

Iron solubility driven by speciation in dust sources to the ocean

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Although abundant in the Earth's crust, iron is present at trace concentrations in sea water and is a limiting nutrient for phytoplankton in approximately 40% of the ocean^{1,2}. Current literature suggests that aerosols are the primary external source of iron to offshore waters, yet controls on iron aerosol solubility remain unclear^{3,4}. Here we demonstrate that iron speciation (oxidation state and bonding environment) drives iron solubility in arid region soils, glacial weathering products (flour) and oil combustion products (oil fly ash). Iron speciation varies by aerosol source, with soils in arid regions dominated by ferric (oxy)hydroxides, glacial flour by primary and secondary ferrous silicates and oil fly ash by ferric sulphate salts. Variation in iron speciation produces systematic differences in iron solubility: less than 1% of the iron in arid soils was soluble, compared with 2–3% in glacial products and 77–81% in oil combustion products, which is directly linked to fractions of more soluble phases. We conclude that spatial and temporal variations in aerosol iron speciation, driven by the distribution of deserts, glaciers and fossil-fuel combustion, could have a pronounced effect on aerosol iron solubility and therefore on biological productivity and the carbon cycle in the ocean.

Aerosol particles constitute a major source of the micronutrient iron, the soluble fraction of which is required by phytoplankton for photosynthesis and nitrogen assimilation¹. Iron is thought to limit the biomass of phytoplankton populations in extensive regions of the ocean referred to as high-nutrient low-chlorophyll (HNLC) regions². Most terrestrial particulate Fe in the open ocean is thought to be derived from aerosols sourced in soils of arid regions, but recently a more complicated picture, with multiple source environments for aerosol Fe, has started to emerge^{5–7}. Although aerosol solubility could be heavily influenced by Fe speciation, which in turn could vary considerably among possible aerosol source environments, no such relationship has yet been clearly established, largely owing to a lack of direct measurements of particle speciation^{2,8,9}.

Here we use solubility experiments and synchrotron-based X-ray absorption spectroscopy (XAS) to examine the relationship between Fe speciation and solubility in samples from different aerosol source environments. African dust, Chinese loess, Alaskan glacial flour and oil fly ash were selected because they are representative of aerosol types transported to many HNLC waters^{4,5,10}. By coupling Fe speciation and solubility data, we provide the first direct examination of the effect of different source areas on the production of unique aerosol Fe species, which we demonstrate controls the solubility of Fe in such particles. It should be noted that other factors such as atmospheric and photochemical processing of particulates, aerosol particle size distribution, microbial processes and the concentration of organic

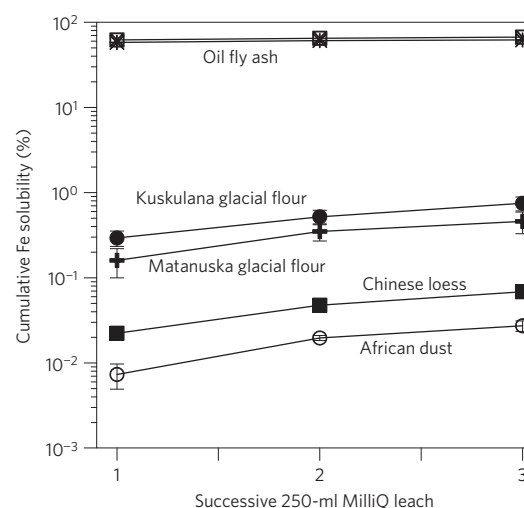


Figure 1 | Cumulative Fe solubility of successive leaches of sediment samples with 250 ml of MilliQ water. Leach experiments: circle, African dust; filled square, Chinese loess; plus symbol, Matanuska glacial flour; filled circle, Kuskulana glacial flour; multiplication symbol, oil fly ash PM; open square, oil fly ash PT1. Order of magnitude differences in cumulative Fe solubility by dust source are evident. The error bars are based on the standard error of triplicate leaches.

ligands in sea water have also been shown to influence particulate Fe solubility, but are not addressed in our experiments^{3,11,12}.

