



## Variability of dust iron solubility in atmospheric waters: Investigation of the role of oxalate organic complexation

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### ABSTRACT

Atmospheric dust deposition is a major external iron source for remote surface ocean waters. Organic complexation is known to play a role in the dissolution of iron-containing minerals. In this paper, we present our study on the effect of oxalate on dust iron solubility in simulated rainwater. Our results reveal that the solubility of iron carried by analogs of different African dusts varies with the dust source. Our experiments indicate a positive linear correlation between iron solubility and oxalate concentration. Soluble iron (SFe) increases from 0.0025(±0.0005)% to 0.26(±0.01)% of total iron, considering all dust sources and with oxalate concentrations ranging from 0 to 8 μM. These results show that the observed variability of iron solubility in aerosols collected over the Atlantic Ocean is, at least partly, due to an increase in dust iron solubility, with the presence of oxalate complexation, rather than to the presence of more soluble anthropogenic iron. Considering the mineralogical composition of those particles, experiments with pure minerals (hematite, goethite and illite) were performed to study the dissolution process. We found that oxalate promotes the solubility of iron contained in clay and hence confirmed that more than 95% of SFe from soil dust is provided by clay (illite). This experimental work enables us to establish a parameterization of iron solubility in dust as a function of oxalate concentration and based on the individual iron solubility of pure iron-bearing minerals usually present in dust particles. Finally, our results emphasize that oxalate contributes to iron solubility on the same order of magnitude as the acid processes. Organic complexation appears to be a process that increases iron solubility and likely enhances the bioavailability of iron from dust.

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### 1. Introduction

Iron bioavailability has been shown to limit or co-limit primary productivity in several oceanic waters, particularly in high-nutrient, low-chlorophyll (HNLC) regions (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000). Among different external iron sources to these and other oceanographic regimes, atmospheric deposition of mineral dust is considered to be critical. This is the case of the Atlantic ocean (Bristow et al., 2010; Trapp et al., 2010), where the atmospheric Fe inputs could be dominated by wet precipitation of North African dust in the Inter-tropical Convergence Zone (ITCZ) areas of the equatorial Atlantic (Helmers and Schrems, 1995; Vink and Measures, 2001; Kim and Church, 2002; Sarthou et al., 2003). However, not all dust iron is bioavailable in the ocean surface waters, and only the soluble forms of iron are bioavailable (Martin et al., 1994; Coale et al., 1996; Boyd

et al., 2000). Iron solubility values are higher in transported aerosols than in dust particles collected close to the sources, implying a substantial atmospheric processing effect (Desboeufs et al., 2001; Jickells and Spokes, 2001; Hand et al., 2004; Mahowald et al., 2005).

Among these atmospheric processes, the importance of organic complexation in atmospheric deposition has been suggested in terms of iron solubility (Mahowald et al., 2005). The oxalic acid ( $pK_{a1} = 0.97$ ,  $pK_{a2} = 3.57$ ) is the most abundant organic ligands of iron ( $K_{Fe}^{2+} = 4.2$ ,  $K_{Fe}^{3+} = 9.4$ , we have made the hypothesis that 1:1 complex is the most abundant in our experiments) in ambient aerosols and in the atmospheric aqueous phase (Sempéré and Kawamura, 1996; Kerminen et al., 2000; Hegg et al., 2002; Yao et al., 2002; Huang et al., 2006). However, there is little information on oxalate concentrations in remote atmosphere. The presence of oxalate has been observed in atmospheric waters over the central and equatorial Pacific Ocean (Kawamura and Usukura, 1993; Kawamura and Sakaguchi, 1999), with values ranging from 0.1 μM to 6 μM. This dicarboxylic acid is also present in aerosol collected over the Atlantic Ocean (Baboukas et al., 2000; Johansen et al., 2000; Turekian et al., 2003; Avery et al., 2006); given that

