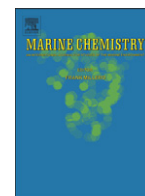


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# Marine Chemistry

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## Review article

# Atmospheric and marine controls on aerosol iron solubility in seawater

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## ARTICLE INFO

### Article history:

Received 9 May 2008

Received in revised form 11 September 2008

Accepted 12 September 2008

Available online 27 September 2008

### Keywords:

Aerosol iron

Solubility

SOLAS

Experimental methods

## ABSTRACT

The fraction of atmospherically deposited iron which dissolves in seawater, or becomes available to phytoplankton for growth, is a key determinant of primary productivity in many open ocean regions. As such this parameter plays an important part in the global oceanic cycles of iron and carbon, and yet the factors that control iron dissolution from aerosol are very poorly understood. In this manuscript we seek to synthesise the available knowledge of these factors, which operate in the atmosphere and in seawater. A conceptual model of the overall aerosol iron solubility is presented, in which we liken the various controls on iron solubility to sets of parallel electrical resistors. We also discuss experimental methods for the determination of iron solubility and make recommendations for future studies in this area.

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## 1. Introduction

Iron (Fe) is a co-factor in many enzyme systems of marine photosynthetic organisms, playing a role in photosynthesis, respiration and nitrogen fixation (Falkowski et al., 1998; Morel and Price, 2003). Yet the solubility of Fe in oxic seawater is extremely low (Liu

and Millero, 2002). Iron concentrations are now recognised to be low enough to limit primary productivity in several ocean regions (e.g. the Southern Ocean and equatorial and sub-Arctic Pacific) (Coale et al., 1996; Boyd et al., 2000, 2007), or to control rates of nitrogen fixation in other regions, due to the relatively high Fe demand of the nitrogenase enzyme (Sanudo-Wilhelmy et al., 2001; Kustka et al., 2003). Although riverine inputs of Fe to the coastal ocean are very large, this input is rapidly removed, so that the primary source of Fe to the remote deep ocean is probably via atmospheric transport of soil dust, most of which originates from desert regions (Jickells et al.,

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2005). Atmospheric dust concentrations, and hence the dry or wet deposition of dust to the ocean, are highly variable in both space and time (Prospero and Lamb, 2003; Jickells et al., 2005), but in the context of this discussion are relatively well understood. Much less well constrained is the fraction of the iron contained in atmospheric deposition which is soluble in seawater and / or available to marine photosynthetic organisms. Indeed, aerosol Fe solubility remains a key uncertainty in our understanding of the marine Fe cycle, and through the links between Fe metabolism and primary production, the marine carbon cycle. (This discussion focuses primarily on the soluble fraction of Fe, although we recognise that there is evidence that some organisms appear to be able to utilise particulate Fe directly (Kraemer et al., 2005)). Calculations based on estimates of total dust iron inputs and total oceanic iron inventory, indicate that the global average aerosol iron solubility is ~1–2% (Jickells and Spokes, 2001), while estimates of aerosol iron solubility based on small-scale experimental work fall over a huge range (0.001–80%; Jickells and Spokes, 2001; Mahowald et al., 2005). It appears that Fe solubility in remote marine aerosols is significantly higher than in soil source materials (Zhuang et al., 1992).

The overall solubility of Fe in seawater is controlled by a number of complex interactions both in the atmosphere and ocean. Some of the factors implicated are: aerosol source / mineralogy (Spokes et al., 1994; Baker et al., 2006b; Sedwick et al., 2007; Cwertyny et al., 2008; Journet et al., 2008), atmospheric chemical / photochemical processing (e.g. Pehkonen et al., 1993; Zhu et al., 1993; Spokes et al., 1994; Spokes and Jickells, 1996; Desboeufs et al., 1999; Mackie et al., 2005), aerosol size (Siefert et al., 1999; Johansen et al., 2000; Chen and Siefert, 2004; Baker and Jickells, 2006), seawater dissolved Fe concentrations (Liu and Millero, 2002), seawater Fe binding ligand characteristics (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Croot and Johansson, 2000), aqueous phase dust concentration (Zhuang et al., 1992; Spokes and Jickells, 1996; Bonnet and Guieu, 2004; Mackie et al., 2005) and biological influences from bacteria and phytoplankton and grazing effects (Barbeau et al., 1996; Marshall et al., 2005; Kustka et al., 2005; Rose et al., 2005). In this work we discuss these various atmospheric and oceanic influences on aerosol iron solubility and suggest a conceptual model with which to describe their combined effects. We also suggest experimental approaches which we hope might prove useful in the study of this complex system.

In the course of writing this review we came across a critical difference between the atmospheric and oceanic communities regarding the term *solubility*. For both sets of researchers solubility is experimentally operationally defined by measuring metal concentrations in the filtrate after passing a sample through a filter (typically 0.2 or 0.4  $\mu\text{m}$ , though increasingly now 0.02  $\mu\text{m}$  or 200 kDa). The results of these experiments are typically reported differently between the communities: Oceanographers report the *concentration* of metal that passed through the filter as the solubility (e.g. 150 pM) and thus solubility in this case might be considered to be the maximum potentially obtainable dissolved metal concentration in the study system. Atmospheric scientists present their results as the *fraction* of metal that will dissolve from an aerosol sample (i.e. the metal content in the filtrate divided by the total metal content of the aerosol added to the solution: e.g. 2%). In this manuscript we use the terms *fractional solubility* for the atmospheric case and *concentration solubility* for the oceanographic case. We also use the term *solubility* in the general sense (i.e. independently of the atmospheric or oceanic definitions) or when either definition could apply.

## 2. Atmospheric controls on iron solubility

We first examine the physicochemical processes affecting aerosol, as these are likely to have an important potential influence on aerosol iron solubility changes in the atmosphere.

