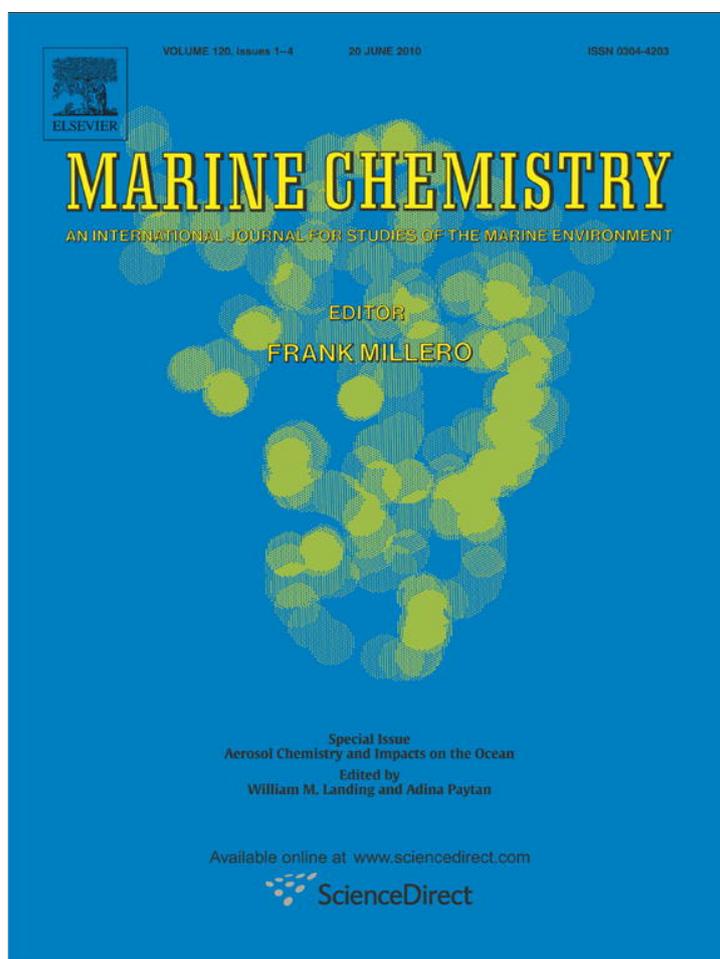


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

The fractional solubility of aluminium from mineral aerosols collected in Hawaii and implications for atmospheric deposition of biogeochemically important trace elements

C.I. Measures ^{a,*}, T. Sato ^{a,b}, S. Vink ^{a,c}, S. Howell ^a, Y.H. Li ^a^a Department of Oceanography, University of Hawaii, Honolulu, USA^b Engineering and Risk Services Corporation, Tokyo, Japan^c Sustainable Minerals Institute, University of Queensland, Australia

ARTICLE INFO

Article history:

Received 1 May 2008

Received in revised form 27 January 2009

Accepted 27 January 2009

Available online 12 February 2009

Keywords:

Dust solubility

Al

Hawaii

ABSTRACT

The partial solubility of mineral aerosols collected on the windward side of Oahu, Hawaii, was determined by suspending aerosol laden filters in samples of filtered surface seawater and determining the amount of dissolved Al released over a period of four days. The results showed that 80% of the dissolvable Al was released rapidly, within the first 24 h, and that a further 20% was released slowly over the next three days. The mass-based fractional solubility varied from 0.087–14.3% with a mean value of 4.6%.

The total dissolvable Al (1st plus 2nd mode) was well correlated with the total charge of nitrate and non seasalt sulphate (nss) ($R^2 = 0.78$, $R^2 = 0.84$) on replicate filters. These results imply that the abundance of atmospheric acids (derived from nitrate and sulphur species) in the atmosphere appears to be one of the major factors controlling the fractional solubility of atmospheric dust in this region. In addition, the results indicate that as this field of study develops there is an urgent need to develop a consensus on the matrix used for defining the solubility of dusts and the development of protocols that eliminate artefacts associated with the determining solubilities that will permit comparison of data between different research groups working in different regions.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Background

Understanding the systematics of the atmospheric deposition and dissolution of mineral dust in the surface ocean is of key importance to geochemistry and biogeochemistry. For the former, the atmospheric deposition route represents an important but poorly quantified part of the geochemical cycle. For the latter, the delivery, and variability of delivery, of biogeochemically important trace elements (e.g. Fe) to the surface ocean may play a vital role in immediate biological processes as well as having longer term consequences for the utilization of macro-nutrients and moderating atmospheric carbon dioxide levels. In the case of Fe, it has been suggested that in several large oceanic regions, limited atmospheric deposition of Fe to the surface waters of the regions is the principal cause of their High Nutrient Low Chlorophyll (HNLC) status (Martin and Fitzwater, 1988). It has been proposed that lack of available Fe, a required micronutrient for biological processes, prevents the complete uptake of surface water macronutrients in these regions and thus limits the effectiveness of the biological pump in partitioning atmospheric carbon dioxide into

the deep ocean (Martin, 1990). The coincidental increase in atmospheric dust and reduction in atmospheric CO₂ over the last four glacial cycles, as recorded in the Vostok ice core, Antarctica, (Petit et al., 1999) has stimulated interest in understanding the role of atmospheric transport in delivering continental materials to the surface ocean, particularly those that may play key roles in biological processes.

