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Dissolution of atmospheric iron in seawater

Sophie Bonnet and Cécile Guieu

Laboratoire d'Océanographie de Villefranche (LOV), La Darse, Villefranche-sur-mer, Cedex, France

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[1] In vitro dissolution experiments were conducted in seawater in order to quantify the partitioning between dissolved and particulate phases of iron associated to Saharan dust and urban particles. The percentage of iron released was very low (0.05 to 2.2%) depending on the particulate load, the aerosol source and the contact time. This percentage decreased with the amount of particles introduced following a power law, indicating that the process could be modeled. Indeed, these dissolution processes were a function of the lability of iron in relation to the particle source, the particle size and adsorption processes. According to these experiments, the dissolved iron induced in a 10 m mixed layer by Saharan events of various magnitudes ranges from 0.07 to 1 nM. Since these concentrations are in agreement with the natural iron requirements for the phytoplankton, such inputs can profoundly influence the primary production, especially in oligotrophic conditions. *INDEX TERMS*: 4801 Oceanography: Biological and Chemical: Aerosols (0305); 1223 Geodesy and Gravity: Ocean/Earth/atmosphere interactions (3339); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 1635 Global Change: Oceans (4203); 1050 Geochemistry: Marine geochemistry (4835, 4850). **Citation**: Bonnet, S., and C. Guieu (2004), Dissolution of atmospheric iron in seawater, *Geophys. Res. Lett.*, 31, L03303, doi:10.1029/2003GL018423.

1. Introduction

[2] Studying the impact of atmospheric inputs in the water column is essential to understanding the biogeochemical cycles in the ocean. The atmosphere is actually an important way for the micro-nutrients such as iron to enter the ocean. Indeed, it is one of the major sources of iron in the ocean and probably the dominant one [Duce and Tindale, 1991]. The atmospheric iron source is associated with the constant emissions produced from the human activities close to populated areas plus additional sporadic 'pulses' of aluminosilicate mineral soil material coming from deserts.

[3] Within the framework of the research project of the European Commission ADIOS (Atmospheric Deposition and Impacts of pollutants, key elements and nutrients on the Open Mediterranean Sea), the objective of the present study was to mimic processes occurring in the Mediterranean water column after the aerosols deposition. In the present paper, we propose (1) a quantification of the dissolution processes in seawater of iron contained both in a Saharan dust and in anthropogenic particles, (2) an identification of the factors controlling the dissolution and (3) a comparison of the dissolved iron concentrations induced by atmospheric inputs with the iron requirements of the phytoplankton. The key point of these experiments

results from the fact that the final particle concentrations used (down to 0.01 mg.l^{-1}) were in agreement with those encountered in the natural environment.

2. Materials and Methods

2.1. Experiment

[4] Saharan soil with iron concentration of $4.5\% \pm 0.49\%$ in weight, representative of the Saharan aerosol carried over the Western Mediterranean Sea, was used for the in vitro experiments. A Standard Reference Material of the National Institute of Standards and Technology named 'Urban particles' with iron content of $3.91\% \pm 0.10\%$ in weight, was used as a proxy for anthropogenic aerosol.

[5] The dissolved iron concentration of the seawater used for the experiments was $0.38 \text{ nM} \pm 0.007 \text{ nM}$; this water has been collected in the Ligurian Sea at 40 meter depth with acid-cleaned polyethylene tubes using an Osmonics solid Teflon diaphragm pump and filtered through a Sartrobran-P-capsule containing a $0.45 \mu\text{m}$ prefilter and a $0.2 \mu\text{m}$ final filter. The Saharan dust and the anthropogenic particles were carefully homogenized in seawater prior to the experiment in order to obtain two mother solutions with particle concentrations of 10 mg.l^{-1} . Various amounts of these mother solutions were introduced into 500 ml filtered seawater inside opaque Teflon flasks in such a way that the 8 final particle concentrations (P_c) ranged from 10 to 0.01 mg.l^{-1} . This handling lasted for less than one minute and we assume that consequences on partitioning between particulate and dissolved fractions is negligible. Two exposure durations were chosen to simulate natural conditions: 24 hours and 7 days. These exposure durations were assumed to be representative of the contact time between the atmospheric particles and seawater [Ridame and Guieu, 2002]. During incubations, the flasks were stirred every 12 hours.