Atmospheric particles occur in the size range 0.01–100  $\mu\text{m}$ , although the vast majority of aerosol mass is in particles larger than

~0.1  $\mu\text{m}$  (Seinfeld and Pandis, 1998; Raes et al., 2000). We consider only these larger particles here, which are often further divided into two size classes that are of importance in the consideration of aerosol iron fractional solubility: the so-called coarse and fine mode particles. Coarse mode particles are generated by abrasion and elevation of bulk materials. In the marine atmosphere sea spray generation as a result of bubble bursting is a significant source of coarse mode aerosol, while the generation of mineral dust aerosol during high-energy wind events over desiccated, exposed (desert) soils is the major mechanism by which iron-containing particles enter the atmosphere. Bulk emission results in highest concentrations, in terms of particle numbers, in the 0.1–1  $\mu\text{m}$  range, while highest mass concentrations are in the >1  $\mu\text{m}$  fraction (Raes et al., 2000). The dominant formation mechanism of fine mode particles is growth through coagulation of, and condensation on, smaller particles. Fine mode particles are thus predominantly formed by gas-to-particle conversions. The fine and coarse modes strongly overlap in the diameter range of ~0.1–1  $\mu\text{m}$  (Raes et al., 2000).

### 2.1. Acid processing

Atmospheric sulphuric and nitric acids are derived from oxidation of precursor gases ( $\text{SO}_2$  from combustion processes or from oxidation of dimethyl sulphide, or  $\text{NO}/\text{NO}_2$  also from combustion). Sulphuric acid is a major component of freshly nucleated particles and hence is found predominantly in the fine mode. In the terrestrial atmosphere nitric acid follows similar behaviour, but in the marine atmosphere it reacts rapidly with sea spray and enters the coarse mode (Andreae and Crutzen, 1997; Dall'Osto et al., 2004).

Thus, in the marine atmosphere, the dominant aerosol generation mechanisms tend to produce a segregated system in which sulphuric acid resides on particles much smaller than those containing most of the aerosol iron, while nitric acid is present in (coarse mode) seaspray. Aerosol size-class distinctions are a little less clear cut than this in practice; for instance the breaking of bubble films at the sea surface introduces sea spray into the fine mode, albeit in much smaller quantities than found in the coarse mode, and high temperature anthropogenic activities can also produce fine mode iron particles. A very small proportion (in mass terms) of mineral dust aerosol also exists in particles <1  $\mu\text{m}$  (Raes et al., 2000). The overlap in size distributions between the fine and coarse modes, and the less than ideal separation efficiency of size-segregating aerosol sampling equipment (Rader and Marple, 1985), makes a complete separation of the two populations impossible.

Aerosol chemical composition is also likely to be an important factor for the enhancement of iron fractional solubility through acid processing. Much aerosol sulphate is in the form of ammonium salts (Quinn et al., 1990; Ooki et al., 2007): data from several meridional transect cruises in the Atlantic Ocean showed a median fine mode  $\text{NH}_4$ : non-seasalt (nss—the fraction of total concentration not derived directly from seaspray emission)  $\text{SO}_4$  ratio of 1.5 (Bell et al., in preparation). The uptake of nitric acid into coarse mode sea spray (the sea salt displacement reaction (Andreae and Crutzen, 1997), Eq. (1)) results in the lowering of sea spray pH to some extent, but eventually leads to loss of HCl to the gas phase (Keene et al., 1998).



Thus neither nss  $\text{SO}_4^{2-}$  nor  $\text{NO}_3^-$  concentrations can be used in isolation to give a reliable indication of aerosol acidity.

Complexation of Fe(III) by organic ligands such as formate, acetate and oxalate promotes the photo-production of more soluble Fe(II), with the organic ligand acting as the electron donor (Erel et al., 1993; Pehkonen et al., 1993; Zhu et al., 1993; Siefert et al., 1994). When these Fe(III) complexes form at particle surfaces photo-reduction results in the release of Fe(II) into solution. In the case of oxalate, Fe(II) can be

consumed during the subsequent production of  $\text{H}_2\text{O}_2$ , and the  $\text{H}_2\text{O}_2$  produced is capable of further oxidation of Fe(II). Reactions with other organic components, for example methanesulphinic acid (Johansen and Key, 2006), may help to stabilise Fe(II) in solution. Aerosol organic components may also have more subtle effects on aerosol iron solubilization, e.g. through the influence of organic surface films on uptake of (acid) gases into the aerosol aqueous phase (Smoydzin and von Glasow, 2007).

Aerosol chemical interactions are also controlled by the so-called mixing state of the aerosol population (Andreae et al., 1986). Most (filtration-based) aerosol sampling techniques allow the determination of the overall chemical properties of an aerosol population (or fraction of that population in the case of size-segregation techniques). If the chemical composition of each particle in the population is the same as the bulk composition of the population, the population is said to be “internally mixed”. An “externally mixed” population is one composed of particles with a diverse range of chemical compositions, which are effectively averaged to that of the bulk by the sampling process. In the context of acid enhancement of aerosol iron fractional solubility, internal mixing of the acidic and mineral dust components of the aerosol population is an essential prerequisite.

Atmospheric aerosol populations rarely exist in purely internally- or externally mixed states, but do tend to progress towards the internally mixed state as the population ages. The processes responsible for this increase in internal mixing include condensation of gaseous species on pre-existing particles and in-cloud processing of particles. In-cloud processes include reactions in the aqueous phase of activated (i.e. wet) particles (e.g. uptake of  $\text{SO}_2$  and subsequent oxidation to sulphuric acid (Pandis et al., 1990)) and scavenging of non-activated (dry) particles into activated particles (Seinfeld and Pandis, 1998). Identification of aerosol mixing state in the field can only be achieved using single aerosol particle mass spectrometers. For instance, aerosol mass spectrometer studies over the Atlantic indicate that mineral dust aerosol is externally mixed close to Saharan sources, but internally mixed with nitrate and sulphate at Mace Head on the west coast of Ireland (M. dall’Osto, pers. comm., 2007). Aerosol mass spectrometers however cannot be used for the determination of aerosol iron solubility.