Our leaching experiments confirm that Fe solubility is highly variable and dependent on dust source (Fig. 1, Table 1). Iron in arid region soils was extremely insoluble with less than 0.1% total solubility after three leaches, a value consistent with previous studies (Fig. 1)^{7,11}. Cumulative solubility after 20 leaches remained low at less than 1% (Table 1). Iron in Chinese loess was roughly twice as soluble as in African dust (Fig. 1). Iron in glacial flour was an order of magnitude more soluble than Fe in arid soils, with total solubility reaching close to 1% after three leaches and up to ~3% after 20 leaches (Fig. 1, Table 1). Furthermore, Fe in glacial flour of the Wrangell Volcanic Field (Kuskulana Glacier) was consistently more soluble than Fe sourced in the metasedimentary and igneous rocks of the Chugach Mountains (Matanuska Glacier) (Fig. 1, Table 1)¹³. Iron in oil fly ash was extremely soluble, releasing almost 70% of the Fe in these samples during the first leach (Fig. 1). Oil fly ash sample PT1 has the lowest Fe content of any sample (0.86%), but released an order of magnitude more Fe in its first leach than did any of the mineral soil leachates (Table 1). Interestingly, in leachates of both glacial flours and the Chinese loess, the amount of Fe released was relatively constant over the duration of the 20-leach

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Table 1 | Iron content and solubility of materials used in this study.

Measurement	Glacial flour		Arid soils		Oil fly ash	
	Kuskulana Glacier	Matanuska Glacier	African dust	Chinese loess	PM	PT1
% Fe (wt)	5.0 (± 0.4)	4.6 (± 0.4)	4.2	4.0 (± 0.5)	3.78	0.86
Leach 1 ($\mu\text{g Fe} \cdot \text{g material}^{-1}$)	121 (± 31)	64 (± 17)	3.4 (± 1.9)	8.1 (± 1.9)	23,333	4,938
Leach 9 ($\mu\text{g Fe} \cdot \text{g material}^{-1}$)	78	44	bd	4.7	97	55
Leach 20 ($\mu\text{g Fe} \cdot \text{g material}^{-1}$)	86	47	bd	7.0	36	9.3
Cumulative % Fe solubility (20 250-ml leaches)	3.2	1.9	0.04	0.54	77	81

Cumulative solubility is based on 20 sequential 250-ml MilliQ leaches. The Fe composition in each material was determined by total digestion, with the exception of the African dust, which was based on a published value²⁶. Error ranges when presented are standard error values based on triplicate analyses. The initials bd indicate below detection limits when Fe counts in routine full run blanks constitute over 10% of the Fe counts measured in a leachate.

experiment, but the amount of Fe released from oil fly ashes in successive leaches decreased rapidly, with an order of magnitude decrease in Fe concentration by the second leach (Table 1).

With these solubility data in mind, we examined the speciation of Fe in each material. With the exception of oil fly ash sample PT1 at 0.86% Fe, the samples chosen for this study differed minimally in bulk Fe content (3.9–4.6%, Table 1). This indicates that the observed order of magnitude differences in Fe solubility between dust sources (Fig. 1) were not due to a difference in the total amount of Fe, but rather related to differences in the chemical form and reactivity of Fe in each sample. Although other studies have suggested that Fe mineralogy may influence aerosol solubility, they have relied on indirect methodologies (inconsistent operationally defined selective extractions, experiments with mineral separates, speculation based on solution compositions or bulk mineralogical characterizations) that have prevented a clear and definitive link between Fe speciation and solubility to be established^{9,14,15}. Here we use XAS, which enables us to directly analyse the partitioning of Fe species in complex heterogeneous matrices and quantify how Fe oxidation state and bonding environment vary among these samples¹⁶. Indeed, analysis of the XAS spectra of our samples indicates that the speciation of Fe in these samples is quite variable and highly dependent on aerosol source area (Figs 2, 3).