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these compounds are highly soluble, we can estimate that the same concentration should be measured in the north Atlantic atmosphere. The main sources of oxalic acid are thought to be the atmospheric photochemical oxidation of anthropogenic, biogenic and oceanic emissions and/or primary traffic emissions (Kawamura and Kaplan, 1987; Kawamura et al., 1996; Turekian et al., 2003). This induces the possibility of a global source of oxalate precursors, specifically in marine VOC emissions (Warneck, 2003). The characteristic size distribution of oxalate and its relationship with sulfate confirmed the in-cloud formation of oxalate (Yao et al., 2002, 2003; Crahan et al., 2004; Sorooshian et al., 2007). Thus, oxalate is present in different atmospheres (remote and rural environments, close to areas of biomass-burning activities, etc.). Due to its formation mechanism, the interaction between oxalate and dust could happen in the atmospheric aqueous phase during their atmospheric transport. Aymoz et al. (2004) observed a correlation between oxalate concentration and dust content in the French Alps during a Saharan dust event, which they concluded would result from the production of oxalate directly on the dust from the oxidation of adsorbed gaseous precursors or from the coagulation of dust and submicron particles. During the ACE-Asia campaign, oxalic and malonic acids were found mostly to be internally mixed with mineral dust and aged sea salts in Asian outflow by direct shipboard measurements (Sullivan et al., 2007). Similar, a mixing of mineral dust and biomass-burning plumes, rich in organic carbon and especially oxalic acid, has been observed throughout West Africa during the dry season (Capes et al., 2008; Paris et al., 2010). Likewise, dust and oxalate have been found conjointly in rainwater samples collected over Sahel region during monsoon period (Galy-Lacaux et al., 2009; Desboeufs et al., 2010). Saydam and Senyuva (2002) also reported oxalic acid formation via the action of fungus found on the surface of dust and encapsulated in a cloud droplet above a certain solar radiation threshold. Consequently, the mixing between dust particles and oxalate is realistic in the atmosphere and especially over Atlantic Ocean in African air masses. As oxalate has been confirmed to be produced by in-cloud chemistry (Crahan et al., 2004; Yu et al., 2005), there is a large probability of finding an atmospheric aqueous complexation of dust iron and oxalate ligand.

Field measurements showed a positive relationship between oxalate and soluble Fe concentrations in specific samples of air masses over the North Atlantic region (Johansen et al., 2000; Chen and Siefert, 2004; Hand et al., 2004; Xia and Gao, 2010), suggesting a positive effect of organic complexation on dust iron dissolution solubility. However, considering anthropogenic sources of oxalate, the authors concluded that it was difficult to exclude the potential effect of anthropogenic iron on the measured soluble Fe concentrations. By contrast, other studies (e.g., Buck et al., 2006, 2010; Paris et al., 2010) have not observed a link between aerosol iron solubility and oxalate. Thus far, it is difficult to conclude on the organic effect on iron solubility due to the limitations of the currently available equipment (Baker and Croot, 2010). Moreover, Yang and Yu (2008) have highlight loss processes that removes

oxalate from the aerosol. The destruction of oxalate during the production of soluble iron (Siefert and Sulzberger, 1991; Zuo and Hoigne, 1992, 1994; Zuo and Deng, 1997; Kunkely and Vogler, 2001; Cwierntny et al., 2008) can explain the lack of correlation between the %SFe and oxalate concentration in field studies. Laboratory studies of Saydam and Senyuva (2002) showed an increase in the quantity of soluble iron with oxalate during in-cloud photochemical reduction simulations. Additionally, the effect of oxalate on iron dissolution has focused on pure iron oxide species and ambient aerosol particles (e.g., Pehkonen et al., 1993; Siefert et al., 1994). For all of these studies, the observed effect of oxalate on iron dissolution can be directly explained by light-induced dissolution of Fe(III)-oxides as demonstrated in the soil chemistry literature (e.g. Furrer and Stumm, 1986; Sherman, 2005). However, Journet et al. (2008) have recently emphasized the role of clays, especially illite, as a major provider of soluble iron during dust deposition in non-reductive conditions at the expense of iron oxide. Considering the positive effect of oxalate on iron oxide dissolution, the contribution of clay to soluble iron inputs could be lower. Consequently, a quantitative relationship between oxalate and dust iron solubility is questionable.

The purpose of this paper is to estimate the potential role of organic complexation as atmospheric process playing on dust iron solubility during transport. We investigated the effect of oxalate on iron dust solubility by experimental dissolution in rainwater conditions. The solubility was estimated from the fine fraction of various Saharan source materials, which mimic dust particles before transport. Furthermore, similar experiments were conducted on pure minerals to characterize the influence of aerosol mineralogical composition on iron solubility in wet deposition.

## 2. Materials and methods

### 2.1. Sources of dust particles

African source materials consisted of the sieved fine fraction of soil (diameter < 20 µm) collected in known dust emission sources from Niger (13°31'N; 2°38' E), Tunisia (33°32' N; 9°58' E), Morocco (59°51' N; 05°48' W) and Algeria (Hoggar region, detailed in Guieu et al. (2002)). This particle size range is considered to be the part of soil that can be carried through the atmosphere for long-range transport. We chose different sources of dust particles as a good representation of the iron-containing mineral aerosols that reach the North Tropical Atlantic Ocean. The various geographic positions provide differences in the mineral composition and iron content. The elemental composition (Table 1), notably the mass iron content in these materials, was determined by X-ray fluorescence spectrometry (Panalytical).