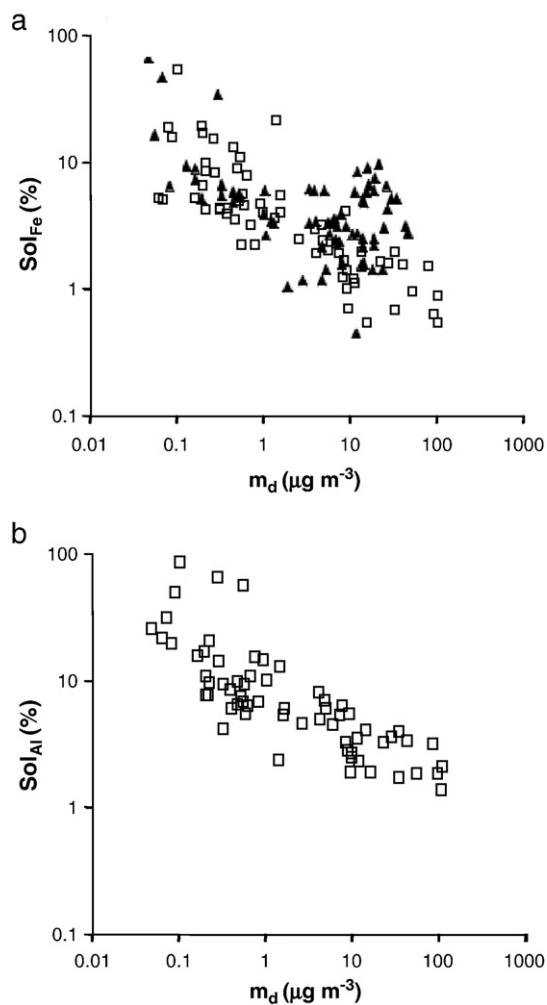
Laboratory simulation studies (Spokes et al., 1994; Spokes and Jickells, 1996; Desboeufs et al., 1999; Mackie et al., 2005) indicate that iron release from aerosol increases rapidly after pH is lowered and is greater at lower pH (Zhuang et al., 1992; Desboeufs et al., 1999), although the release is largely reversible when pH is raised (Spokes et al., 1994; Mackie et al., 2005). The rate determining step for acid enhancement in the atmosphere may therefore be the rate of internal mixing of dust and (free) acid species. This mixing probably occurs by different mechanisms in different environments. Saharan dust advected over the Atlantic is entrained into air that already contains anthropogenic acids emitted from southern Europe and North Africa (Savoie et al., 1989; Raes et al., 2000), so that the acid species are probably largely established in the aerosol population before dust entrainment. Asian dust is often transported over regions of intense industrial emissions before passage over the Pacific, so that in this case the dust probably provides a significant surface area for direct uptake of acid species from the gas phase. In both cases at least part of the acid taken up by dust particles will be neutralised by  $\text{CaCO}_3$  minerals in the dust (Zhu et al., 1992; Li et al., 2006), although these minerals are present in variable quantities depending on dust source (Bergametti et al., 1989; Chiapello et al., 1997). Biomass burning and fossil fuel combustion have been suggested to be potential sources of aerosol Fe (Guieu et al., 2005; Luo et al., 2008) with perhaps higher Fe fractional solubility than that of mineral dust, similarly to other anthropogenic sources of aerosol Fe (Spokes et al., 1994; Sedwick et al., 2007). This enhanced solubility may result from alteration of the Fe-containing particles during combustion or subsequent processing of the particles in the combustion plume.

Motivated by the potential link between acid processing and iron solubility, a number of workers have sought to correlate aerosol iron fractional solubility and acid species concentrations in field data (e.g. Hand et al., 2004; Baker et al., 2006a,b). These attempts have not provided strong correlations, prompting some to question the significance of acid processing as a control on iron fractional solubility in the environment (Baker and Jickells, 2006). However it seems likely that at least two factors would combine to obscure any such relationship in field data, even if acid processing were the primary atmospheric control on iron fractional solubility. First none of these studies had access to information regarding the mixing state of the aerosol collected, so that physical contact between the iron- and acid-bearing components of the aerosol could not be confirmed. Second, (potential) solubility enhancement during transport over the ocean must also occur simultaneously with deposition of acids and dust particles (whether of enhanced solubility or not) so that simple correlations between acid concentrations and iron solubility seem unlikely. A recent modelling study exemplifies this problem. Luo et al. (2005) simulated aerosol iron fractional solubility enhancement by various mechanisms, but failed to find any significant correlations between fractional solubility and sulphate concentrations even when sulphur chemistry was the sole driver of solubility enhancement in the model.

## 2.2. Physical controls

Chen and Siefert (2004) and Baker and Jickells (2006) have noted an inverse relationship between iron fractional solubility in Atlantic aerosol and atmospheric mineral dust concentrations (Fig. 1a). Noting the similarity in iron fractional solubility of samples collected over the remote North and South Atlantic (regimes with very different acid concentrations), Baker and Jickells (2006) proposed a physical control on aerosol iron solubility: preferential removal of larger particles during long-range transport leads to alteration of the mineral aerosol size-spectrum. Thus at lower dust concentrations the modal size of the dust population is smaller and the population has a correspondingly larger surface area to volume ratio, and hence a greater proportion of its iron content close enough to the particle surface to dissolve. While there was some observational data to support the suggested changes in size distribution at mid- to high-dust concentrations (see Baker and Jickells, 2006), acquisition of such data at low dust concentrations is hampered by both the low quantities of mineral dust involved and the likelihood, after long-range transport, of mineral particles being internally mixed with other aerosol components. Thus at low mineral aerosol concentrations determination of the size of the mineral particles, as opposed to the size of the internally mixed, mineral-containing particles, is particularly difficult.