[6] 250 ml of each sample was then filtered after each incubation time through an acid-cleaned $0.2 \mu\text{m}$ Nucleopore membrane (polycarbonate, diameter 47 mm). Each filtered 'sample' was then acidified to pH 2 with 250 μl Ultrapur-Merk HCl (30%) for preservation until analysis. The samples were stored in acid-washed high-density polyethylene (Nalgene) bottles. All handling was performed in a clean laboratory under a laminar flow hood.

2.2. Analysis of Dissolved Iron (DFe)

[7] Dissolved iron concentrations were determined according to a chemiluminescence method adapted from Obata *et al.* [1993]. Two calibration curves were generated by adding increasing amounts of a standard iron solution to seawater with dissolved iron concentration equal to 1 nM: one curve for the low concentrations up to 2 nM (LD = 0.03 nM; blank = 0.10 nM) and the other for the high concentrations between 2 and 8 nM (DL = 0.13 nM; blank = 0.27 nM). For the

concentrations higher than 8 nM, the samples were diluted with the seawater. The detection limit was defined as 3 times the standard deviation of 10 replicates of the blank.

[8] The accuracy of the method was assessed using a NASS-5 standard (3.58 ± 0.60 nM certified value, 3.71 nM ± 0.001 nM determined, $n = 3$).

3. Results

3.1. Dissolved Iron Concentrations

[9] After 24 hours of contact time between seawater and Saharan particles, concentrations of DFe remained almost constant regardless of the amount of dust added. Values of ΔDFe ($[\text{DFe}]_{\text{after the introduction of particles}} - [\text{DFe}]_{\text{initial}}$) were negligible (Figure 1). For anthropogenic particles, ΔDFe was a function of the amount of particles introduced, with ΔDFe ranging from DL to 13.66 nM.

[10] After 7 days, the ΔDFe vs Pc relationship was linear with high correlation coefficients ($r^2 = 0.93$ and $r^2 = 0.99$ for Saharan and anthropogenic particles, respectively). The ΔDFe were much higher for the experiment involving anthropogenic particles: ΔDFe ranged from 0.15 to 4.87 nM for Saharan dust and 0.16 to 38.77 nM for anthropogenic particles.

3.2. Solubility of Iron in Seawater

[11] The percentages of iron released in seawater by Saharan and anthropogenic aerosols were extremely low (0.05 to 2.2%) and were inversely correlated to the amount of particles introduced following a power law (Figure 2). This was not observed for Saharan dust after 24 hours, for which very low and stable dissolution rates were found. The highest dissolution was reached after 1 week contact time for the lower Pc (0.01 mg.l⁻¹): 1.6 and 2.2% respectively for Saharan and anthropogenic particles.

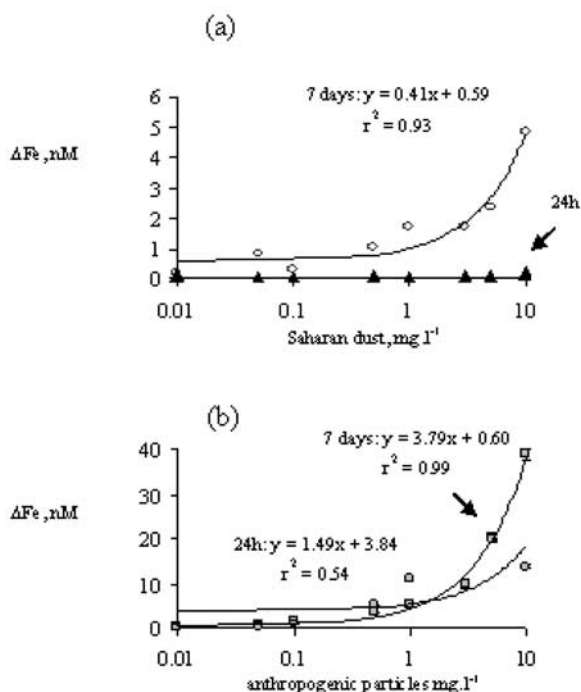


Figure 1. ΔDFe as a function of the amount of particles introduced in seawater for contact times of 24 hours and 7 days. (a) Saharan particles (b) anthropogenic particles.