However, until recently, quantifying the vertical flux of atmospheric materials to the planetary surface has been limited to land-based sampling and the extrapolation of these values out into the adjacent oceanic regions (Duce et al., 1991). A more recent approach (Measures and Brown, 1996) uses the chemical imprint of dissolved Al from the dust in surface ocean waters to allow direct estimation of dust deposition to the ocean in regions remote from land masses. Measures and Vink (2000) showed good agreement between the dust deposition calculated from this Al model (MADCOW) and those from independent sources including the Duce et al. (1991) predictions.

However, the fractional solubility of dust in the surface ocean is one of the largest uncertainties in applying this model to open ocean surface waters since there are only limited studies and data regarding the fractional solubility of Al from dust in seawater (see below). This lack of data results in a poor understanding of the factors controlling the solubility of atmospheric minerals when they are deposited in the ocean. Currently, the MADCOW model uses an assumed solubility

* Corresponding author.

E-mail address: chrism@soest.hawaii.edu (C.I. Measures).

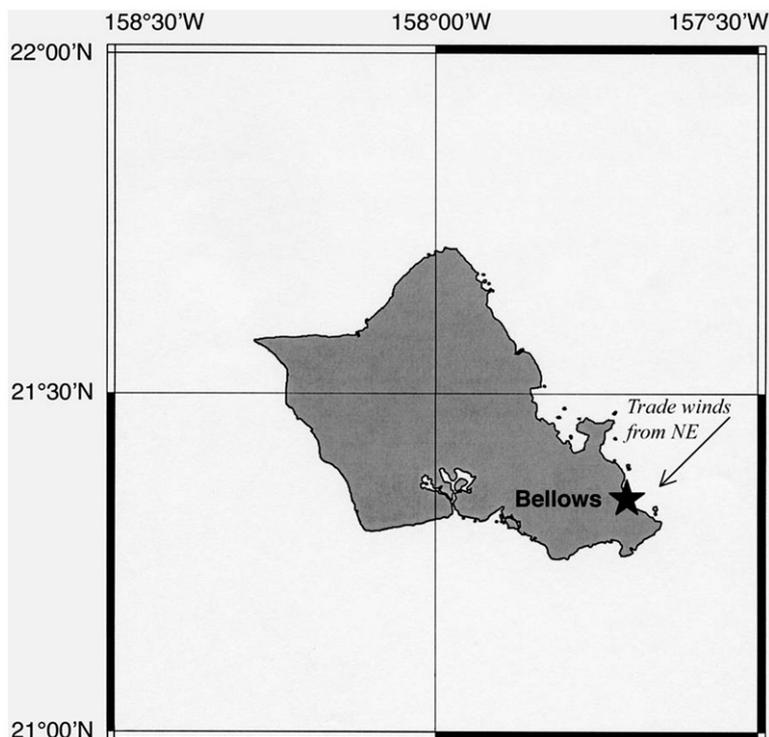


Fig. 1. Location of the Bellows sampling site, Oahu, and the predominant trade wind direction.

range of 1.5–5.0%. Thus estimates of deposition have an uncertainty of a factor of 3.3 based on the estimated solubility values alone. In order to improve the accuracy of the dust deposition model, it is necessary to improve our knowledge of the fractional solubility of Al from atmospheric aerosols and to understand the processes that control its variations. Only then will it be possible to extrapolate this understanding to predict how changes in the solubility of mineral dust over annual and longer periods might affect the delivery of geochemically important trace elements such as Fe to the surface ocean, and to incorporate these geochemical forcing functions into predictive models of global climate.

The work described here was designed to obtain some initial estimates of aerosol mineral solubility and to provide insights into the mechanisms that underlie variations in solubility. Hawaii's location in the central Pacific makes it an ideal site to examine aerosol solubility since the materials collected there have had long transport paths from their source regions in Asia and thus are likely to provide good examples of the characteristics developed during extended atmospheric chemical reaction processes. In addition, they are probably (but not certainly) representative of aerosols that affect large areas of the North Pacific basin, which also includes an important HNLC region. Thus the solubility characteristics of aerosols collected in Hawaii will be directly relevant to the delivery of the biogeochemically important trace element Fe.

1.2. Previous estimates of Al solubility from aerosols

Historical estimates (Hodge et al., 1978) that the solubility of aluminosilicate material was of the order of ~1% had resulted in little interest in the contribution of atmospheric aerosols to the geochemical cycle of Al. However, in 1987, Maring and Duce (1987) reported that 8–10% of the Al from the aluminosilicate in five aerosol samples collected at Enewetak Atoll dissolved (defined as passing a 0.45 μm filter) when the samples were suspended in filtered surface seawater. The majority of that dissolution (5–6%) occurred within 1 h of suspension, with a further 3–4% occurring more slowly over 60 h.

