

Iron content and solubility in dust from high-alpine snow along a north-south transect of High Asia

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ABSTRACT

This study describes the dissolved and insoluble iron fraction of dust (mineral aerosol) in high-alpine snow samples collected along a north-south transect across High Asia (Eastern Tien Shan, Qilian Shan, and Southern Tibetan Plateau). This dust provides the basic chemical properties of mid- and high-level tropospheric Asian dust that can supply the limiting iron nutrient for phytoplankton growth in the North Pacific. The iron content in Asian dust averages 4.95% in Eastern Tien Shan, 3.38–5.41% along Qilian Shan and 3.85% in the Southern Tibetan Plateau. The iron fractional solubility averages about 0.25% in Eastern Tien Shan, 0.05–2% along Qilian Shan and 1.5% in the Southern Tibetan Plateau. Among the controlling factors that can affect iron solubility in Asian dust, such as dust composition and particle grain size, acidity seems to be the most significant and can increase the iron solubility by one or two orders of magnitude with acidification of pH = 0.66. Our results reveal that iron solubility of dust in the remote downwind sites is higher than that in high-alpine snow, confirming the strong pH-dependence of iron solubility, and indicating that Asian dust shows a large variation in iron solubility on a regional scale.

Keywords: Asian dust, high-alpine snow, iron content, iron solubility

1. Introduction

The iron contained in the long-range transported Asian dust (mineral aerosol) that is deposited in the high-nutrient low-chlorophyll Pacific Ocean acts as the limiting nutrient for the growth of phytoplankton, which can take up atmospheric CO₂ according to the ‘Iron Hypothesis’ (Martin, 1990; Ridgwell, 2003 and references cited therein). The annual Asian dust flux into the North Pacific is estimated to vary between 68 Tg (Jickells et al., 2005) and 480 Tg (Duce and Tindale, 1991). Observation reveals that oceanic diatom activity in the North Pacific is highly correlated with dust events, indicating that Asian dust events stimulate biological productivity (Yuan and Zhang, 2006). The iron content and solubility are two key issues concerning the effect of atmospheric dust on atmospheric CO₂ content (e.g. Jickells et al., 2005). Although iron abundance in the upper continental crust (UCC) averages

3.5% (Taylor and McLennan, 1995), dust compositional differences in those source areas may exist and make it much more complex to estimate the total eolian iron flux to the oceans. In addition, not all the iron in mineral dust is available for oceanic bioactivities. Only the dissolved fraction of iron is bio-available and can act as a nutrient. The atmospheric dust load over the world and deposition to the oceans has been modelled. However, accurate iron deposition fluxes to the oceans (Duce and Tindale, 1991; Jickells et al., 2005; Mahowald et al., 2005) differ greatly due to the significant variability of iron solubility (Fan et al., 2006).

There are numerous studies on the iron supply of dust to remote oceans, which reveal that iron fractional solubility (the dissolved iron as a fraction of total iron content) varies over a large range. Although the soluble iron fraction in soils is as low as about 0.5% (Fung et al., 2000) or about 1% near the dust source (Fan et al., 2006), measurements of iron in the aerosol at remote ocean locations indicate a much higher solubility that can reach up to 10–40% (Fang et al., 2006), or even 80%

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(Mahowald et al., 2005), implying that atmospheric processing could change the solubility of iron as it moves from the source regions to remote oceans (Desboeufs et al., 2001). As the end member of the Asian dust, dust in the Greenland Ice Core Project (GRIP) ice core shows iron solubility averaging about $40 \pm 20\%$ (Laj et al., 1997). Until now, both iron abundance and especially iron solubility of dust are not well understood, leading to a large uncertainty in assessing the exact iron flux and the impact of dust on the global biogeochemical cycle in models.

Iron solubility of Asian dust has been studied by many researchers (e.g. Chuang et al., 2005; Ooki et al., 2010; Kumar and Sarin, 2010). Although Asian arid lands are the major source of eolian iron to Pacific oceanic bioactivity, most studies focus on the near-surface or sea surface aerosols, but few studies focus on the mid- to high-level tropospheric Asian dust that can be carried to remote oceans. The eolian dust in high-alpine snow near the Asian dust emission areas, which is a good analogue of the long-range transported Asian dust, has not been studied, and the basic characteristics of iron in the dust are poorly understood at present. In this study, we report the iron

abundance and solubility of Asian dust, and the regional differences from snow and firn core samples from High Asia; we also report the sensitivity experiment result that a change in acidity of the aqueous solutions to which the dust particles would be exposed can affect the iron solubility of dust in those samples. The purpose of this study is to provide some fundamental properties of Asian dust, focusing on the initial solubility of iron in Asian dust near the source regions.

2. Field sampling and measuring methods

Three sites are chosen for sampling the iron fraction in mineral dust along a north-south transect in High Asia, including Urumqi Glacier No. 1 (UG1) in Eastern Tien Shan; Qiye, Dunde and Lenglongling in Qilian Shan, on the northern margin of the Tibetan Plateau; and Qiangyong Glacier in the southern part of the Tibetan Plateau. Eastern Tien Shan and Qilian Shan are enclosed by Northern Chinese deserts, while Qiangyong is located at the boundary of the Tibetan Plateau and the Indian subcontinent (Fig. 1).