In both arid soil samples, XAS spectra indicate that most Fe is present in the oxidized or ferric(III) form (Fig. 2). Iron in the African dust sample is entirely associated with the pedogenic minerals ferrihydrite, goethite and haematite (Fig. 2). This is surprising, as other studies have suggested that Fe is structurally associated with silicate minerals in these dusts^{9,14}. Iron in Chinese loess also consists of a large fraction of ferrihydrite and goethite, but a significant fraction (~20%) is also associated with the primary mixed-valence silicate mineral hornblende, a phase that must be derived from the parent material of the loess (Fig. 2). In general, speciation data from arid soil samples indicate that Fe species in these dust sources are primarily partitioned as secondary ferric weathering products produced during pedogenesis in oxidizing soil environments, and the low solubility of Fe in these dusts is associated with the insolubility of these ferric precipitates. The higher solubility of the loess relative to the African dust is probably due to the presence of measurable ferrous silicate species (Fig. 2, Table 1)¹⁷. The relative abundance of these Fe(II)-bearing phases will be influenced by environmental factors related to soil formation (such as weathering regime and soil parent material composition), which will produce spatial variability in the speciation and solubility of Fe in arid dust storms^{17,18}. In addition, the ubiquity of ferrihydrite and low abundance of haematite (routinely differentiated and

quantified by extended X-ray absorption fine structure (EXAFS) analyses; Supplementary Fig. S1) in these samples suggests that ferrihydrite must be considered by the ocean modelling community as a common Fe phase associated with atmospheric deposition, as it differs substantially in solubility and chemical structure compared with haematite, which is often assumed the dominant iron form in dust input from arid regions^{19,20}.

Ferrous Fe(II) constitutes most (72–79%) of the Fe in glacial flour, and speciation is dominated by the primary mixed-valence mineral phases hornblende and biotite, along with lesser fractions of secondary clays and ferrihydrite (Fig. 2). These Fe species are typical of the bedrock mineralogy of the Chugach and Wrangell St Elias ranges and also indicate recent chemical alteration of glacial sediment²¹. Hence, dust storms from glacial valleys will have markedly different Fe species compositions compared with dusts from arid region soils. In glacial dust, Fe species primarily reflect the Fe mineral composition of mechanically weathered bedrock of the glacial catchment, rather than ferric alteration products in soils that have been exposed to earth surface processes for extended time periods. We attribute the higher relative solubility of glacial flour (Fig. 1) to most of the Fe being reduced and associated with primary or secondary silicate phases, which at circumneutral pH values should be more soluble than ferric (oxy)hydroxides^{17,22}. The composition of the glacially weathered bedrock clearly influences Fe speciation and related solubility. Kuskulana glacial flour contains a significant fraction (26%) of Fe-bearing smectite, a typical weathering product of volcanic ash deposits such as those found in the Wrangell Volcanic Field²³. Iron-bearing clays have been shown to be a relatively soluble phase with regard to Fe, and the presence of a significant fraction of ferrosmeectite in Kuskulana glacial flour could explain its higher Fe solubility relative to Matanuska glacial flour, which is derived from a catchment lacking large ash deposits (Figs 1, 2)¹³. These data confirm that Fe in clay minerals can be particularly important in providing bioavailable Fe to HNLC waters¹⁴, and that weathering environments conducive to the production of these phases in surficial materials are particularly fertile sources of bioavailable Fe dust loads. This work clearly demonstrates that glacially derived dust is a potentially important, albeit intermittent, source of relatively soluble Fe to HNLC waters proximal to terrestrial environments affected by active glacial weathering, owing to the dominance of relatively soluble Fe(II)-bearing silicates in these dusts. The transport of this type of material could explain the episodic diatom blooms that Boyd *et al.* hypothesized were induced by Fe fertilization from Alaskan-based dust at Ocean Station Papa in the North Pacific²⁴.

