On the contrary iron seemed to show a very independent behaviour, not influenced by solar radiation, H_2O_2 or oxalate concentration. We suggest that complexation of iron by NOM stabilised the iron in reduced form and prevented further oxidation: this form of iron is less reactive than iron free cation or Fe(III)-hydroxo-complexes. In this case the role of iron and, by analogy, of all the transition metals in atmospheric liquid phase has to be carefully considered.

4. Conclusions

Monitoring of dissolved iron with its speciation was carried out at the puy de Dôme summit over four years. The values of total iron ranged from 0.1 to 9.1 μM with the major frequency occurring at low levels, which are representative of the tropospheric background conditions (about 11–90 $\mu g\ l^{-1}$). The total iron concentration was linked with the parameters that are representative of the air mass nature (conductivity, pH, redox potential). The pH and presence of organic complexants seemed to be the most significant factors impacting the total dissolved iron content.

The iron speciation seemed to be an independent factor: light intensity, presence of complexants (also oxalate) or oxidants (H_2O_2) did not influence the Fe(II)/Fe(Total) ratio, which was constant at about 0.75 ± 0.24. Experiments of real sample irradiation confirmed that no evolution of iron speciation was driven by light intensity or wavelength. The ratio between the two oxidation states underwent very little variation, but did not show a tendency towards evolution; we observed the same percentage of Fe(II) typical for cloudwater freshly sampled. We propose that NOM colloids play a very significant role in stabilising iron in its reduced oxidation state and preventing its further re-oxidation.

This evidence contrasts with some experimental studies on water surface and with results predicted from atmospheric chemistry models, that describe a significant diurnal cycle with excess of Fe(II) during the day and oxidation to Fe(III) during the night. The Fe(II)-NOM complexes are a less reactive form than iron free cation or Fe(III)-hydroxo-complexes. Thus the role of iron and, by analogy, of all the transition metals in atmospheric liquid phase has to be carefully considered.

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