### 2.2. Mineralogical composition

The distribution of iron in dust between the oxides/hydroxides (oxide iron or free iron) and aluminosilicated phases (structural

**Table 1**

Elemental composition of the different studied soil \*Mean values between our measurements and those of Guieu et al. (2002).

	%Fe	%Al	%Si	%P	%Ca	%Na	%K	%Mg	%Ti	%Mn
Banizoumbou	3.1%	4.9%	33.0%	0.03%	0.30%	0.22%	1.2%	0.23%	1.1%	0.06%
(+/-)	0.2%	0.8%	0.7%	0.01%	0.14%	0.01%	0.2%	0.05%	0.2%	0.01%
Matmata	1.9%	4.2%	19.6%	0.03%	14.6%	0.23%	1.2%	1.4%	0.4%	0.04%
(+/-)	0.3%	0.1%	0.2%	0.01%	0.3%	0.03%	0.1%	0.2%	0.1%	0.00%
Hoggar*	5.0%	6.5%	26.5%	0.11%	1.8%	0.00%	1.8%	0.93%	0.80%	0.12%
(+/-)	0.0%	0.8%	0.01%							
Maroc	5.3%	8.4%	19.7%	0.07%	6.4%	0.21%	3.1%	3.0%	0.47%	0.09%
(+/-)	0.2%	0.5%	0.2%	0.03%	0.2%	0.08%	0.5%	0.3%	0.02%	0.02%

iron) was determined by the aerosol-adapted CBD (Citrate–Bicarbonate–Dithionite) method described by Lafon et al. (2004). The method uses the CBD reagent to dissolve free iron oxides selectively via reduction. This method is based on successive Ultrasonication and 80 °C water bath of filter containing dust particles (Lafon et al., 2004). Even if ultrasonication produces superoxide and H<sub>2</sub>O<sub>2</sub>, this method has been validated and is commonly used for the determination of the distribution of iron in dust.

In terms of the mineralogical origin of iron, X-ray diffraction analysis (Caquineau et al., 2002) and the diffuse reflectance method revealed the presence of different iron-containing minerals in the investigated soils. However, these analyses are not chemically quantitative and did not enable us to determine exactly the distribution of total iron among these different minerals. The characteristics of the studied soil samples described above are detailed in Table 2.

### 2.3. Pure minerals

In addition to soils, we also worked with three pure standard mineral phases: illite (AP135, Fithian Illinois); hematite from IRD Bondy; and Goethite (HS36, Biwabik, Minnesota) as described in Journet et al. (2008). Illite is one of the most abundant iron-containing minerals in dust particles (e.g. Chester and Johnson, 1971; Chester et al., 1972; Falkovich et al., 2001; Journet et al., 2008). Iron content in illite is generally under 5%. The Fe mass percentages in our commercial minerals are 3.38%, 57.48%, and 62.87% for illite, hematite and goethite, respectively.

### 2.4. Dissolution experiments

In order to measure the iron solubility, 15 ± 0.2 mg of material (soils or pure minerals) was placed into 1 L (Bottle LDPE or PP) of ultrapure water (Elga®) acidified at pH = 4.7 with 20 mL of sulfuric acid (Ultrapure, Normaton 2, Prolabo®). This pH value is characteristic of atmospheric conditions and is commonly used to mimic the release of trace metals from aerosol in rainwater (Desboeufs et al., 2001; Sarthou et al., 2003; Baker et al., 2006). The oxalate concentrations ranged from 0 to 8.10<sup>-6</sup> mol L<sup>-1</sup>, which are typical values found in rainwater (Sempéré and Kawamura, 1996; Tang, 1998; Hegg et al., 2002; Avery et al., 2006; Yang and Yu, 2008). Another set of experiments was carried out on Niger dust with ultrapure water acidified to pH 2 without oxalate to estimate the role of acid processing of dust on iron solubility.

For all of the experiments, after 60 min of contact time with automatic shaking and the solutions were filtered through a 0.2-µm Nuclepore® polycarbonate filter. The contact time have been determined in order to be in realistic conditions of a droplet lifetime (Junge, 1964; Sofikitis et al., 2004). We worked under artificial laboratory light (Philips - MASTER TL-D Super 80 18W-840 UNP),

**Table 2**

Chemical and mineralogical characteristics of iron in the studied source material (fine fraction of soils). The %Fe(oxide)/Fe(tot) corresponds to the % of total iron present as oxide in opposition to iron contained in aluminosilicate minerals (Clays, feldspar.) defined as structural Fe.