Iron in oil fly ash exists entirely in the ferric form (Fig. 2). However, EXAFS spectra are quite different from ferric iron in

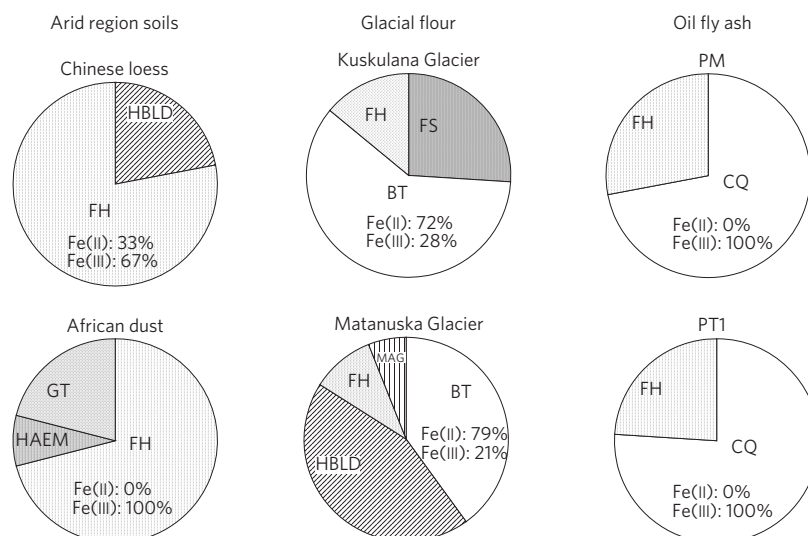


Figure 2 | Iron speciation of aerosol source samples used in this study. The oxidation state of Fe in each sample was determined on the basis of the calculated centroid of the pre-edge feature for each spectra. Iron species partitioning was determined by EXAFS analyses of spectra collected on beamline 11-2 at Stanford Synchrotron Radiation Laboratory. Iron species observed in these samples consist of biotite (BT), coquimbite (CQ), ferrihydrite (FH), ferrosmeectite (FS), goethite (GT), hornblende (HBLD), magnetite (MAG) and haematite (HAEM).

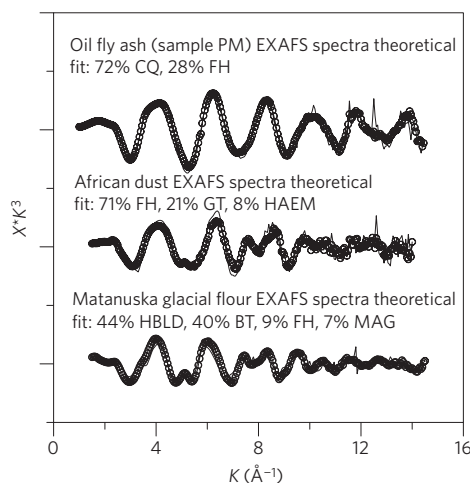


Figure 3 | Representative EXAFS spectra and theoretical fits used to determine Fe species partitioning in aerosol source materials. Fits (open circles) of sample EXAFS spectra (lines) were determined by least-squares fitting with combinations of spectra of known reference materials using the SixPACK interface. Standards consist of hornblende (HBLD), biotite (BT), ferrihydrite (FH), magnetite (MAG), goethite (GT), haematite (HAEM) and coquimbite (CQ). The error generated by SixPACK suggests that these fits are accurate within 5% for each phase. The error for the relative abundance of goethite and ferrihydrite in African dust is probably higher owing to similarities in structure and associated XAS spectra of these two minerals¹⁶.

arid soils (Fig. 3). Most of the oil fly ash Fe is associated with ferric sulphate salt ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9(\text{H}_2\text{O})$) typical of those found in acid sulphate environments²⁵. Such salts will be extremely labile in circumneutral solutions and Fe associated with these phases would be leached immediately. Indeed, the fraction of soluble Fe that is released by the fly ash samples in initial leaches is roughly equal to the total XAS-determined fraction of Fe associated with coquimbite, again confirming the relationship between Fe solubility and speciation in these samples (Figs 1 and 2). These data confirm field and modelling efforts that have suggested that fossil-fuel combustion products may be a particularly bioavailable source of Fe to HNLC waters⁴, in this case owing to the presence of unique and labile Fe species, Fe(III) sulphate salts.