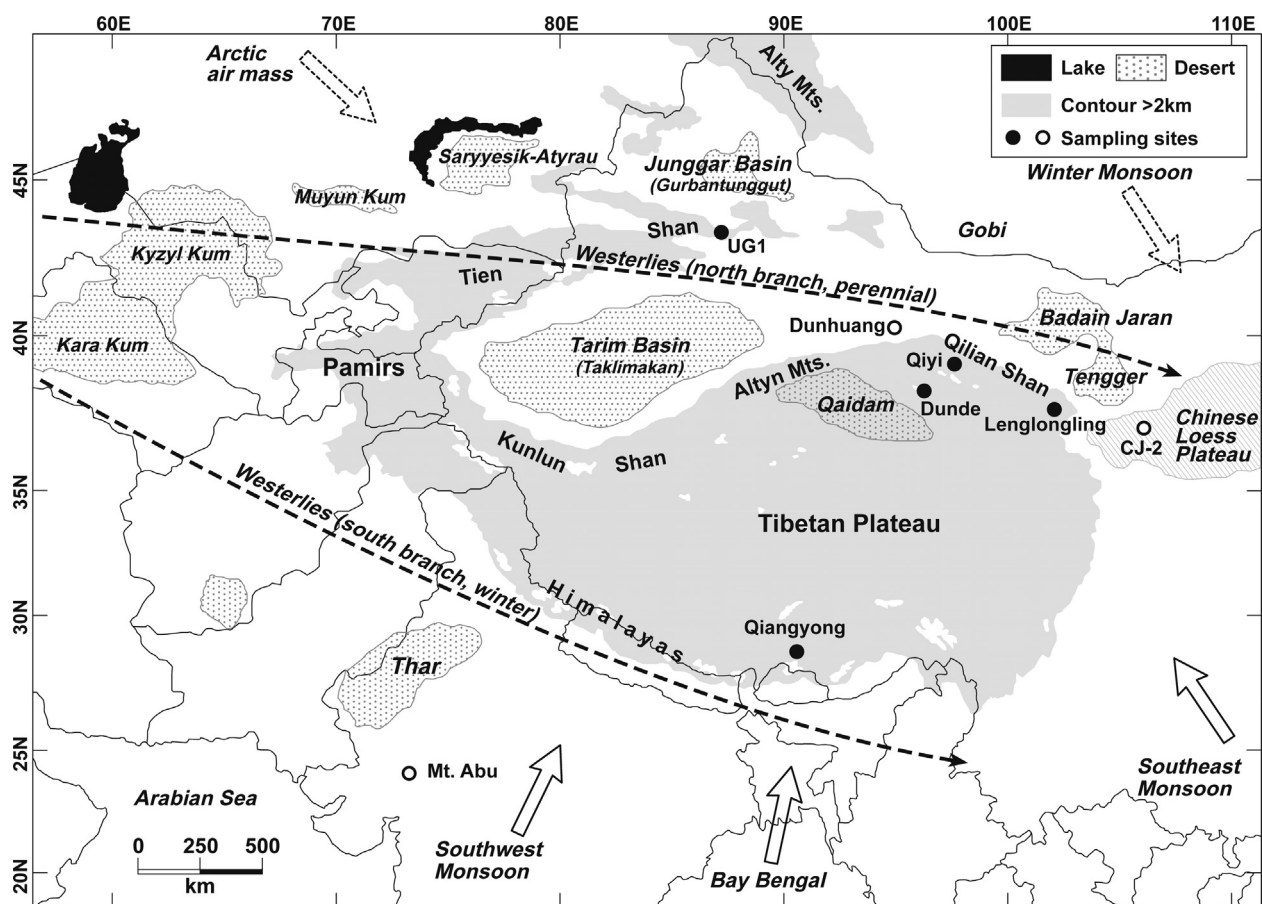


Fig. 1. Location of sampling sites.

In April 2009, a 8.64 m firn core was drilled at Qiangyong Glacier (28°51'N, 90°13'E, 6100 m a.s.l.), Southern Tibetan Plateau. This core was cut and divided into 42 successive subsections at intervals of about 20 cm. We estimate that this core covers the past 5 yrs and each sample may have temporal resolution of monthly timescale. The outer part of each subsection, about 0.5 cm (the diameter of the firn cores is only 6.5 cm), was scraped away using a stainless steel scalpel under a class 100 clean cabinet in a class 1000 clean cold room (−5 °C). The inner part of each ice core slice was collected for element, ions and dust concentration analysis, and further divided into 5 cm intervals for high-resolution dust concentration measurement. The scraped outer part was collected at 5 cm intervals for oxygen isotope analysis.

Since March 2006, we have collected surface snow samples, weekly or bi-weekly, using acid pre-cleaned low-density polyethylene (LDPE) bottles at the Program for Glacier Process Investigation observation site (43°06'N, 86°49'E, 4130 m a.s.l.) in a percolation zone of the eastern branch of UG1, as described in detail previously (Li et al., 2006; Wu et al., 2010). In this study, a total of 25 samples collected from February to December 2008 were used to measure the dissolved and insoluble iron fraction of the dust. In July 2009, surface snow samples were collected, using the same procedure as at UG1, from the western (Qiyi Glacier, 39°14'N, 97°46'E, 4800 m a.s.l.) and eastern (Lenglongling, Chinese Glacier Inventory No. 5Y416F003, 37°31'N, 101°49'E, 4300 m a.s.l.) parts of Qilian Shan. We have measured the insoluble dust composition from a shallow Dundee ice core (Wu et al., 2009). Unfortunately, the filtrate of Dundee sample was not collected, and the iron solubility of dust in this core cannot be provided in this study.

All the snow and firn core samples were melted at room temperature just before filtration and were filtered (in a class 1000 clean room) on LCR hydrophilic polytetrafluoroethylene (PTFE) membrane filters (Millipore Corp.) with a diameter of 47 mm and a pore size of 0.45 µm. Therefore, only the particles with diameters larger than 0.45 µm were collected on the filter, while the filtrate (water-extracted fraction and particles finer than 0.45 µm) was collected in acid pre-cleaned LDPE bottles and allotted for element analysis.

Considerable caution was applied to avoid contamination through the field sampling and laboratory pretreatment and analysis. The filters were digested with super-pure HNO₃–HF at 150–190 °C in PTFE screw-top bombs. All element measurements were made using inductively coupled plasma-mass spectrometry (ICP-MS, X-7, Thermo-Elemental Corp.) in the Institute of Tibetan Plateau Research (ITP), Chinese Academy of Sciences. The digestion, measuring procedure and accuracy of this method have previously been described in detail (Wu et al., 2009).

The dust fraction with diameter <0.4 µm is thought to be the dissolved fraction (e.g. Zhuang et al., 1990; Duce and Tindale, 1991; Wu et al., 2001). In this study, a 0.45 µm pore filter was used to separate the dissolved and insoluble fractions. Therefore, the filtrate going through the filter can be taken as the dissolved fraction, while the residue on the PTFE filter is the insoluble fraction. We combined the iron content in the insoluble (dust particles on PTFE filters) and dissolved fractions (filtrate) in these samples to get the total iron content and to calculate iron fractional solubility, which is defined as $\text{Fe}_{\text{dissolved}}/(\text{Fe}_{\text{dissolved}} + \text{Fe}_{\text{insoluble}}) \times 100\%$. The concentrations of dissolved Fe(II) and Fe(III), the former being much more soluble than the latter (Fung et al., 2000), were not measured separately, and the difference between them is ignored for the solubility calculation in this study.