	%Fe	(+/-)	%Fe(oxide)/ Fe(tot)	Major iron-containing minerals
Niger	3.1%	0.2%	70%	Illite, goethite, hematite
Tunisia	1.9%	0.3%	55%	Illite, palygorskite, goethite, hematite
Algeria	5.0%	0.0%	51%	Illite, smectite, goethite, hematite
Morocco	5.3%	0.2%	47%	Illite, smectite, goethite, hematite

without UV-light emissions and therefore we avoid any UV light-induce dissolution.

Dissolved iron (DFe) concentrations were analyzed by GFSAA ATI-Unicam 929 with a detection limit of 0.03 µg L<sup>-1</sup> (Sofikitis et al., 2004). All experiments were performed in triplicate and under ultra-clean conditions. The pH values for all the samples were measured in solution after filtration (noted pH<sub>final</sub>) to characterize the experimental conditions after dissolution of carbonate-containing minerals, notably the calcite identified in Tunisian and Moroccan soils. Iron solubility % (SFe) was calculated as follows: (SFe) = (DFe/Fe<sub>tot</sub>) × 100, with Fe<sub>tot</sub> as the total mineral concentration of iron present in the material.

## 3. Results and discussion

### 3.1. Different source provides different iron solubility

The amount of dissolved iron (DFe) obtained by the dissolution experiments of different types of soils was used for the calculation of iron solubility. The solubilities (SFe) without oxalate ranged from 0.0025%(±0.0005%) to 0.04%(±0.01%) (Table 3). Our results are low and on the same order of magnitude as those found in the literature, indicating that soluble iron in soils represents about ~0.001%–0.5% of the total iron in typical environmental conditions (Fung et al., 2000; Bonnet and Guieu, 2004; Hand et al., 2004; Desboeufs et al., 2005). As previously reported in the literature, our results exhibited a large variability (a factor of 10) in iron solubility depending on the soil studied. However, these differences are not related to the experimental protocol and therefore are directly associated with the intrinsic properties of the studied particles. The values of Fe solubility are not related to either the total iron content or the percentage of oxide iron summarized in Table 2. In addition, no pH effect due to the neutralizing capacity of the material containing calcite ( $R^2 = 0.4$  between SFe and pH after adding of soil material) was observed. Cwiertny et al. (2008) revealed a difference in solubility related to desert dust source materials but in extreme conditions (pH 1). A simple solubility relationship was not observed for the basic source material characteristics for the soil samples used in their study. Therefore, we conclude that it is difficult to consider a single initial value of solubility for iron dust from each source region, even without the atmospheric processing effect. The results obtained for fine fractions of soil are also in agreement with recent works by Paris et al. (2010), which emphasize a high variability of iron solubility from dust aerosol sampled over African dust emission sources. Consequently, the source of dust seems to be a parameter that is equally or even more important than atmospheric processes in explaining the wide range of iron dust solubilities estimated in the literature. Therefore, we wanted to estimate the atmospheric process and its impact on iron dust dissolution.

**Table 3**

Iron solubility obtained for the experiments to various adding of oxalate and pH<sub>final</sub> obtained in average for the different dissolution experiments conducted at pH<sub>initial</sub> = 4.7. The pH around 7 measured for the soils of Tunisia and Morocco is due to the strong buffering power of calcite in these source materials.

Oxalate (µM)	%SFe Niger	(+/-)	%SFe Tunisia	(+/-)	%SFe Algeria	(+/-)	%SFe Morocco	(+/-)
0	0.04%	0.01%	0.01%	0.00%	0.01%	0.00%	0.0025%	0.0005%
1	0.08%	0.01%						
3	0.13%	0.01%	0.04%	0.00%	0.08%	0.00%	0.07%	0.01%
5	0.19%	0.01%	0.08%	0.01%	0.11%	0.01%	0.13%	0.01%
8	0.26%	0.01%	0.12%	0.01%	0.16%	0.01%	0.21%	0.02%
Average	4.71		7.1		5.0		7.0	
pH <sub>final</sub>								