Our results also suggest that the speciation of Fe in particles affects the residence time required for particles to release the bulk of their bioavailable Fe loads. Iron associated with ferric sulphate salts in oil fly ash will immediately dissolve on entering the water column owing to high species solubility (Table 1, Fig. 2). However, consistent release of Fe by mineral soil dusts containing Fe(II)-bearing primary and secondary silicate minerals over 20-leach experiments may imply a relatively constant supply of soluble Fe while these materials are suspended and recirculated through the photic zone of HNLC waters (Fig. 2, Table 1). Furthermore, the total bioavailable Fe of mineral soil Fe may be influenced by the residence time and circulation of these ferrous silicates within the photic zone of HNLC waters.

The implications of this work for understanding the input of Fe to the ocean are profound. Aerosol Fe solubility is strongly influenced by the partitioning of Fe species in particle loads, which can produce variations in Fe solubility of at least three orders of magnitude in the particulates chosen for this study, and can explain a substantial component of the large range of aerosol Fe solubility observed in nature. In the context of global change, as the glaciers of the world recede, it is likely that the flux of this relatively soluble Fe source will change. Increased industrialization and fossil-fuel combustion in developing countries (such as China and India) could provide an increase in soluble aerosol Fe species to regions of the ocean. Global expansion of arid regions would increase the flux of aerosol Fe to the ocean, but these aerosols would provide relatively insoluble Fe species compared with those supplied by glaciers or fossil-fuel combustion. Clearly, global change has the potential to have an enormous impact not only on the flux of particulate Fe, but also on the speciation and related solubility of the Fe input to the ocean from the atmosphere, with implications for marine productivity and the carbon cycle.

Methods

Sample collection and preparation. Alaskan glacial flour samples were collected at the toe of the Matanuska Glacier in the Chugach Mountains and the Kuskulana Glacier in the Wrangell Volcanic Field. African dust was collected from a buoy in the northeast Atlantic Ocean, as described in detail by others²⁶. Chinese loess was provided by B. Puecker-Ehrenbrink, from the Shanxi region of the Chinese loess plateau. Oil fly ash samples were provided courtesy of M. Seggiani and were collected from Italian power plants fuelled by heavy oil²⁷. Samples were dry-sieved to a 10–50 μm size class. Bulk elemental chemistry of all samples (except the African dust, which already has a published value²⁶) was determined by typical HF/HNO₃ whole elemental digestion⁷.

Leaching experiments. A major difficulty in assessing the solubility of Fe in marine aerosols on the basis of available literature is the lack of consistency in the operational definition of soluble or bioavailable Fe fractions, making interstudy comparisons of aerosol Fe solubility difficult^{8,28}. We used leaching procedures similar to other studies so that the solubility of glacial flour and oil fly ash can be compared with other larger data sets of Fe solubility in aerosol particles^{7,28}. Ultrapure MilliQ was used as a leachate, which is obviously a different geochemical matrix relative to sea water. However, its utility for reproducibility across studies and for comparison between different particles has been thoroughly discussed by Buck *et al.*, who outline a strong rationale for selecting this leachate matrix²⁸. Furthermore, recent work has shown that differences in calculated aerosol Fe solubility between sea water and MilliQ leach solutions are minimal when compared with the range of values observed in this study by aerosol type¹².