A portion of the unfiltered samples was analysed for oxygen isotope ratio (Finnigan MAT 253), electrical conductivity (DDB-303A, Shanghai REX Instrument Factory), acidity (PHS-3E PH meter, Shanghai REX Instrument Factory), microparticle size and concentration (1–30 µm diameter, Multisizer 3 Coulter Counter, Beckman Coulter Inc.) and ions (Dionex 2000/2500, Dionex Corp.). These measurements were also performed in ITP.

Three sets of experiment were conducted in order to investigate the effect of pH on iron solubility. First (Experiment 1), the post-filtration filtrate was measured by ICP-MS without and with acidification (to pH = 2) to check the impact of acidification on dissolved iron concentration. In this study, we use the unacidified filtrate to calculate the iron fractional solubility.

Second (Experiment 2), more than 50 g of melted pre-filtration snow samples (two from Qiyi and one from Lenglongling) were divided, after gently shaking to avoid sedimentation of coarse particles, into 7 or 10 aliquots (each weighing about 4 or 5 g) and then pure water (18.2 Ω, Milli-Q A10, Millipore Corp.) diluted super-pure HNO₃ (CNW Technologies GmbH) at different concentrations (varying from 0.0001 to 16 mol l^{−1}) was added to the aliquots. After a reaction period of a week (approximately the time (4–7 d) for the Asian dust to be transported from the source region to the North Pacific) at room temperature (in sealed bottles), the dissolved iron concentration in the aliquots was measured by the same ICP-MS. This experiment is designed to quantitatively detect the dissolved iron concentration at different pH values (acidity increases gradually).

Third (Experiment 3), about 5 g of melted pre-filtration UG1 and Qiangyong samples were extracted, after gently shaking to avoid sedimentation of coarse particles, and the dissolved element concentration without acidification was measured. Then, 0.2 ml of super-pure HNO₃ (CNW Technologies GmbH, diluted to 26% V/V with pure water)

was added to each pre-filtered sample; this drops the acidity of the solution to $\text{pH} = 0.66$. After a reaction period of a week (in sealed bottles) at room temperature, iron concentration was measured using the same ICP-MS. We therefore obtained the non-acidified and acidified results from the two sets of pre-filtered samples. Due to the very small portion of these aliquots, we cannot filter these pH-acidified solutions in Experiments 2 and 3. Therefore, we provide the dissolved iron concentration in those filtrates instead of the iron solubility. Experiments 2 and 3 were set up to discuss the effect of acidity on the iron solubility. The complete experimental design is shown in Fig. 2.

3. Results and discussion

3.1. The iron abundance of Asian dust in snow and ice

The three sampling sites, named Tien Shan, Qilian Shan, and southern Tibetan Plateau, provide a north-south transect that crosses Western China and covers possible dust transport pathways by the high-level Westerlies over High Asia. The dust-borne iron content provides the basic information for the assessment of the maximum iron potential input to oceanic bioactivities. The iron abundance of the UCC, which averages 3.5% (Taylor and McLennan, 1995), is usually thought to be the analogue of eolian mineral aerosols' iron content over remote oceans. The loess material of the Chinese Loess Plateau has an iron content of 3.4% (loess layers) to 3.8% (paleosol layers) on average (Ding et al., 2001), while the simulated Asian dust standard (CJ-2) has an iron abundance of about 3.0% (Nishikawa et al., 2000).

Whether the iron content of Asian dust keeps consistent is of significance in assessment of the iron supply to Pacific and Indian oceans. The iron content in UG1 dust collected in 2008 averages 4.97% (varying from 3.45 to 7.56%).

The iron abundance in the Dundee ice core, Qiyi and Lenglongling snow samples is 3.38 (from 2.53 to 4.09%, Wu et al., 2009), 5.41 and 3.86%, respectively, while in the Qiangyong firn core, the iron content averages 3.91% (varying between 0.94 and 5.94%). The iron contents of Asian dust from the three sites are different, but none varies more than a small fractional amount from the iron content of the UCC (Table 1). Previous models of the flux of dust-borne iron transport to the oceans are largely smoothed (e.g. Uematsu et al., 2003; Hand et al., 2004), assuming an iron content ratio of 3.5%. This simple assessment based on the assumption of a uniform iron content would eventually cause some errors in modelling the global iron (and other elements) flux. Our results provide a regional variability in iron content across the north-south section of Asia, which can improve iron flux modelling.

3.2. The initial iron solubility of high-alpine Asian dust: Experiment 1

Anthropogenic pollutants (e.g. combustion emission) have higher iron fractional solubility (e.g. Sedwick et al., 2007) and might contribute to those high-alpine sites. The enrichment factors (EF, using Al as the reference element), which are widely used to check for anthropogenic contributions (EF usually greater than 5 or 10), of iron are close to 1.5, indicating that there are no substantial distortions from human contribution. Therefore, the iron in those alpine snow samples is predominantly originated from crust and anthropogenic effect on iron solubility is small, although only the insoluble fraction was checked.