As with acid processing reactions, it may not be possible to unambiguously confirm that particle size effects are solely responsible for the relationship shown in Fig. 1a. Decreasing mineral aerosol concentration is largely a function of atmospheric transport, so that some other transport-related process may also contribute to the observed trend in iron fractional solubility. For instance, atmospheric transport is associated with a shift in dust mineralogy from (large) quartz to (smaller) clays (Glaccum and Prospero, 1980) and it has recently been observed that clays appear to have higher Fe fractional solubility (Journet et al., 2008). Indeed the fractional solubility trend may arise as a result of a combination of chemical and physical processes. The passage of dust particles through clouds likely results in the dissolution of iron minerals on the particle surface and subsequent reprecipitation of iron in the form of smaller, less structured and more soluble particles (Zhu et al., 1992; Sulzberger and Laubscher, 1995). The similarity of Fig. 1a to the corresponding relationship for aluminium (Al, an element without redox chemistry) (Fig. 1b) does however appear to imply that the contribution of redox processes to aerosol iron fractional solubility is relatively minor,



**Fig. 1.** Percentage of soluble aerosol a) iron and b) aluminium at pH 4.7 as a function of mineral aerosol atmospheric concentration ( $m_d$ ) over the Atlantic Ocean. Data from Chen and Siefert (2004) (solid triangles) and Baker and Jickells (2006) (open squares). (Dust concentration for the data of Chen and Siefert (2004) has been converted from Total Fe concentration by assuming that dust contains 3.5 wt.% of Fe).

although redox chemistry will be an important influence on dissolved Fe speciation.

The solubility of Fe in rainwater (defined as the fraction of rainwater Fe that passes through a 0.45  $\mu\text{m}$  or 0.2  $\mu\text{m}$  filter) is often reported to be higher than that of Fe in aerosol (Jickells and Spokes, 2001 and references therein; Baker et al., 2007), and this may be due to the relatively low pH of rainwater. The physical mode of Fe deposition to the ocean might also be expected to have some influence on Fe solubility, since wet and dry deposited Fe presumably pass through the sea surface microlayer in different ways and might thus interact differently with the high concentrations of organic matter in that layer. We are not aware however of any studies which demonstrate such an effect.

### 3. Oceanic controls on iron solubility

#### 3.1. Solubility of iron in seawater

The concentration solubility of Fe(III) in natural waters is under strong pH control with a pronounced minimum around pH 8 where the sparingly soluble neutral species  $\text{Fe}(\text{OH})_3$  is formed (Jolivet et al., 2004). This minimum in iron concentration solubility at ambient seawater pH is the major reason why dissolved iron is found in such

low concentrations compared to other natural waters. Many studies over the years have examined via dialysis or filtration experiments the concentration solubility and inorganic speciation of iron in natural waters (Byrne and Kester, 1976; Fox, 1988; Schwertmann, 1991). There has been a recent resurgence of such studies in seawater, starting with work by Kuma et al. (1996), that inspired firstly review articles (Millero, 1998; Byrne et al., 2000) and then new laboratory experiments in NaCl (Liu and Millero, 1999), in seawater solutions (Liu and Millero, 2002; Sunda and Huntsman, 2003), and direct assessment in open ocean seawaters (Kuma et al., 1998a,b, 2000; Nakabayashi et al., 2001, 2002; Tani et al., 2003). These studies have helped to more precisely determine both the concentration solubility of Fe in seawater but also the hydrolysis constants for the different inorganic Fe species present as a function of pH, temperature and ionic strength (Liu and Millero, 2002; Sunda and Huntsman, 2003). Fe(III) solubility is strongly controlled by the concentration of these inorganic iron species, usually denoted as  $\text{Fe}'$ , and they are also important for estimates of iron bioavailability (Hudson and Morel, 1990; Hudson et al., 1992).

The reduced form of iron, Fe(II), while being more soluble than Fe(III), is rapidly oxidized (seconds to minutes) in oxygenated seawater by  $\text{O}_2$  or  $\text{H}_2\text{O}_2$  (Millero et al., 1987; Millero and Sotolongo, 1989; Gonzalez-Davila et al., 2006). This oxidation is also strongly temperature dependent with longer half-lives (hours to days) in cold polar waters (Croot and Laan, 2002; Croot et al., 2005). While concentrations of Fe(II) are expected to be low (sub pM) in most waters, it does provide a route by which Fe can be cycled from insoluble to more soluble phases (see below).

Direct measurements of iron concentration solubility in coastal seawaters indicate that concentrations of up to  $\sim 4$  nM of Fe can be supported before precipitation occurs (Kuma et al., 1996, 1998b, 2000). In open ocean waters much lower iron concentration solubility values are found, typically around 1–2 nM (Kuma et al., 1996; Nakabayashi et al., 2002; Tani et al., 2003), but this is still well above the concentration solubility limit of 0.1–0.2 nM found in seawater free of organic complexing agents (Kuma et al., 1996; Liu and Millero, 2002; Sunda and Huntsman, 2003). These values have important implications for aerosol deposition as it strongly indicates that the amount of organic ligands present in the seawater is a major control on soluble iron supply.