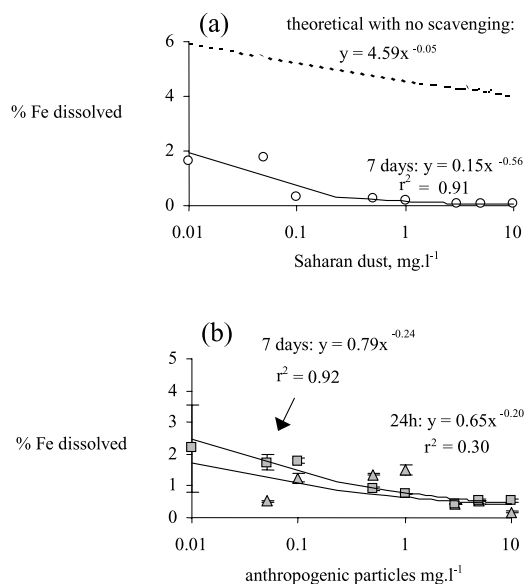


Figure 2. Percentage of iron under dissolved form as a function of the amount of particles introduced in seawater for contact times of 24 hours and 7 days. (a) Saharan particles (b) anthropogenic particles. $\text{DFe} (\%) = (\text{DFe} - \text{DFe}_{\text{initial}}) \times 100 / \text{Fe}_{\text{tot}}$ nM where DFe is the percentage of iron released in seawater, Fe_{tot} (nM) is the concentration of total iron [$(\text{Pc} \times \text{Fep} \times 0.001) / 55.85$] if 100% of the anthropogenic or Saharan iron dissolves. With: Pc = amount of particles introduced (mg.l⁻¹); Fep = particulate concentration of iron in each kind of particles (anthropogenic: Fep = 3.9% and Saharan: Fep = 4.5% in weight); 55.85 g.mol⁻¹ = atomic weight of iron.

[12] For anthropogenic particles, the iron dissolution process was relatively rapid, the solubility of iron being not statistically different after 24 hours or 7 days (t -test, $p > 0.01$, $n = 8$). For Saharan particles the dissolution rates after 24 hours were lower than those after 7 days (t -test, $p < 0.01$, $n = 8$).

[13] Iron solubility was also a function of the aerosol source: over the range of Pc considered, the mean solubility with anthropogenic particles (1.11%) was twice as much as the solubility with Saharan particles (0.53%) after 7 days.

4. Discussion

4.1. State of the Art

[14] Many authors have studied the dissolution processes of iron in natural or artificial rainwater or cloudwater but few experiments have been conducted directly in seawater or in ultra-pure water at pH 8 to mimic the dry deposition mode of particles (Table 1). However, a significant number of Saharan events carry very high amounts of dust in only a few drops of rainwater [Loye-Pilot and Martin, 1996]. In this case, the raindrops are evaporated immediately so the rainfall is not measurable and the main dissolution process will occur in seawater. Nevertheless, strict dry deposition is also a highly effective mechanism of dust deposition in several regions (up to 56% in the eastern Mediterranean Sea; Kubilay et al. [2000]. Although Zhuang et al. [1990] have reported a high dissolution rate of iron ($\sim 50\%$) in filtered seawater at pH 8, most authors suggest that iron solubilization from atmospheric aerosols is extremely low.