The calculated iron fractional solubility in high-alpine snow and firn core varies over a large range of two orders of magnitude, from 10^{-2} to several percent (see Table 1). The Qiangyong samples have a higher (about five times in arithmetic average and four times in geometric average)

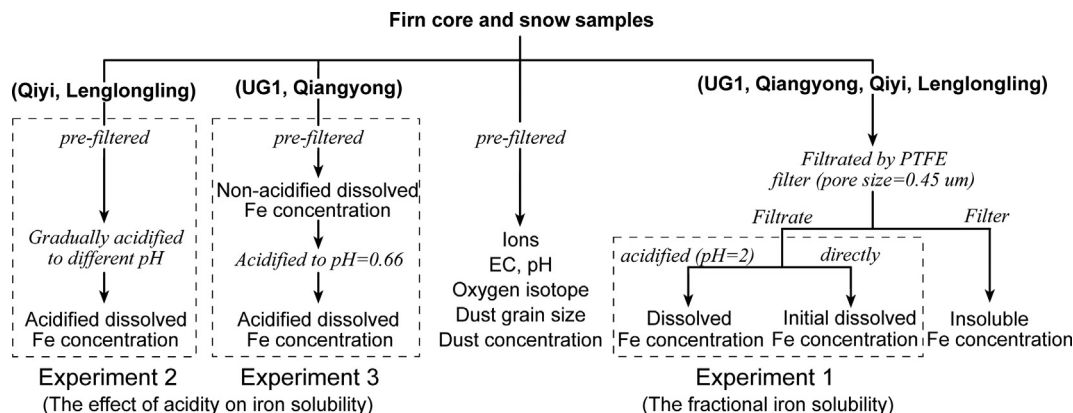


Fig. 2. The flowchart of experimental design in this study.

Table 1. The iron content and fractional solubility of Asian dust from different sites and dust types

Site and dust type	Sample number	Fe content (%)	Fe solubility (%, arithmetic mean)	pH	References
Dunde ice core, dust	16	3.38 ± 0.50			Wu et al. (2009)
Qiyi snow, dust	2	5.41 ± 0.08	0.05	6.37	This study
Lenglongling snow, dust	2	3.86 ± 0.56	2.16	5.65	This study
Qiangyong firn core, dust	42	3.91 ± 0.90	1.18 ± 1.12 (0.67 Geo. mean)	5.86 ± 0.21	This study
Tien Shan (UG1) snow, dust	25	4.97 ± 0.70	0.25 ± 0.18 (0.18 Geo. mean)	6.62 ± 0.41	This study
UCC		3.50			Taylor and McLennan (1995)
Simulated Asian dust (CJ-2)		3.02 ± 0.12	0.33		Nishikawa et al. (2000) and Ooki et al. (2009)
TSP aerosol at Dunhuang			0.05–1.2		Chuang et al. (2005) and Duvall et al. (2008)
Aerosol on East China Sea			0.2–1.5		Hsu et al. (2010)
TSP aerosol at Gosan, Korea			0.1–3.4		Chuang et al. (2005) and Duvall et al. (2008)
Bulk aerosol at Hokkaido			1.2–2.2		Ooki et al. (2009)
North Pacific, aerosol	54		9 ± 8		Buck et al. (2006)
dust in GRIP ice core			40 ± 20		Laj et al. (1997)
Aerosol at Mt. Aba, Western India			8.1 (2.5–16.1), winter		Kumar and Sarin (2010)
Aerosol at Mt. Aba, Western India			1.6 (0.06–6.1), summer		Kumar and Sarin (2010)
Aerosol in Aqaba, Middle East			5 (0.5–19)		Chen et al. (2006)

iron solubility than UG1 snow. Along the Qilian Shan, Qiyi has the lowest iron solubility (0.05%) compared to that at Lenglongling (2.16%). This regional difference between Qiyi and Lenglongling is probably largely due to the post-depositional processes that can affect the dissolved iron concentration in snow (see Section 3.5). Iron solubility is highly variable and dependent on dust sources on a continental (e.g. Africa vs. Asia) scale (Mahowald et al., 2005). Our observed results indicate that it also varies pronouncedly on a regional scale in different Asian dust emission areas. Furthermore, at each site, the iron solubility also shows great variability over time. The iron solubility varies from 0.01 to 0.72% in UG1 snow and from as low as 0.04% to as high as 4.62% for Qiangyong firn core samples.

The source, origin and inherent properties of the dust impact the iron solubility (Trapp et al., 2010). Based on the results of air mass track modelling and geochemical characteristics of dust, the Tarim Basin (Taklimakan) and Junggar Basin are main sources for UG1 dust (Wu et al., 2010); and Tarim Basin and Qaidam Basin are the major sources for Dunde dust (Wu et al., 2009). For dust in the Southern Tibetan Plateau (such as Mt. Everest), the Northwest India arid regions (Thar desert and Indus-Gangetic Basin) are the possible sources. Our results indicate that specific source areas contribute to the regional difference in iron solubility, which will improve the

assessment of the bio-available iron supply from Asian arid lands to remote oceans.

Besides source provenance, there are also several factors that can affect the iron solubility of eolian dust, such as particle size (Baker and Jickells, 2006; Ooki et al., 2009), mineralogy (Journet et al., 2008), cloud processes and acidity during the dust transport (e.g. Desboeufs et al., 2001) and anthropogenic activities (Chuang et al., 2005; Sedwick et al., 2007). The pH value of natural precipitation is about 5.6 due to CO_2 partial pressure. There is a large change in elevation between the high-altitude sampling sites (about 4 km a.s.l. for Tien Shan, 4.5 km a.s.l. for Qilian Shan and 6 km a.s.l. for Qiangyong samples) and the Beijing laboratory (about 50 m a.s.l.) where the pH measurement was performed, which could cause the measured pH value to change by ~ 0.1 unit due to the change in CO_2 partial pressure. Therefore, CO_2 partial pressure seems to have no substantial effect on the pH measurement.

The calcium content (or the Ca/Al ratio) of dust is a good tracer for carbonate mineral, which can increase the pH value and substantially limits the iron dissolution (Ito and Feng, 2010). Both Qiangyong and Tien Shan samples show decreasing iron solubility with increasing Ca/Al ratio, and Tien Shan samples have a higher Ca/Al ratio than that of Qiangyong (Fig. 3a). The pH value of the UG1 and Qiangyong samples differs. In UG1, the pH value averages