### 3.2. Oxalate effect on dust particles

Fig. 1 shows a plot of the solubility over the oxalate concentrations for the studied soils. A positive linear correlation was observed between SFe and the oxalate concentration for all of the considered soil materials, suggesting a direct effect of oxalate on dust iron solubility. These results are in agreement with field observations (Chen and Siefert, 2004), which showed the highest iron labile fraction for the highest oxalate/Fe<sub>tot</sub> ratio. Previous laboratory work on the reactivity of iron indicated a positive effect of oxalate on light-induced dissolution of Fe from iron oxides/hydroxides (Sulzberger and Laubscher, 1995). Thus, photochemical reduction of Fe(III)-containing aerosols in the presence of an electron donor, such as oxalate, could explain the increase of iron solubility in aerosol (Zuo and Hoigné, 1992; Pehkonen et al., 1993). However, photochemical reduction of Fe(III)-oxalate complexes also leads to the formation of H<sub>2</sub>O<sub>2</sub> (Zhu et al., 1993; Sedlak et al., 1997). In dark conditions, the soluble Fe(II) formed is partially or totally oxidized back to Fe(III) by H<sub>2</sub>O<sub>2</sub> produced in the presence of light. Therefore, these authors concluded that oxalate has few effects on iron solubility in a global diurnal cycle, with higher production of Fe(II) during the day than at night. In our case, the experiments were conducted without additional white light but in artificial laboratory light, which is a new approach to study the contribution of oxalate on iron dust dissolution enhancement. Our results seem to emphasize that the light-induced reductive dissolution is not the principal process explaining the increase in iron solubility. At contrast, ligand-promoted dissolution by bidentate ligands as described by Stumm and Morgan (1996) could lead to increased iron solubility. These ligands can form relatively strong metal-organic surface complexes, which destabilize the Fe–O bond and lower the energy barrier for dissolution (Stumm and Morgan, 1996). This type of dissolution increases Fe bioavailability through the generation of dissolved forms of Fe(III) as Fe(Ox)<sub>n</sub>. Recent work of Xu and Gao (2008), show by an adsorption isotherm method, that the iron dissolution from hematite increases with increasing oxalate concentrations in link with the amount of adsorbed oxalate, as Fe(III)-oxalate complex, on the surface of hematite. Thus, they emphasized that the oxalate adsorbed on the surface of hematite conditions the iron dissolution. Due to the linear regression found in our work and based on conclusions of Xu and Gao (2008), we can suppose that the iron solubility is limited by the oxalate loading on

dust surface, suggesting a dissolution mechanism of iron by surface complexation with oxalate. Nevertheless, our experimental conditions are not comparable to the ones of previous studies, which have established the mechanism of ligand-promoted dissolution. First, at the contrary of Xu and Gao (2008), the oxalate concentrations applied are in a same order of magnitude than total iron content, then probably higher than soluble Fe pool in the soil particles. Moreover, unlike previous studies on iron dissolution mechanism in presence of ligands and iron oxides/hydroxides, we used a complex material composed by various minerals. These mineral probably release numerous elements in solution such as transition metals (Cu, Mn, Cr.) which could form oxalate complex and hence influence its effect on iron dissolution. Consequently, we need much more studies to conclude on the involved mechanism. As revealed by the slope of the plot in Fig. 1, the effect of oxalate was not similar for the various studied materials. With the same experimental conditions, the complexation had different effects on the iron dust solubility (Table 3). With the addition of 8 μM oxalate, the solubility of iron from the Niger samples increased from 0.04% ± 0.01%–0.26% ± 0.01% (Factor 6.5), whereas the solubility of iron from the Morocco samples was enhanced from 0.0025% ± 0.0005%–0.21% ± 0.02% (Factor 105). These observations suggest different effect of oxalate complexation with iron, as a function of dust source. The iron complexation with oxalate is pH-dependent, with higher complexation capacity to low pH (Xu and Gao, 2008). The buffering effect of dust particles is known and can affect the dissolution of iron (Ito and Feng, 2010). Among our samples, the samples from Morocco and Tunisia present a buffering capacity due to the carbonate content (Table 3). If we study the case of Niger and Morocco samples, the most effective dissolution occurs for the second one, which presents a more neutral final pH (Table 3). Thus, the pH dependence does not explain the observed difference on oxalate effect. These results emphasize the possible link between the intrinsic properties of iron within the dust and its solubility.