Leaching experiments were conducted in a class 100 laminar flow hood within a class 10,000 clean laboratory. All components of the leach process were soaked in 20% trace-metal-grade HCl for 1 week, conditioned in pH ~2 MilliQ for 2 days (acidified with Optima-grade HNO₃), and then rinsed profusely in MilliQ ultrapure water. 1–3 mg of sediment sample was then weighed and transferred to an acid-cleaned 0.4 µm polycarbonate filter. Then 250 ml of MilliQ was pushed through the filter by slight pressure with N₂ gas, usually taking ~40 s per leach. This procedure was repeated up to 20 times to determine if Fe released from these sediments changes with successive leaches. The pH of MilliQ was monitored during one leach sequence for each sample, but pH changes were minimal (<0.2 units) owing to the small volume of sample relative to solution and the short duration of the leach experiment (~40 s). Three aliquots of each sample were leached three times for each of the six samples to address sample heterogeneity within such small sample aliquots. We quantify this variation on the basis of the standard error of calculated Fe solubility. Less than 0.4-µm filtrates were collected in clean Nalgene high-density polyethylene 250-ml sample bottles and acidified to pH ~2 with Optima-grade HNO₃. Leachates were analysed for Fe and other trace-element concentrations using a Finnigan Element II high-resolution inductively coupled plasma mass spectrometer in medium-resolution mode at Woods Hole Oceanographic Institution's Plasma Facility. All leachates were spiked with a 2 ppb In internal standard. Multiple full-leach blanks were collected during each leach experiment and these blanks usually contained less than 10% of the Fe counts of sediment leachates (with the noted exception of 20-leach African dust leachates after the sixth leach, which are not included for total solubility measurements).

Synchrotron analyses. Samples were analysed by synchrotron-based XAS at Stanford Synchrotron Radiation Laboratory on Beamline 11-2. A Si(220) = 90° monochromator crystal was used for these experiments, which was calibrated with Fe metal foil to 7112 eV. The *k*-weighted chi function of each normalized spectra was then fitted using least-squares fitting of known mineral standard spectra using the SixPACK interface at a *k*(Å⁻¹) range of 1.5–14.5 (Fig. 3)²⁹. EXAFS fits were optimized by minimizing the residual and chi squared values of theoretical fits of combinations of Fe species standards. The errors for fits were generated by SixPACK. The only adjustable parameter was the combination of standards used to fit the data, which must sum to unity. Typical fits are shown in Fig. 3 and example pure mineral standard spectra are shown in Supplementary Fig. S1. The redox ratio of Fe in each sample was obtained by calculating the position of the centroid of the normalized background-subtracted pre-edge feature following methods used by numerous other researchers studying the valence of Fe in soil and sediment matrices^{6,30}. The error is undetermined for these measurements.