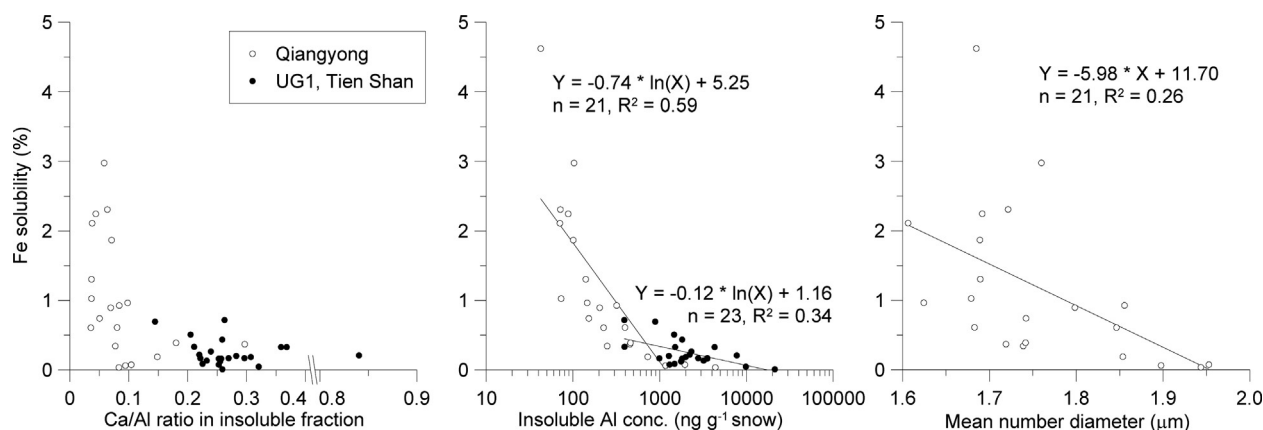


Fig. 3. The correlation between iron solubility and (a) Ca/Al ratio, (b) dust (using Al element) concentration and (c) particle grain size in Qiangyong (cycles) and Tien Shan samples (dots).

6.62 ± 0.41 (ranging from 5.63 to 7.20); while in Qiyi and Qiangyong, the pH value averages 6.37 and 5.86 ± 0.21 (varying between 5.04 and 6.27), respectively. Both average pH values for UG1 and Qiangyong snow are greater than that of the natural precipitation in high mountains due to the contribution of the alkaline Asian dust into the glacier, which neutralises the natural (CO_2) and anthropogenic acid species (e.g. SO_2) (Wake et al., 1992). Eastern Tien Shan snow shows a greater pH value than that of Qiangyong and Qilian Shan, in accordance with the proximity to the Central Asian arid regions. Both in Qiangyong and Tien Shan, iron solubility clearly decreases with increasing dust (defined as the insoluble Al element) concentration, and a correlation function can be fitted (Fig. 3b). Therefore, the differences in the initial (means the non-acidified) iron solubility at those sites (UG1, Qiyi and Qiangyong) might be partly attributed to the different pH values and total dust concentration.

The Coulter Counter measurement enables a numerical comparison of the dust (insoluble) particle grain size between the different sites. The mean number diameter of UG1 snow samples collected in 2009 (unfortunately, the 2008 samples have not been measured by the Coulter Counter) averages $1.98 \mu\text{m}$ and is greater than that of Qiangyong samples ($1.80 \mu\text{m}$). Compared to Qiangyong samples, the dust particles are coarser in UG1 and could partly contribute to its lower iron solubility, although the 2009 samples are used instead of the 2008 ones for the grain size comparison. Iron solubility of Qiangyong samples display a decreasing trend with increasing dust grain size (Fig. 3c). This inverse relationship, which provides the direct correlation between particle size and iron solubility, is in accordance with previous studies that small particles seem to have higher solubility than coarse ones (e.g. Baker and Jickells, 2006).

As far as we know, very few data on iron solubility have been reported for Asian dust that is close to the source region and at the beginning of its transport. In addition, dust in high-alpine snow and ice has not been studied for iron solubility. Our data represent the results of the initial iron solubility compared to those that have been affected by many factors at the leeward sites (Table 1). Eolian dust has iron solubility that ranges from 0.01 to 80% and that is highly heterogeneous in space and time (Mahowald et al., 2005). The iron solubility of Asian dust in high-alpine snow samples seems to be in a comparable range of that collected at the source region, such as the total suspended particles (TSP) aerosol at Dunhuang (0.05–1.2%, Chuang et al., 2005; Duvall et al., 2008) and simulated Asian dust standard CJ-2 (0.33%, Ooki et al., 2009), but seems lower than aerosol collected in Korea (Chuang et al., 2005; Duvall et al., 2008), Japan (Ooki et al., 2009) and the North Pacific (Buck et al., 2006) (see Table 1). Iron solubility averages 5% (0.5–19%) in pure water for dust aerosol from Gulf Aqaba, West Asia (Chen et al., 2006), while averages 1.6% (0.06–6.1%) in Western India during summer months (Kumar and Sarin, 2010). These data indicate that Asian dust has a large variability in iron solubility at different regions and iron solubility also has a large range at each site.

3.3. Acidification sensitivity experiment on iron solubility: Experiment 2

Among these factors that impact iron solubility of dust, acidity has been taken as a key control factor of iron solubility (e.g. Meskhidze et al., 2003). Acidification can significantly affect the dissolved iron fraction (e.g. Zhuang et al., 1992; Desboeufs et al., 1999), but no such work has been reported for the dust in snow and ice cores at high-altitude locations in High Asia region, which is a good representative for the long-range transported Asian dust.

In this study, only the acidity impact on iron solubility is discussed. In Experiment 2, three samples, two collected at Qiyi and one at Lenglongling from Qilian Shan, were chosen to detect the impact of stepwise acidification on iron solubility at different pH values. In the acid sensitivity experiment, the reaction period is set up to 7 d, which is approximately the time (1 week) for the Asian dust to be transported from the source region to the North Pacific (e.g. Husar et al., 2001), and is assumed to be long enough for the iron contained in a deliquescent mineral dust particle to be mobilised (e.g. 80–120 h at pH = 4.7–5 for loess from Cape Verde, Desboeufs et al., 1999). Therefore, our results might represent the balanced concentration of dissolved iron at different pH values and simulate a possible range for the iron solubility of Asian dust during its transport.