#### 3.2. Solubility control by organic complexation

The maximum concentration solubility of iron in seawater is controlled by the presence of strong iron-binding ligands. Most of the information we have on iron complexing ligands in seawater has been provided by cathodic stripping voltammetric competitive ligand exchange (CSV-CLE) methods (Gledhill and van den Berg, 1994; Rue and Bruland, 1995; Croot and Johansson, 2000) which only provide information on ligand concentration and conditional stability constants. One study using solid-phase extraction techniques was able to identify functional groups belonging to siderophore forming compounds (Macrellis et al., 2001). Further evidence for siderophores comes from laboratory studies performed by Butler and co-workers who have isolated and structurally identified many different siderophore compounds from marine bacteria in culture (Reid and Butler, 1991; Martinez et al., 2000, 2001, 2003; Butler et al., 2001; Ito and Butler, 2005). More recently siderophores, marine and terrestrial, have been identified in marine waters by capillary electrophoresis (Kosakowska et al., 1999; Mucha et al., 1999) and electrospray mass spectrometer techniques (Gledhill, 2001, 2007; McCormack et al., 2003; Gledhill et al., 2004).

However not all iron-binding ligands need be siderophores, as evidence exists for other potential complexing agents which, though weaker than siderophores, may be present in sufficient concentrations to increase iron concentration solubility. Potential ligands in this class

include degradation products of chlorophylls (Hutchins et al., 1999b), heme complexes (Gledhill, 2007) and oxidation products of carbohydrates (Walters and Hedges, 1988; Nakabayashi et al., 1993; Hung et al., 2001) which may form dissolved or colloidal organic complexes of iron. Indeed ligands in the colloidal size range, such as transparent exo-polymeric (TEP) substances (Passow, 2002), which are known to influence thorium speciation (Azetsu-Scott and Niven, 2005), may be particularly important in supplying bioavailable iron to phytoplankton (Boye et al., 2005).

The presence of iron-binding ligands in seawater can also enhance the dissolution of solid iron phases (Yoshida et al., 2002; Kraemer, 2004; Kraemer et al., 2005). Such dissolution may be further enhanced in the sea surface microlayer due to the presence of ligands, surfactants (Carrasco et al., 2007) and enhanced photochemical processes (Borer et al., 2005). The role of the sea surface microlayer in enhancing aerosol dissolution is complicated to assess but remains an important aspect of study, as all aerosols must pass through this barrier.

Fig. 2 illustrates the potential influence of organic chelators present in seawater on the percentage of the aerosol iron dissolved. The results shown in Fig. 2 are a maximum however, as normally the iron-binding ligand will already be chelated with iron and kinetic effects will also be very important. Recent data from off the coast of West Africa, collected before and after a Saharan dust storm, point to the importance of this effect (Rijkenberg et al., 2008).

### 3.3. Importance of nanoparticle and colloid size

Studies of iron concentrations in seawater have traditionally been based on assessing the dissolved phase operationally defined by a 0.4 or 0.2  $\mu\text{m}$  filter. Later studies have shown the importance of both soluble and colloidal iron concentrations within this operational defined dissolved phase (Kuma et al., 1998b; Nishioka et al., 2001; Wu et al., 2001). In the absence of organic chelation iron can form stable nano-particle clusters (Gilbert et al., 2007). For a pure iron colloid or nanoparticle the dimensions of the particle influences solubility because as a particle becomes smaller, the surface area to volume ratio increases. The larger surface area allows a greater interaction with the solvent and increases the solubility (Schwertmann, 1991). Iron has also been found associated with organic colloids (>3 nm) in river water (Hasselov et al., 1999) and coastal seawaters (Stolpe et al., 2005) but it is unclear whether this is iron bound to an organic matrix or a mixture of iron colloids and organic colloids.

### 3.4. Post-deposition processing of particles: residence time, photochemistry, superoxide and grazing

Post-depositional processes can also solubilize iron from recently deposited aerosols before they have passed through the mixed layer.

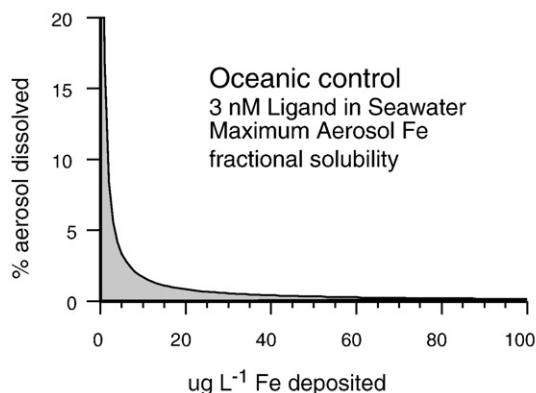


Fig. 2. Simple mass balance model for thermodynamic control of aerosol dissolution with 3 nM strong Fe ligand in seawater assuming oceanic control of iron solubility.

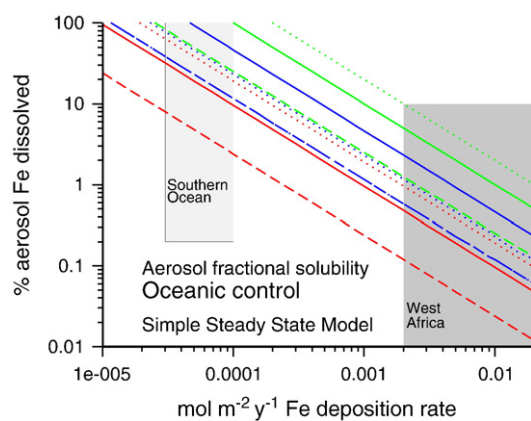
Critical to understanding and quantifying these processes is determining the residence time of different iron species in the euphotic zone to assess the potential relevance of each process for supplying soluble iron. Estimates for the residence time of particulate Fe in surface waters under the Saharan dust plume (Croot et al., 2004b) suggest a dependence on the particle flux with residence times as short as 6 days in high flux regions. Residence times for dissolved Fe in surface waters are typically on the order of a year (Jickells, 1995; Croot et al., 2004b; Chase et al., 2006), while estimates for Fe', based on ligand kinetics, are significantly shorter at 2–6 h (Wu and Luther, 1995; Witter and Luther, 1998) indicating a strong cycling of inorganic Fe within the water column.