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References

- Martin, J. H., Gordon, R. M. & Fitzwater, S. E. The case for iron. *Limnol. Oceanogr.* **36**, 1793–1802 (1991).
- Moore, J. K., Doney, S. C., Glover, D. M. & Fung, I. Y. Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean. *Deep-Sea Res. I* **49**, 463–507 (2002).
- Mahowald, N. M. *et al.* Atmospheric global dust cycle and iron inputs to the ocean. *Glob. Biogeochem. Cycles* **19**, gb4025 (2005).
- Luo, C. *et al.* Combustion iron distribution and deposition. *Glob. Biogeochem. Cycles* **22**, gb1012 (2008).
- Jickells, T. D. *et al.* Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* **308**, 67–71 (2005).
- Lam, P. J. & Bishop, J. K. B. The continental margin is a key source of iron to the HNLC North Pacific Ocean. *Geophys. Res. Lett.* **35**, L07608 (2008).
- Sedwick, P. N., Sholkovitz, E. R. & Church, T. M. Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea. *Geochem. Geophys. Geosyst.* **8**, gc001586 (2007).
- Wu, J., Rember, R. & Cahill, C. Dissolution of aerosol iron in the surface waters of the North Pacific and North Atlantic oceans as determined by a semicontinuous flow-through reactor method. *Glob. Biogeochem. Cycles* **21**, gb4010 (2007).
- Desboeufs, K. V., Sofikitis, A., Losno, R., Colin, J. L. & Ausset, P. Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. *Chemosphere* **58**, 195–203 (2005).
- Hinkley, T. K. Composition and sources of atmospheric dusts in snow at 3200 meters in the St-Elias-Range, Southeastern Alaska, USA. *Geochim. Cosmochim. Acta* **58**, 3245–3254 (1994).
- Desboeufs, K. V., Losno, R. & Colin, J. L. Factors influencing aerosol solubility during cloud processes. *Atmos. Environ.* **35**, 3529–3537 (2001).
- Aguilar-Islas, A. M., Wu, J. & Rember, R. Dissolution of aerosol-derived iron in seawater: The influence of aerosol type and dissolved iron size fractionation. *Mar. Chem.* (in the press).
- Plafker, G., Nokleberg, W. J. & Lull, J. S. Bedrock geology and tectonic evolution of the Wrangellia, Peninsular, and Chugach Terranes along the Trans-Alaska Crustal Transect in the Chugach Mountains and Southern Copper River Basin, Alaska. *J. Geophys. Res.* **94**, 4255–4295 (1989).
- Journet, E., Desboeufs, K. V., Caqueneau, S. & Colin, J. L. Mineralogy as a critical factor of dust iron solubility. *Geophys. Res. Lett.* **35**, L07805 (2008).
- Spokes, L. J., Jickells, T. D. & Lim, B. Solubilization of aerosol trace-metals by cloud processing—a laboratory study. *Geochim. Cosmochim. Acta* **58**, 3281–3287 (1994).
- O'Day, P. A., Rivera, N., Root, R. & Carroll, S. A. X-ray absorption spectroscopic study of Fe reference compounds for the analysis of natural sediments. *Am. Mineral.* **89**, 572–585 (2004).
- Cwierntny, D. M. *et al.* Characterization and acid-mobilization study of iron-containing mineral dust source materials. *J. Geophys. Res.* **113**, D05202 (2008).
- Jenny, H. *Factors of Soil Formation; a System of Quantitative Pedology* (McGraw-Hill, 1941).
- Fan, S. M., Moxim, W. J. & Levy, H. Aeolian input of bioavailable iron to the ocean. *Geophys. Res. Lett.* **33**, L07602 (2006).
- Michel, F. M. *et al.* The structure of ferrihydrite, a nanocrystalline material. *Science* **316**, 1726–1729 (2007).
- Anders, A. M., Sletten, R. S., Derry, L. A. & Hallet, B. Germanium/silicon ratios in the Copper River Basin, Alaska: Weathering and partitioning in periglacial versus glacial environments. *J. Geophys. Res.* **108**, F16005 (2003).
- Cornell, R. M. & Schwertmann, U. *The Iron Oxides* (Wiley-VCH, 2003).
- Prudencio, M. I. *et al.* Clay mineral assemblages in weathered basalt profiles from central and southern Portugal: Climatic significance. *Catena* **49**, 77–89 (2002).
- Boyd, P. W. *et al.* Atmospheric iron supply and enhanced vertical carbon flux in the NE subarctic Pacific: Is there a connection? *Glob. Biogeochem. Cycles* **12**, 429–441 (1998).
- Jerz, J. K. & Rimstidt, J. D. Efflorescent iron sulfate minerals: Paragenesis, relative stability, and environmental impact. *Am. Mineral.* **88**, 1919–1932 (2003).
- Eglinton, T. I. *et al.* Composition, age, and provenance of organic matter in NW African dust over the Atlantic Ocean. *Geochem. Geophys. Geosyst.* **3**, gc1050 (2002).
- Seggiani, M., Vitolo, S., Pastorelli, M. & Ghetti, P. Combustion reactivity of different oil-fired fly ashes as received and leached. *Fuel* **86**, 1885–1891 (2007).
- Buck, C. S., Landing, W. M., Resing, J. A. & Lebon, G. T. Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise. *Geochem. Geophys. Geosyst.* **7**, Q04m07 (2006).
- Webb, S. M. SixPACK: A graphical user interface for XAS analysis using IFEFFIT. *Phys. Scripta T* **115**, 1011–1014 (2005).
- Wilke, M., Farges, F., Petit, P. E., Brown, G. E. & Martin, F. Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *Am. Mineral.* **86**, 714–730 (2001).

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Author contributions

A.W.S., J.C. and E.R.S. designed the study. A.W.S. and J.C. conducted the leaching experiments. A.W.S. interpreted the leach data with input from J.C. and E.R.S. A.W.S. and B.C.B. collected and interpreted XAS spectra. A.W.S. wrote the manuscript with valuable input from all authors.

Additional information

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