The results of the stepwise acidification experiments (Experiment 2) reveal that the dissolved iron concentration in the acidified snow samples increases markedly with pH decrease (Fig. 4; Table 2). As mentioned earlier, we provide the dissolved iron concentration and ratio to step 1, instead of iron solubility, in those aliquots because of their small amount. The Lenglongling sample displays rather scattered characteristics and has a lower determination coefficient ($R^2 = 0.87$) than Qiyi ($R^2 = 0.96$ and 0.98) in the power fitting. This might be due, at least partly, to the low absolute iron concentration in Lenglongling sample. Although some particulate iron might be measured as the dissolved one in those aliquots, generally, the dissolved iron concentrations can increase by one order of magnitude after acidification, compared to the initial ones, due to the dissolution of acid-leachable iron-bearing minerals. In addition, the increasing ratio increases much faster when the pH value drops below 3, especially for the two Qiyi samples. A similar result that dissolved iron content increases more markedly at lower pH has also been reported for the Pacific marine aerosol and Chinese loess (Zhuang et al., 1992).

The natural mineral dust particles (predominantly aluminosilicate) are less soluble compared to the carbonates and sea salts, notably the ones constituting the matrix network (Fe, Mn), and their dissolution is highly influenced by pH (Desboeufs et al., 2005). The anthropogenic acid substance emissions from East Asia, such as sulphuric, nitric and/or hydrochloric acids, can decrease the Asian dust pH even to below 2, promote to the mobilisation of iron in mineral dust and promote iron solubility (Meskhidze et al., 2003). Our results are in accordance with previous studies on Asian dust (e.g. Zhuang et al., 1992) in that iron dissolution is a pH-dependent process and iron solubility increases with higher acidity.

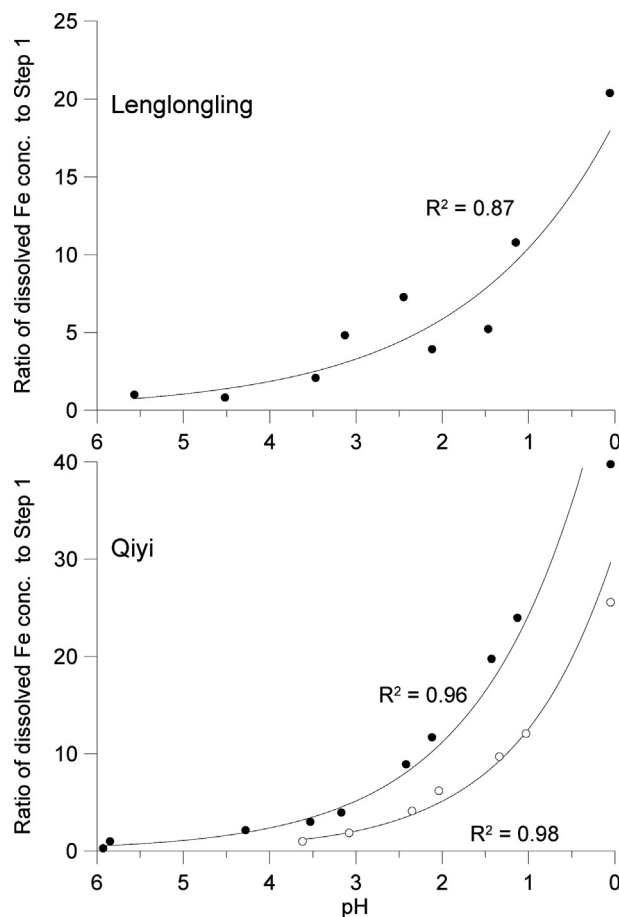


Fig. 4. The absolute dissolved iron concentrations at different pH and the relative increasing ratios (to step 1) in snow from Lenglongling (one sample, top) and Qiyi (two samples, bottom), Qilian Shan, Northern Tibetan Plateau (Experiment 2). Note that some particulate iron might also be measured as the dissolved one in those pre-filtered samples.

3.4. The iron solubility of acidified Asian dust: Experiment 3

Since iron solubility is highly dependent on acidity (pH value), we have conducted another experiment to measure iron solubility under acidified conditions for all UG1 and Qiangyong samples. The acidified (pH ≈ 1) iron solubility, which is thought to be the upper limit of the dissolved iron in dust (Fung et al., 2000), is compared with the initial iron solubility in order to give a comprehensive understanding of the basic characteristics of Asian dust.

The dissolved Fe concentrations before and after acidification of UG1 and Qiangyong samples are shown in Fig. 5, with the dust mass (Al concentration) and pH value profiles. After acidification (pH = 0.66), both the dissolved iron concentrations of Qiangyong and UG1 samples increased by a factor of 10–100 times compared

Table 2. The dissolved iron concentration (unit: ng g^{-1}) after stepwise acidification

Lenglongling			Qiyi sample 1			Qiyi sample 2		
Step	pH	Dissolved Fe	Step	pH	Dissolved Fe	Step	pH	Dissolved Fe
1	5.57	1.1	1	5.93	9.4	1	3.62	62.5
2	4.52	0.9	2	5.85	32.9	2	3.08	116.5
3	3.47	2.4	3	4.28	70.5	3	2.35	257.5
4	3.13	5.5	4	3.53	98.9	4	2.04	387.6
5	2.45	8.3	5	3.17	130.3	5	1.34	607.3
6	2.12	4.8	6	2.42	293.5	6	1.03	755.1
7	1.47	6.0	7	2.12	385.2	7	0.05	1598.0
8	1.15	12.3	8	1.43	649.6			
9	0.06	23.2	9	1.13	788.6			
			10	0.05	1308.0			

to the initial ones. The ratio of the acidified to the initial dissolved iron concentration averages 87 ± 72 and 153 ± 218 for UG1 and Qiangyong samples (Table 3), respectively. There is no substantial difference in the geometric mean (67 vs. 74) and median (67 vs. 67) value of this ratio between the two datasets, indicating that the increase of dissolved iron concentration has a very similar amplitude. Given that these samples were acidified for a period of 7 d and to the same pH, we can assume that the HNO_3 -extractable iron fraction had been fully dissolved, and the impact of grain size and acidity on solubility seems to have had no substantial effect in both sites.

This experiment result is in accordance with the stepwise acidification (Experiment 2) and further confirms that the increase in acidity can markedly increase iron solubility by a factor of at least 10 for the Tien Shan and Qiangyong snow samples. This acid-induced increase in dissolved iron concentration indicates that some water-insoluble but acid-leachable iron-bearing minerals must have been dissolved during acidification. Although we are not sure about the form of iron in these samples, this result clearly indicates that the iron solubility of Asian dust is very susceptible to acids. In addition, this change in amplitude (of one or two orders of magnitude) of iron solubility by acidification seems to be much more obvious than the difference in iron content of Asian dust (see Table 1).