Table 1. State of the Art

Authors	Type of particles	Ultrapure water	Seawater	pH	Amount of particles (mg.l ⁻¹)	Dissolution (%)
<i>This study</i>	Saharan		X (filtered)	8	0.01 to 10	0.001–1.6
<i>Guieu and Thomas</i> [1996]	Saharan	X		6–8	10 to 1000	0.001–0.02
<i>Spokes and Jickells</i> [1996]	Saharan	X		8	32	<0.013
<i>Zhuang et al.</i> [1990]	Saharan		X (filtered)	8	/	50
<i>This study</i>	Anthropogenic		X (filtered)	8	0.01 to 10	0.2–2.2
<i>Hardy and Crecelius</i> [1981]	Anthropogenic		X (filtered)	8	/	1–8
<i>Crecelius</i> [1980]	Anthropogenic		X (filtered)	8	1	7–8

To our knowledge, this study reports the first data for iron dissolution associated with realistic Pc i.e., representative of atmospheric input after dilution in surface seawater. The solubility of iron decreases with the increasing amount of particles introduced following a power law. Typically, this type of result could be integrated into models which take into account the atmospheric compartment.

[15] Our study suggests that dissolution is lower for iron attached to Saharan particles than to anthropogenic particles. To our knowledge, only two studies have reported on the dissolution rates of iron from anthropogenic aerosols and these indicated that the dissolution is higher (up to 8%) than for natural mineral dust [*Crecelius*, 1980; *Hardy and Crecelius*, 1981]. Our results also show the same tendency with the ‘Urban particulate matter’ but with a much lower percentage of dissolution (maximum 2.5% for lowest Pc).

4.2. Factors Controlling the Solubility

[16] **Scavenging.** Two simultaneous physico-chemical processes occur when aerosol particles enter the seawater: dissolution of iron from the aerosol particles and adsorption of DFe at the surface of these particles. Considering the adsorption capacity of 27 nmol.mg⁻¹ of mineral particles [*Zhuang and Duce*, 1993], the theoretical concentration of DFe as a function of the amount of particles added if the scavenging processes did not exist was calculated. These theoretical concentrations would be ~20 times higher than what was actually measured in the experiment involving Saharan particles after 1 week (Figure 2a). Concerning the undetectable dissolution of iron from Saharan dust after 24h, scavenging may have been equal to dissolution which can explain the net dissolution rate equal to zero.

[17] **Lability related to the origin of the aerosol.** Our experiments showed that the solubility of iron associated to anthropogenic particles is twice as much as the solubility of iron associated with Saharan particles. Most authors have shown the same feature with other metals [*Guieu et al.*, 1994] in the case of Mn, *Chester et al.* [1993] in the case of Cu, Zn and Pb). According to these last authors, higher solubility of metals from urban-rich than from crust-rich aerosols is due to the fact that metals are more exchangeable

in anthropogenic particles. In our study, we can suspect that most of the iron contained in the urban particles is present under exchangeable oxides forms located at the surface of the particles, whereas in the desertic particles a large part of the iron is contained in refractory aluminosilicates. Even if the Saharan mineral soil used in the present study is more iron-rich than the urban particulate matter (4.5% against 3.9%), the fraction of exchangeable iron being greater in the urban particles could explain the observed differences.

[18] **Relation to particle size.** It has been recognized that anthropogenic particles are finer than natural ones. Hence large particles are dominant in mass in the atmosphere but small anthropogenic particles are more important considering the number of particles. *Lindberg and Harris* [1983] showed that the solubility in seawater of Cd, Mn, Pb and Zn was inversely proportional to the particle size of the aerosols. The reason for this behavior is unclear but may result from the fact that the surface to volume ratio is inversely proportional to the size of the particles and that the chemical composition of a given aerosol is not constant as a function of its size, the amount of H⁺ ions delivered in seawater being higher with small size particles. Anthropogenic particles such as those used in our experiments are sulfate-rich. After their immersion in the seawater, sulfuric acid is delivered into the aqueous phase enhancing the dissolution processes of iron adjacent to the micro environment of the particle.

[19] **pH.** High iron solubilities were reached at pH 1 to 2. These values are typical of cloudwater but only rise to ~5% of the total aerosol iron in Saharan aerosols [*Spokes et al.*, 1994; *Spokes and Jickells*, 1996] and up to 17% for urban aerosols [see for example *Dedik et al.*, 1992]. The average iron solubility in rainwater, which typically has pH values from 4 to 7, has been established to ~15% [see for example *Colin et al.*, 1990].