### 3.3. Iron mineralogy and oxalate effect

The slopes in Fig. 1 revealed no positive correlation between the percentage of iron oxides and oxalate. Consequently, the oxalate effect is not directly related to iron oxide content in soils. In contrast, our results showed lower effects from additional oxalate

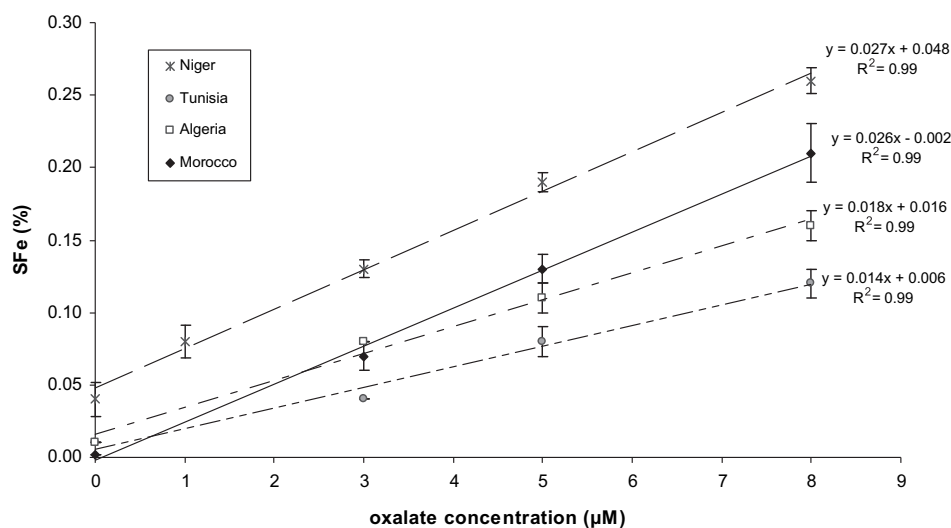


Fig. 1. Comparison of soluble iron with oxalate concentration for different source materials.

with higher proportions of iron from crystalline iron oxides, suggesting that other iron-bearing minerals could control the iron solubility in dust particles. This idea is in accordance with the work of Journet et al. (2008) and Schroth et al. (2009) showing that the solubility of iron contained in clays rather than in oxides/hydroxides species controlled the dust iron solubility. The values of the Fe(oxides)/Fe(tot) ratio are most important for the Niger soil, meaning that the iron is mainly issued from oxides/hydroxides, as commonly observed in dust from the Sahel region (Lafon et al., 2006; Formenti et al., 2008; Lazaro et al., 2008). By contrast, the other soils presented ratio values around 50%, which is typical of Saharan dust (Lafon et al., 2006; Formenti et al., 2008; Lazaro et al., 2008). Spectral diffuse reflectance analysis of these soils indicated that the iron oxides are hematite and goethite, with goethite being the most abundant. Of the structural iron-containing minerals in desert dust (Kandler and Schutz, 2007; Coz et al., 2009), our X-ray analysis revealed the presence of illite, smectite or palygorskite only. It was difficult to study the link between the dust iron solubility and mineralogical state of iron because of the variety of clays present in the studied source material (Table 2). The distinguishing feature of the Niger soil made these samples very useful for further studies because illite was the only clay containing iron.

Dissolution experiments were carried out on pure illite, goethite and hematite following the same protocol as used for the fine fraction of soils. The materials used for the experiments in this section are commercial pure minerals (see Materials and Methods section), and it has been highlighted that it contains no significant amorphous iron (Journet et al., 2008). This parameter was required to better compare with iron dust dissolution results and stick to the work of Journet et al. (2008). Even at a more neutral pH, these experiments confirmed the work of Journet et al. (2008), which highlighted greater solubility of iron coming from illite than that from iron oxides/hydroxides. In terms of amount of dissolved iron, we found that even if hematite or goethite are mainly composed by iron, illite provides the greater quantity of dissolved iron (Table 4). Additionally, our results showed that regardless of the oxalate concentrations, the iron solubility from illite is much higher than that of hematite and goethite, which display similar solubility values (Fig. 2). Therefore, in our experimental conditions the formation of amorphous iron, which is more soluble didn't seem to be the factor that influences the amount of dissolved iron, contrarily to the work of Shi et al. (2009, 2011). Iron solubility in the pure phases as well as in the soil material presents a positive linear correlation with the oxalate concentration (Fig. 2). The slopes of the plot in this figure indicate that the effects of oxalate on the solubility of iron from oxide or from illite are not similar. Iron dissolution from illite is more sensitive to oxalate than Fe-bearing clay, indicating that ligand-promoted dissolution seems to be more efficient for iron aluminosilicated minerals than for iron oxides and hydroxides. Therefore, as observed by Journet et al. (2008) at extreme pH, it appears that crystalline iron oxides have a very low solubility in comparison to iron from illite, even with a pH value and oxalate content corresponding to realistic atmospheric conditions. The higher iron solubility with illite is explained by the

differences in the iron coordination in clays and in crystalline iron oxides (Chester et al., 1993; Journet et al., 2008; Schroth et al., 2009). Iron, in hematite and goethite is bound to oxygen atoms. In illite iron has been identified, in substitution of aluminum in the octahedral site or potassium in the inter-sheets structure (Johnston and Cardile, 1987). Then the higher solubility for this mineral is explained by the weaker bounds of iron in the structure than in crystalline iron oxides.