3.5. Uncertainties in the measurement of iron solubility

Most previous research found that acidifying the liquid samples (e.g. $\text{pH} = 3$, Dick and Peel, 1985; $\text{pH} \approx 2$, Chen et al., 2006) before ICP-MS/AES measurement might increase the initial dissolved fraction of the iron. In contrast, our measurement without acidification might decrease the dissolved iron fraction. Therefore, our calculated initial iron solubility seems to be underestimated

compared to previous results. This comparison itself is of some uncertainty because those iron solubilities, which are highly pH dependent (see discussion below), were not measured at the same acidity. Previous results and our Experiments 2 and 3 indicate that iron solubility displays a positive correlation with acidity. In most previous experiments, dissolved iron concentration is measured after acidification. According to a previous study, this type of uncertainty in iron concentration might reach up to several times (Knüsel et al., 2003). It should be noted that Knüsel et al. also attribute this difference partly to the incomplete dissolution of iron-bearing particles. Therefore, those previous results might overestimate the actual iron solubility in natural water (rain or snow). Theoretically, the decrease of pH value to 2 for the Qiyi and Lenglongling samples will result in an increase by several to tens of fold in dissolved iron concentration for those pre-filtration samples (Fig. 4). However, acidification can extract the fraction of dissolved iron (and other elements) that is adsorbed on the surface of dust particles, the LDPE (though much better than high-density polyethylene (HDPE)) storage bottles, the filtration system and even the PTFE filters. Therefore, our result showing the initial dissolved iron might be less than the actual value, and the iron solubility might be underestimated due to these uncertainties.

However, the acidification impact on the post-filtrated solutions might be less but still not clear. In this study, the non-acidified dissolved iron in the solutions before and after filtration was measured in order to check this impact. As shown in Fig. 6, the selected Qiangyong samples show obvious variation. Although Qiangyong samples display higher iron solubility than Tien Shan, the absolute dissolved Fe concentration in the filtrate is much lower and close to the detection limit (Fig. 5), which might cause some uncertainty in measurement. Tien Shan samples collected in 2008 display very similar iron solubility between the two

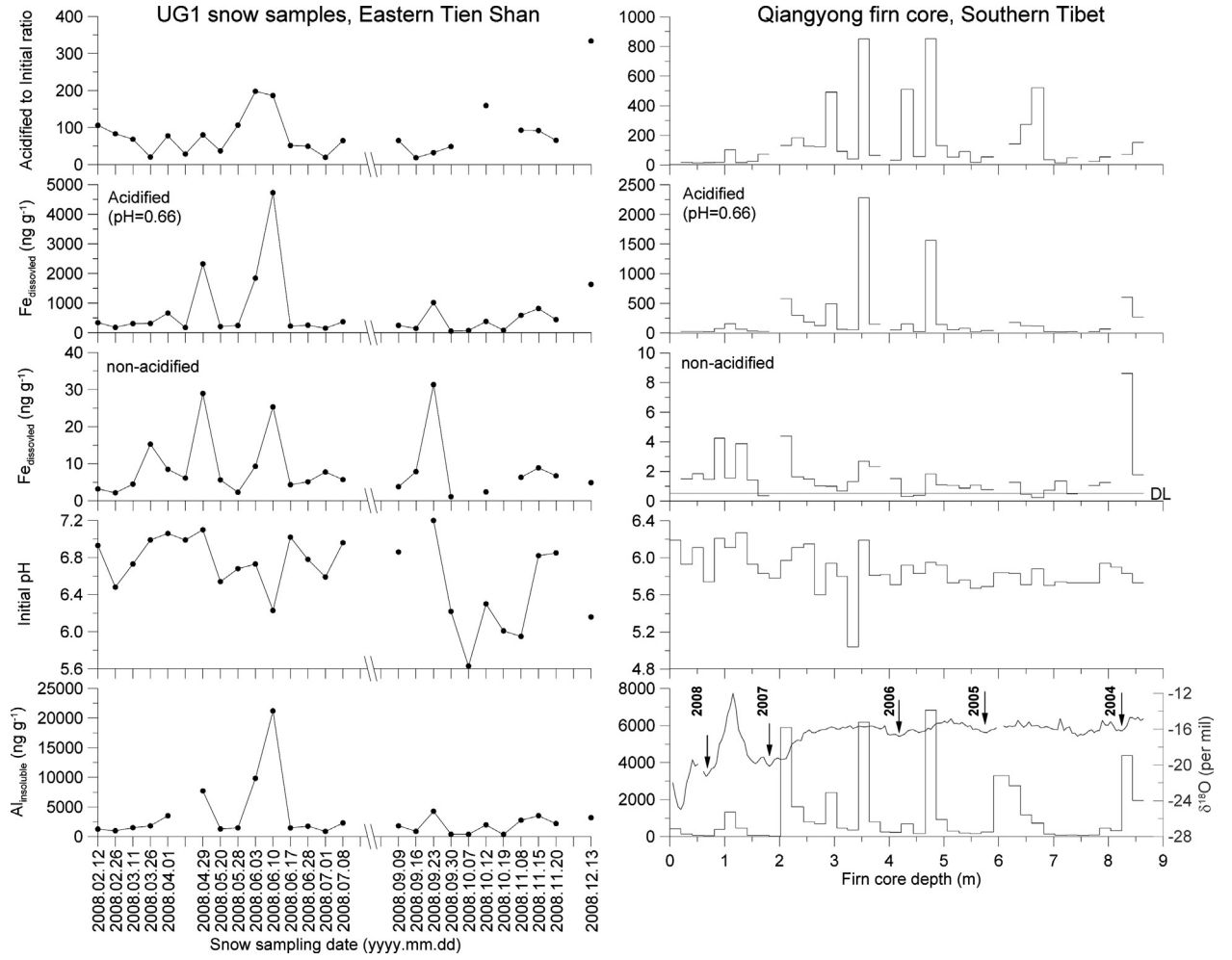


Fig. 5. Comparison of iron concentrations of acidified and non-acidified UG1 (Tien Shan) (left) and Qiangyong (right) samples (Experiment 3). $Al_{insoluble}$ and $Fe_{dissolved}$ mean the insoluble aluminium mass (index of dust) and dissolved iron concentration in melted samples, respectively. DL means the detection limit. The seasonal variations in Qiangyong $\delta^{18}O$ and dust ($Al_{insoluble}$) concentration profiles favour the dating, which is indicated by vertical arrows and numbers.

methods, indicating that the acidification has not significantly changed the dissolved Fe concentration. Although this result may be limited by the number of data (especially for Qiangyong samples), our results suggest that there

seems a small discrepancy (in the same order of magnitude) in the iron solubility between the two methods for Tien Shan. Therefore, the initial iron solubility (avoiding the impact of acidification) used in this study is reasonable.