[20] The much lower iron solubility obtained in our experiments may be related to the high pH of seawater (8.18), the iron hydroxide solubility in these conditions being extremely low. *Zhu et al.* [1992] suggested that ferric ion solubility from hematite varies from a factor 10¹³ when the pH varies from 1 to 8.

Table 2. Concentration of Dissolved Iron as Calculated by the Power Law, Induced by Extremely Low to Strong Saharan Dust Events (According to Data From *Ridame* [2001] and *Loye-Pilot and Martin* [1996])

Magnitude of the Saharan event	Final dust concentration in the 10 m mixed-layer (mg.l ⁻¹)	Dissolution (%)	Input of dissolved Fe (nM) for the mixed layer (10 m) calculated from the power law (Figure 2a)
Extremely low	0.001	7.2	0.07
Very low	0.005	2.9	0.15
Low	0.01	2	0.2
Medium	0.1	0.5	0.5
Strong	0.5	0.2	1

[21] In addition, variations in pH during the experiments are a possibility. Even though, due to the buffering capacity of seawater, no pH variation could have been detected in our samples along the duration of the experiment, we strongly suspect that the pH values in the close micro-environment around the particles could have been modified, influencing the dissolution processes. In the experiment conducted with Saharan dust, by dissolution of CaCO_3 the pH may have increased [Loye-Pilot *et al.*, 1986; Guieu and Thomas, 1996] or decreased in the experiments conducted with anthropogenic type particles (due to the sulfuric acid associated with urban particles [Loye-Pilot and Morelli, 1988]: these effects may have respectively limited or enhanced the iron dissolution processes in the micro environment of the particles.

4.3. Saharan Input of DFe vs Phytoplankton Iron Requirements

[22] Iron limitation has not been demonstrated for the Mediterranean sea, but Sarthou and Jeandel [2001] have established a typical nutrient-like profile in the Ligurian Sea (NW Mediterranean) in May, during a period of phytoplankton bloom, suggesting that the low iron concentrations at the surface may limit the primary production or control the phytoplankton species composition. Although most of the particle flux is under biological control [Buat-Ménard *et al.*, 1989], the residence time of the particles of atmospheric origin remains very long in the mixed layer because of the physical barrier created by the thermocline [Migon *et al.*, 2002] and thus a particle residence time of at least 7 days is probably realistic. This allows the calculation of the potential DFe induced following different scenarios (from extremely low to strong Saharan events) in a 10 meter mixed layer (Table 2). Despite the very low dissolution rates, the mineral particles can release significant quantities of DFe (0.07 to 1 nM) into the ocean surface waters. These values can be compared to the natural iron requirements for phytoplankton. The K_{μ} value (half saturation constant for growth) represents for a given nutrient, the concentration below which the phytoplankton growth is limited by this nutrient. The K_{μ} for iron depends on many factors such as the size of the cells, the species composition of phytoplankton or the co-limiting factors such as light or nitrogen form and availability. Subsequently, data proposed in the literature are highly variable. For example, considering only natural community, K_{μ} was estimated to 0.03 nM Fe in the Equatorial Pacific phytoplankton community which is dominated by small algal cells [Price *et al.*, 1994]. In contrast, in environments dominated by large diatoms, K_{μ} was estimated to 1.2 nM Fe [see for example Timmermans *et al.*, 2001]. Hence the phytoplankton requirements, particularly for environments dominated by small species, seem to be in agreement with the potential inputs of DFe in the surface layer after a Saharan event. Saharan inputs could thus profoundly influence primary production, especially during the season characterized by a stratified water column and low primary productivity. Under these conditions, the atmosphere becomes the main pathway of macro and micro-nutrients to the surface mixed layer.

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S. Bonnet and C. Guieu, Laboratoire d'Océanographie de Villefranche (LOV), La Darse, BP 08, 06238 Villefranche-sur-mer, Cedex, France. (sbonnet@obs-vlfr.fr; guieu@obs-vlfr.fr)