We conclude that illite is a major mineral provider of soluble iron in dust. Soluble iron input from dust deposition is currently modeled from hematite dissolution (Meskhidze et al., 2003, 2005) and/or estimated from a set value (Gao and Anderson, 2001; Gao et al., 2003; Fan et al., 2006). Consequently, based on the new information highlighted in this paper concerning mineralogical and chemical atmospheric processes, the mineralogical composition of iron should be considered in the atmospheric iron deposition model. To create pertinent models, it is necessary to constrain the iron solubility parameter depending on the mineral type.

### 3.4. Iron dissolution parameterization

The influence of oxalate on iron solubility has been recently modeled globally (Luo and Gao, 2010). This model links oxalate to NSS-Sulfate then to an anthropogenic source. In this paper, we have highlighted that oxalate is produced by many anthropogenic or natural precursors, and the mixing with dust particles in the atmosphere is possible. Consequently, we suggest a simple calculation of iron dust solubility that could be included in the dissolved iron module (e.g., Meskhidze et al., 2005). A linear positive relation was obtained for iron solubility from dust and from pure mineral (Figs. 1 and 2). Therefore, we assume that the total iron solubility can be parameterized as the sum of iron solubility of each pure mineral

$$SFe_{Dust} = \sum(\%Fe_{Mi} \times SFe_{Mi}),$$

with  $M_i$  corresponding to pure iron-bearing minerals in the soil sample.

Considering that structural iron in Niger soil (Table 2) is mainly illite and that goethite is representative of iron oxide, the theoretical SFe for Niger soil can be calculated from the experimental pure mineral solubility:

$$SFe_{Niger} = (\%Fe_{illite} \times SFe_{illite}) + (\%Fe_{hematite} \times SFe_{hematite}).$$

The SFe is similar for goethite and hematite, with no significant difference observed between the calculated values if goethite is considered instead of hematite. We applied this relationship for each oxalate concentration (Fig. 2), and the results show a good agreement between the calculated and measured values of iron solubility for all oxalate concentrations. Our results show that more than 95% of total soluble iron from Niger soil results from illite-iron dissolution, and the oxide species having a low contribution to the total iron solubility. The agreement between the calculated and measured values shows that iron solubility parameterization from the dissolution of pure iron-containing minerals could be used to estimate the iron solubility in dust particles. All of these results indicate that the solubility of iron in aerosol samples is not linked to the amount of iron oxides, even in presence of atmospheric processing with oxalate complexation. Based on these results, the variability observed in response to an increase of oxalate concentration between various soil samples seems to be related to the different mineralogical forms of iron. Thus, even if oxides and hydroxides are the minerals with the highest Fe content, iron-containing clays are probably the main contributor of the atmospheric input of dissolved iron to the ocean,

**Table 4**

Iron solubility and dissolved iron amount, obtained for the experiments with pure iron-containing mineral to various adding of oxalate and for the different dissolution experiments conducted at  $pH_{initial} = 4.7$ .

Oxalate ( $\mu M$ )	%SFe Hematite	DFe ( $\mu g$ ) Hematite	%SFe Goethite	DFe ( $\mu g$ ) Goethite	%SFe Illite	DFe ( $\mu g$ ) Illite
0	0.0006%	$5.4 \times 10^{-2}$	0.0006%	$7.2 \times 10^{-2}$	0.17%	$8.7 \times 10^{-1}$
3	0.0009%	$8.1 \times 10^{-2}$	0.0008	$1.0 \times 10^{-1}$	0.41%	2.1
5	0.0014%	$1.3 \times 10^{-1}$	0.0010%	$1.2 \times 10^{-1}$	0.62%	3.2
8	0.0021%	$1.9 \times 10^{-1}$	0.0012%	$1.5 \times 10^{-1}$	0.83%	4.2