Table 3. Statistics of the initial and acidified dissolved iron concentration (unit: $ng\ g^{-1}$) and ratio between them for Qiangyong and UG1 samples

	UG1 Fe dissolved ($n=24$)			Qiangyong Fe dissolved ^a ($n=36$)		
	Initial	Acidified (pH = 0.66)	Ratio	Initial	Acidified (pH = 0.66)	Ratio
Arithmetic mean	8.6	735.3	87	1.6	228.8	153
Geo. mean	6.2	412.3	67	1.2	90.4	74
Median	5.9	326.2	67	1.3	72.6	67
SD	8.3	1031.8	72	1.6	450.8	218
Minimum	1.1	53.6	19	0.2	18.2	14
Maximum	31.4	4726.6	616	8.6	2283.6	853

^aSome particulate iron might also be measured as the dissolved one for these pre-filtrated samples.

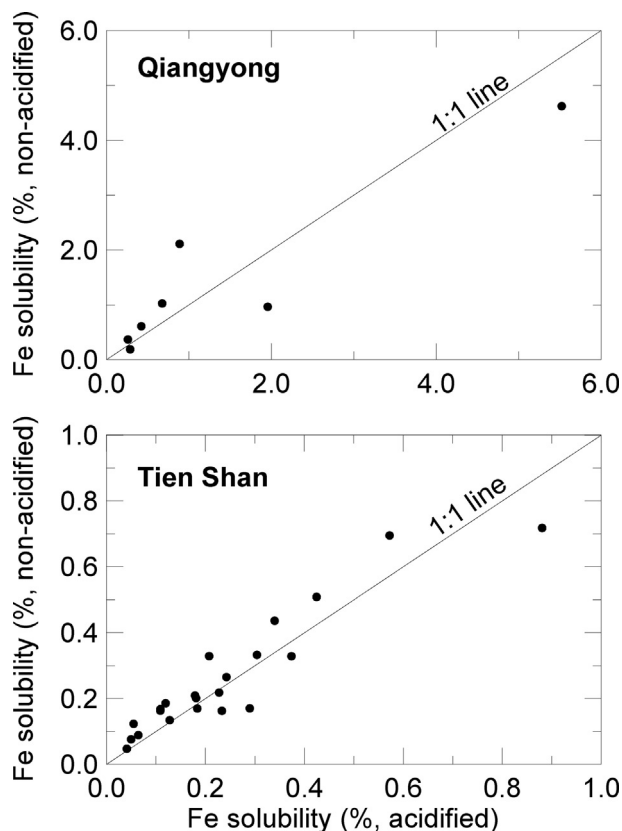


Fig. 6. Comparison of iron fractional solubility between acidified and non-acidified post-filtrate for the Qiangyong and UG1 (Tien Shan) samples.

If snow samples have experienced melting, then the calculated iron solubility would likely be distorted by elution, and the distortion will be larger if melting becomes stronger. The 2009 Qiyi samples are from old snow that, as known from field observations, has experienced strong melting, while the Lenglongling samples are from perfectly fresh snow (i.e. it was snowing when samples were collected) and might represent the actual initial state of iron solubility in Qilian Shan. Some UG1 snow samples, from relatively a lower altitude (4130 m a.s.l.), also experienced melting during the summer season due to high temperature, which would change the concentration of dissolved iron (and other elements) by elution and penetration (Li et al., 2006). Few ice layers, with thicknesses of 0.5–1 cm, were found in Qiangyong firn core, suggesting that melting is infrequent and weak at this site because of the high altitude (6100 m a.s.l.) and high accumulation rate, although it is located much further south than Qilian Shan and Tien Shan. The issue of post-depositional processes impacting on the dissolved impurities will be discussed in our future work.

4. Conclusions

For the first time, our results provide the water-soluble and water-insoluble iron fractions of Asian dust collected at Eastern Tien Shan, Qilian Shan and the Himalayas. They also provide the iron content and solubility along a north-south transect over inner Asia and the transport route for Asian dust that is carried by the North and South branches of the westerly jets. Both the iron content and solubility have a regional variability in High Asia. Several summaries and conclusions can be drawn:

1. The iron content in High Asian dust averages 4.95% in Eastern Tien Shan, while it ranges from 3.38 to 5.41% along Qilian Shan, and averages 3.85% in the Southern Tibetan Plateau. Our results present the initial iron solubility of Asian dust near its source regions. The iron solubility of dust in High Asian alpine snow, averaging from 0.05 to 2.16%, has regional difference of two orders of magnitude, which is much more significant than that of the iron content in dust. Previous results as well as ours indicate that Asian dust shows a large variation in iron solubility at a given site. And, even at a given site, the value of iron solubility also shows a large range, covering one or two orders of magnitude.
2. Dust composition, as indicated by the Ca/Al ratio, and particle grain size, and acidity seem to affect the iron solubility to some degree. The increase in iron solubility is likely to be caused by the acid-dissolved iron content from the iron-bearing minerals and can reach up to two orders of magnitude when the acidity increases to pH = 1.
3. Although our data might be underestimated because of non-acidification in pre-treatment, the iron solubility of Asian dust is lower in its initial state than those at remote sites but increases pronouncedly with greater transport distance and time period, suggesting that acidification and cloud processes along with grain-size sorting during transport seem to be very important for increasing the bio-available (dissolved) iron carried to the remote ocean.

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