Chief amongst the post-depositional processes which influence iron biogeochemistry is photochemical reactions in the sunlit surface ocean which are important for maintaining bioavailable iron in the mixed layer. Several studies have shown that colloidal iron can be directly photo-reduced, producing Fe(II) (Waite and Morel, 1984; Wells et al., 1991) which is subsequently oxidized to Fe(III) and either reforms smaller Fe colloids or is bound to an organic chelator. Organic iron complexes in seawater may also undergo photo-reduction (Kuma et al., 1995; Barbeau et al., 2001, 2003; Barbeau, 2006; Rijkenberg et al., 2006) with reduction of the iron and oxidation of the ligand, however in some cases the modified ligand may still be able to bind Fe (Barbeau et al., 2001). The presence of high concentrations of organic Fe complexes in seawater can lead to high steady state Fe(II) and dissolved iron concentrations (Kuma et al., 1992; Ozturk et al., 2004).

Indirect reduction of iron species in seawater can occur via production of the reactive oxygen species superoxide ( $\text{O}_2^-$ ). This is produced through photochemical formation of excited states of dissolved organic matter which react with  $\text{O}_2$  in seawater (Zafriou, 1990; Voelker and Sedlak, 1995; Rose and Waite, 2006). Superoxide can act as both a reducing agent and an oxidizing agent for iron (Rush and Bielski, 1985) and is also formed by oxidation of Fe(II) by  $\text{O}_2$  (Millero et al., 1987). Photochemically produced  $\text{O}_2^-$  has been shown to be able to reduce particulate Fe (Voelker and Sedlak, 1995; Fujii et al., 2006). Superoxide can also be produced via enzymatic action in bacteria and phytoplankton (Marshall et al., 2005) and recent investigations have focused on whether  $\text{O}_2^-$  is produced in response to iron stress in order to convert colloidal iron into more bioavailable forms (Kustka et al., 2005; Rose et al., 2005). However present evidence suggests this is a relatively inefficient process (Shaked et al., 2005). A combination of photo-reduction and photo-production of  $\text{O}_2^-$  has been implicated in the apparent extended lifetime of Fe(II) in iron enrichment experiments in the Southern Ocean (Croot et al., 2001, 2005).

Iron contained in colloids and particles, including Fe in phytoplankton, may be ingested by zooplankton, where the action of digestive enzymes results in part of the Fe becoming soluble. Upon release from the zooplankton gut this Fe may subsequently be taken up by phytoplankton (Hutchins et al., 1993, 1995; Hutchins and Bruland, 1994; Barbeau et al., 1996). The dissolution of iron colloids by micro-zooplankton grazing has been shown to be important in iron cycling in coastal waters (Barbeau et al., 1996; Barbeau and Moffett, 1998, 2000). The low pH environment found in the food vacuoles of protozoan grazers (Fok et al., 1982) suggests that these species are more important for dissolving iron colloids than larger zooplankton (Hutchins et al., 1993, 1995; Hutchins and Bruland, 1994), such as krill (Tovar-Sanchez et al., 2007) where the stomach pH is higher. Grazing of phytoplankton by zooplankton may also release iron-binding ligands further increasing iron concentration solubility (Sato et al., 2007).

No matter what processes are occurring that dissolve the aerosol particle the maximum amount of iron that can be solubilized is determined by the concentration solubility of iron in seawater (assuming that the aerosol has the potential to supply this amount of iron). Fig. 3 illustrates the results of a simple model which combines



**Fig. 3.** Simple model of steady state aerosol iron fractional solubility under oceanic control of iron dissolution assuming a constant deposition rate. The diagonal lines represent isolines for the product ( $\eta$  units:  $\text{m y}$ ) of residence time and mixed layer depth (solid:  $\eta = 25$ , dotted:  $\eta = 50$ , dot-dash:  $\eta = 100$ , dashed:  $\eta = 400$ ). The maximal percentage solubility was determined by dividing the maximum molar amount of soluble iron in the mixed layer (either as solely inorganic or as  $1 \text{ nM FeL}$ ) by the molar amount of Fe deposited over the residence time and assuming steady state. The red lines indicate values of  $\eta$  where only inorganic solubility in tropical waters ( $25 \text{ }^\circ\text{C}$ ) is considered, the blue lines are for inorganic solubility in polar waters ( $4 \text{ }^\circ\text{C}$ ) and the green lines for solubility controlled by  $1 \text{ nM FeL}$ . The areas denoted by the light and dark gray shading indicate the range of aerosol deposition rates for the Southern Ocean and Saharan West Africa.

the residence time of iron in surface waters, the mixed layer depth and the aerosol Fe deposition rate to illustrate the differences in aerosol dissolution between solely inorganic concentration solubility and in the presence of organic chelators under steady state conditions. It is clear in Fig. 3 that in regions of low deposition higher aerosol fractional solubilities would be expected.

### 3.5. Scavenging of dissolved iron by particles

Scavenging of soluble and colloidal iron by particles is a major sink for dissolved iron in seawater (Johnson et al., 1997). However investigations of direct scavenging effects on iron or other trace metals in the ocean are, with the exception of the thorium isotopes, limited to a few conceptual studies (Honeyman et al., 1988; Clegg and Whitfield, 1990; Jannasch et al., 1996). Most approaches to understanding Fe scavenging have been model-based, either as general particle size compartment models (Clegg and Whitfield, 1990) or more recently by a constant scavenging rate for  $\text{Fe}'$  (Parekh et al., 2004; Dutkiewicz et al., 2005) optimised by comparison to deep water dissolved Fe profiles (Parekh et al., 2004). There are no reports of any field studies designed to examine the scavenging of dissolved iron by particles and only a handful of studies have examined iron scavenging in the laboratory (Honeyman and Santschi, 1991; Waychunas et al., 2005). Scavenging of iron will be strongly influenced by the chemical composition of the particle surface, with biota (e.g. cell surfaces) especially important. Of all the processes affecting aerosol dissolution in the ocean this is easily the least understood, but has key importance for experimental design as high mass loadings will see a particle concentration effect acting to lower the soluble and colloidal iron concentrations (Zhuang et al., 1992; Spokes and Jickells, 1996; Bonnet and Guieu, 2004).