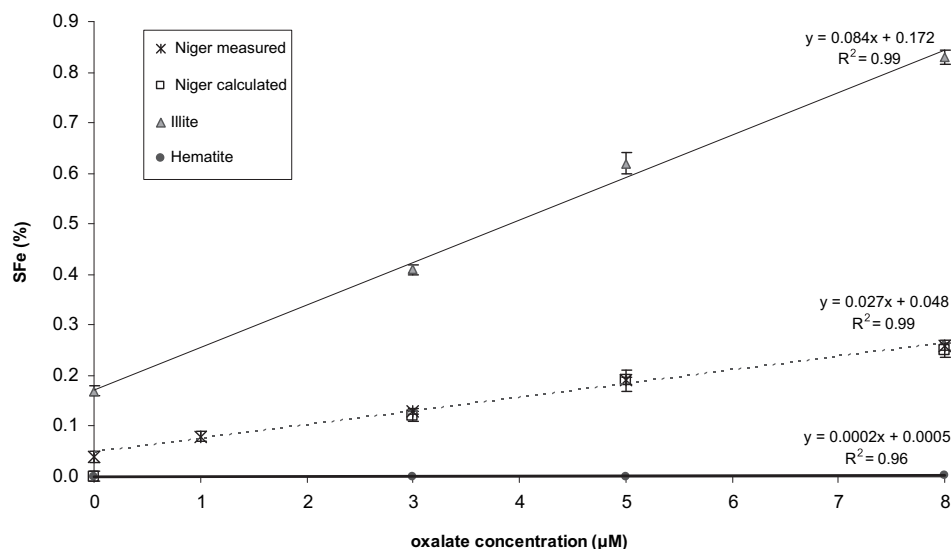


Fig. 2. Comparison of measured or calculated soluble iron with oxalate concentrations for Niger soil, illite and hematite.

even in the presence of atmospheric transport processing. The observation of the oxalate effect for all of the studied soils, but dependent on the soil source, highlights that organic complexation could play a significant role in dust iron dissolution, especially in the absence of influence from anthropogenic soluble iron.

### 3.5. Comparison with acid processing effect

The pH effect is known to influence dust dissolution significantly (Desboeufs et al., 1999). Recent modeling studies have shown that the acidification due to coating of  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  on the dust surface could be the atmospheric process responsible for a transformation of insoluble iron into soluble iron forms (Meskhidze et al., 2003; Solmon et al., 2009). These models are more representative of pollution event, but as oxalate might be partly produced by anthropogenic source it is interesting to compare proton-promoted dissolution to ligand-promoted dissolution. To assess the respective contribution of organic complexation and pH to iron dust dissolution, similar experiments were conducted on Niger soil without any addition of oxalate at the extreme pH of 2. The Niger soil does not contain calcite, a mineral known to buffer the aqueous phase during dissolution experiments and hence to induce an underestimation of the pH effect. The iron solubility found at  $\text{pH} = 2$  was  $0.24\% \pm 0.02\%$ . Therefore, the soluble fraction of Fe was on the same order of magnitude at  $\text{pH} = 4.7$  in the presence of  $8 \mu\text{M}$  oxalate as the soluble Fe fraction at  $\text{pH} = 2$  without oxalate (Table 3). However, rainwater usually has a pH of approximately 4.7 with a concentration of  $8 \mu\text{M}$  oxalate (e.g. Decesari et al., 2005). These observations suggest that organic complexation could have a similar, or even higher, effect than a reduced pH induced by a  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  coating on dust, on the flux of soluble iron to the ocean. Thus, these findings confirm the importance of considering oxalate complexation as a critical atmospheric process that impacts iron dust solubility.

## 4. Conclusion

Dissolution experiments were carried out on various desert source materials with a range of oxalate concentrations, mimicking atmospheric aqueous phase conditions. Our results show a large variability of iron solubility depending on the oxalate concentration and source material, due to the mineralogical distribution of iron in

the samples. The oxalate effect is linear with SFe for all of the studied dust, which could be directly related to the mechanism of ligand-promoted dissolution for iron oxides/hydroxides as well as iron illite. Our results confirm the recent conclusions of Journet et al. (2008) and Schroth et al. (2009) on the higher solubility in atmospheric conditions of iron trapped in the crystal lattice of clay than of iron contained in goethite or hematite. Therefore, we support the use of clay dissolution as the major source of dissolved Fe in biogeochemical models. From the experimental work, we established a parameterization enabling the estimation of iron solubility from mineral material based on the individual iron solubility of different minerals constituting the material. This parameterization was validated considering the effect of oxalate. Moreover, we highlight that the contribution of oxalate complexation on iron dissolution from dust particles could be as important as the acid processing effect. It is important to notice that oxalate is not a unique organic complexant of iron present in the atmosphere (Okochi and Brimblecombe, 2002). To improve the estimation of dissolved iron flux to the ocean, it is important to study the effect of identified atmospheric organic ligands on iron dust dissolution and to investigate the dissolution process of illite and other clays containing iron (such as montmorillonite) in the presence of organic ligands and at different pH values.

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