### 3.6. Bioavailability of iron—the importance of speciation

The key factor driving the present studies into the solubility of atmospheric aerosols is in determining the supply of soluble iron to remote oceanic regions in connection with the iron limitation of primary productivity. The emphasis has been on soluble forms, since the paradigm has been that only these forms are bioavailable. The

most bioavailable form is believed to be the reduced form of iron,  $\text{Fe}(\text{II})$ , (Anderson and Morel, 1980; Shaked et al., 2005) which can be taken up directly into phytoplankton by metal ion transporters. The inorganic soluble species of  $\text{Fe}(\text{III})$  ( $\text{Fe}'$ ) are also bioavailable but are typically present at sub-optimal concentrations for phytoplankton growth (Brand et al., 1983; Sunda et al., 1991; Sunda and Huntsman, 1995). Organic complexed forms of Fe appear to vary in their bioavailability to different phytoplankton groups (Hutchins et al., 1999b; Maldonado et al., 2005) and require reduction of the Fe-organic prior to uptake (Maldonado and Price, 2001; Shaked et al., 2005). Strong Fe complexes such as the siderophore ferrioxamine B are apparently not bioavailable to most phytoplankton (Hutchins et al., 1999a; Wells, 1999) though some studies indicate Fe uptake is possible (Soria-Dengg and Horstmann, 1995; Soria-Dengg et al., 2001).

Amorphous colloidal iron hydroxides as well as colloidal  $\text{FePO}_4$  and  $\text{FeS}$  are less bioavailable than  $\text{Fe}'$  and the utilisation of these colloids by phytoplankton has also been found to vary with different phytoplankton taxa (Rich and Morel, 1990; Naito et al., 2005). Colloidal crystalline iron oxyhydroxides have been found to not support the growth of diatoms in laboratory experiments (Rich and Morel, 1990). Experiments with natural seawater colloids indicates that this size range can be an important source of Fe for phytoplankton (Nishioka and Takeda, 2000; Chen et al., 2003).

There have been only a few field or laboratory studies using natural aerosols to assess bioavailability. This includes natural dust samples (Blain et al., 2004; Mills et al., 2004; Herut et al., 2005), volcanic ash (Duggen et al., 2007) or soils processed to mimic aerosol particles (Visser et al., 2003). In all of these studies there have been differences in the response from the phytoplankton by species type, nutrient status and aerosol type.

Thus while soluble Fe is clearly the most bioavailable form of iron, aerosol iron can apparently supply important amounts of colloidal or nano-particulate iron which can be transformed via post-depositional processes into soluble Fe. Thus studies of aerosol deposition fluxes need to consider the size and chemistry of the deposited material.

## 4. Conclusions

### 4.1. A conceptual model of aerosol iron solubility control

In the preceding sections we have outlined some of the atmospheric and oceanic factors that control overall aerosol iron solubility. We liken the influence of these atmospheric and oceanic factors to a pair of resistors connected in series in an electrical circuit. Each is independent of the other, but together they control the overall “resistance” to iron dissolution in the water column. Thus we consider overall solubility to be determined by the combined effects of these two “partial solubilities”.

Similarly we compare the atmospheric and oceanic partial solubilities to sets of resistors connected in parallel (Fig. 4), with each partial solubility being controlled by the “lowest resistance” (i.e. the process leading to the most iron dissolution) of each set. In Fig. 4 we identify the atmospheric resistors as aerosol source / mineralogy, (photo)chemical processing, physical processing and kinetics / transport / mixing, but we recognise that several of these are probably interconnected. For instance, both chemical and physical processing are related to kinetics / transport / mixing. The oceanic resistors (dissolved iron concentration, iron-binding ligands, biota, suspended particulate concentration / adsorption, kinetics) are also interconnected, with examples being the release of iron-binding ligands by phytoplankton in response to atmospheric iron inputs (Croot et al., 2004a), or the release of iron-binding ligands by grazing (Sato et al., 2007).

Both partial solubilities are a function of air- or water-mass past histories and different combinations of atmospheric and oceanic partial solubilities (and hence different overall solubility) can be

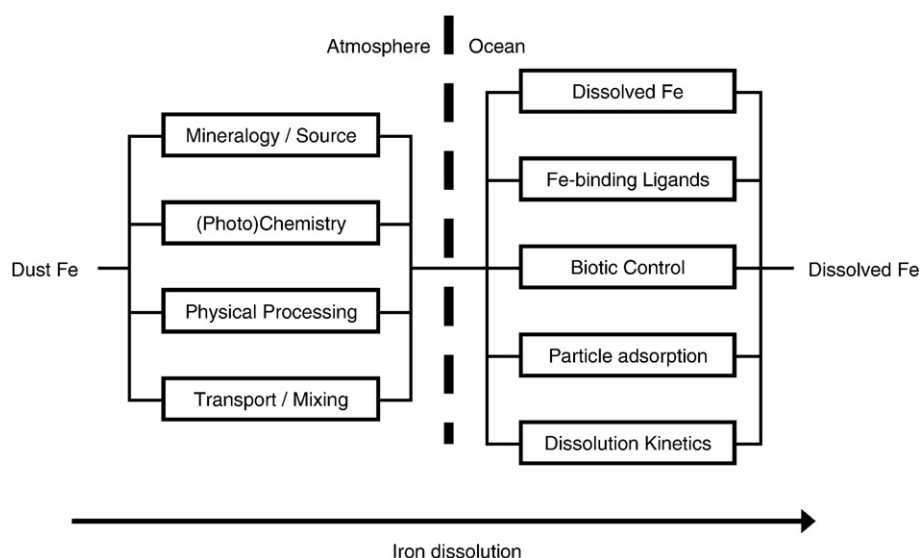


Fig. 4. Conceptual model of aerosol iron solubility controls, represented as electrical resistors. Descriptions of the individual resistors can be found in the text.

achieved via processes as simple as changing wind direction transporting aerosols of different characteristics to a water mass. When the concentration solubility of iron is oversaturated in the ocean with respect to the most soluble iron phase, then no more soluble Fe can dissolve from the aerosols. This is derived from simple thermodynamics and in this case the oceanic partial solubility dominates. However in most regions of the world, where deposition rates are low, this situation is probably never reached and so the solubility of the aerosols is the product of the atmospheric and oceanic partial solubilities.

#### 4.2. Experimental determination of aerosol iron solubility

In this discussion we have attempted to illustrate the complex factors that control overall aerosol iron solubility. This complexity undoubtedly contributes to the wide range of aerosol iron solubility estimates reported in the literature (Mahowald et al., 2005). However some of this variability in reported estimates must also be due to the diverse experimental approaches used for determination of aerosol iron solubility. Aqueous phases ranging in character from ultrapure water to pH buffered solutions to seawater have been used for leaching, while freshly collected, or stored, aerosol or sieved desert soil have been used to represent the solid component. For instance, Chen et al. (2006) recently demonstrated that the amount of Fe that could be leached from aerosol samples collected over the Gulf of Aqaba was significantly lower using seawater than when ultrapure water was used as the leachate. Differences in filter pore size (e.g. 0.45, 0.2 or 0.02  $\mu\text{m}$ ) used to separate solid and aqueous phases after leaching also strongly influence the fraction of Fe defined as soluble. These same methodological differences also exist in methods developed for assessing the leachates of volcanic ash as a recent review has shown (Witham et al., 2005). This diversity in experimental methods undoubtedly hinders efforts to make progress in this field, and we therefore examine experimental methods here in more detail.

In many ways the most “obvious” means to determine aerosol iron solubility is the direct exposure of an ambient aerosol sample to an aliquot of surface seawater. Such experiments, although conceptually simple, are extremely difficult in practice, requiring great skill to avoid potential contamination and to measure the tiny quantities of iron released with sufficient accuracy (Buck et al., 2006; Wu et al., 2007). The results of these experiments are also highly conditional on both their contributing atmospheric and oceanic partial solubilities (i.e. the

aerosol and seawater samples used in the experiment). These experiments provide the closest possible simulation of aerosol iron dissolution in the ocean but, given our current poor understanding of the partial solubility controls, we argue that they are impossible to interpret in the wider biogeochemical context, or to extrapolate to other conditions.

We suggest that more progress can be made towards understanding the controls on aerosol iron solubility using experiments designed to probe the atmospheric or oceanic partial solubilities individually. For (laboratory) determination of atmospheric partial solubility a protocol based on a simple leaching solution which is not subject to iron solubility constraints (as is seawater) would provide a means to short-circuit the oceanic partial solubility. Approaches similar to this have been successfully employed by several workers (Siefert et al., 1999; Johansen et al., 2000; Johansen and Hoffmann, 2003; Chen and Siefert, 2004; Hand et al., 2004; Baker et al., 2006a,b). Information obtained from these experiments should ideally also be augmented with a wide range of chemical (acid and alkali concentrations, mineralogy, pH) and physical (particle size, aerosol number / volume concentration) data, together with aerosol provenance information and, if possible, aerosol (external / internal) mixing status from supporting aerosol mass spectrometer measurements.

To some extent the characterisation of the iron biogeochemical parameters of the seawater sample (e.g. dissolved iron concentration, iron-binding ligands) can be used as a proxy for the determination of oceanic partial solubility. However the biotic and kinetic “resistors” are not so easily probed in this manner. In these cases, and for the determination of overall oceanic partial solubility, we consider that both standardised aerosol materials and a standard artificial seawater solution for use in dissolution experiments would be useful tools. Standard “aerosol” materials representative of the major desert dust sources and urban / industrial aerosols could be prepared relatively simply. For instance, fine fractions (<20–40  $\mu\text{m}$ ) of desert soils, which can be easily collected in large quantities, could serve as a first approximation for desert dust aerosols. Artificial seawater solutions with ultra-low iron levels are commonly used in several laboratories for the preparation of iron standard solutions (e.g. Fe chemostat growth experiments). A similar solution containing a standardised amount of a well characterised iron complexing ligand (e.g. desferrioxamine B, NTA, EDTA) could serve as a standard oceanic partial solubility leaching solution when run under a set of standard operating conditions. Both aerosol and seawater standards could then be used as benchmarks against which to compare aerosol iron

dissolution in ambient seawater. Analysis of the aerosol standard materials with both atmospheric and oceanic standard solubility protocols would enable the links between the two partial solubility protocols to be established.

In our view the establishment of standard tools (reference materials and protocols) is essential if progress is to be made in understanding aerosol iron solubility. Community discussion towards this goal is urgently required. Ultimately the fraction and chemical speciation of aerosol Fe that is bioavailable in seawater must be determined. This will require work on the biochemistry and kinetics of Fe uptake by a range of organisms, but such work lies outside the scope of this manuscript.

## Acknowledgements

Much of the content of this manuscript formed the basis for a Discussion Session at the SOLAS Open Science Conference, Xiamen in March 2007. We thank all the participants in that session, and Cécile Guieu and Rémi Losno in particular, for their contributions to the discussion. ARB was supported by NERC grant NE/E010180/1. PLC was supported by DFG grant CR145/11 and by SOPRAN (BMBF). We thank two anonymous reviewers for their comments on the manuscript.

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