These researchers reported that the presence or absence of dissolved organic matter in the seawater had no noticeable effect on dissolution. However, they found that substitution of pH 8 seawater with pH 5.5 distilled water (to represent rainwater) resulted in a much more rapid dissolution process, although the magnitude of dissolution did not increase.

At the same time, Prospero et al. (1987), using rainwater samples collected in Miami, calculated a flux-weighted fractional solubility of approximately 5% for Al in Saharan origin aerosols, by using the dissolved Al in 0.45 μm filtered rainwater and the mass of the accompanying aerosol. The range of values reported, however, was 0.5 to 48% ($n = 18$). This large range provided two additional insights into the mechanistic aspects of dust solubility. First, the solubility of Al in dust increased with decreasing total dust concentrations. Second, the solubility increased with decreasing pH in the wet samples.

Spokes et al. (1994) examined the effects of pH cycling on aerosols by suspending urban and Saharan aerosols in distilled water and cycling the pH up and down to mimic in-cloud acidification processes. Determination of dissolved Al in the 0.2 μm filtered sub-samples showed that at pH = 5.6 the Saharan aerosols were less soluble than the urban ones (0.6 and 3.1% respectively) but that both aerosol types showed enhanced solubility at a typical in-cloud pH = 2 with fractional solubilities as high as 9 and 26.5% for the Saharan and urban aerosols respectively.

It is clear from the results of previous workers that there is a relationship between the solubility of the aluminosilicate material and the pH of the solution. Since the transport path of many of the aerosols that arrive in Hawaii take them through regions of Asia where large amounts of precursors of atmospheric acids are added to the atmosphere (e.g. SO_2 , NO_x , etc.) one of the goals of the work presented here was to build on those previous results and to examine what, if any, relationship exists between the occurrence of atmospheric acids and the fractional solubility of aerosol aluminosilicate. In addition, since our primary interest is in the geochemical effects of this aerosol deposition in seawater, a further goal was to develop a protocol for assessing the fractional solubility of mineral aerosols in an

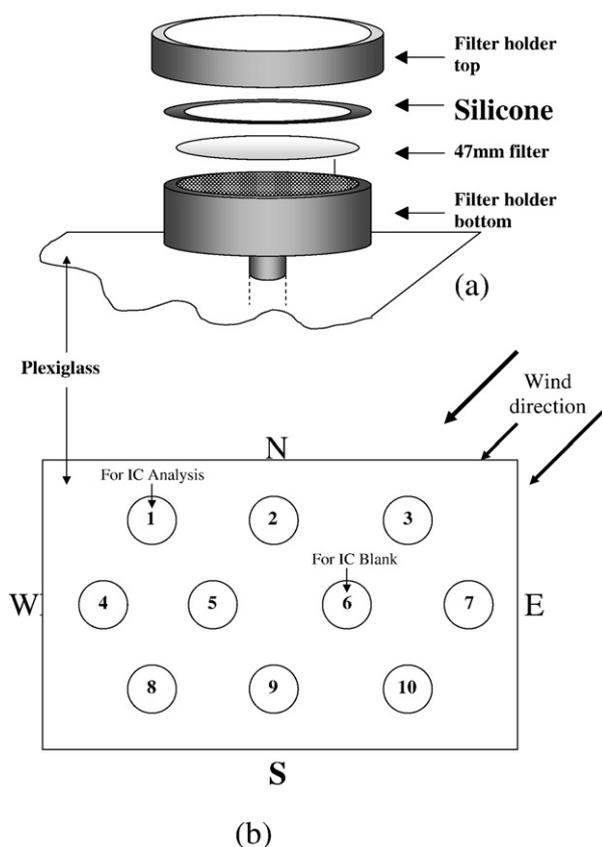


Fig. 2. Filter sampler (a) and position of filter samplers (b).

aquatic environment as close as is currently analytically feasible, to that experienced by aerosols deposited into the alkaline, high ionic strength surface ocean replete with organic ligands that might facilitate solubility.

2. Methods

Further, more detailed, descriptions of the methodologies used in this work can be found in Sato (2002). Here we present the outline of the major protocols used, reserving detailed description for the chemical methodologies.

2.1. Aerosol sampling

Atmospheric sampling was conducted at Bellows Air Force Station on the windward side of Oahu, Hawaii (Fig. 1), at the top of a 20 m tower (Upright manufacturing, Hoffman and Duce, 1972).

The aerosol sampler (Fig. 2) consisted of 10 open-faced filter holders (Nalgene cat#335), loaded with a 47 mm 0.4 μm Millipore polycarbonate filter (cat# HTTP-047-00) and a silicone O-ring. The silicone O-rings were placed between the filters and filter holders to make each holder airtight, and PVC tubing was used to make airtight connections between each hole in the Plexiglass and the base of the filter holder. To protect filter samples from atmospheric precipitation, a plastic cover was placed 24 mm above the surface of the filter sampler. Cable ties were used to stabilize the cover on the sampler. The face of the sampler was horizontal within $\pm 2^\circ$. To avoid potential contamination from the Al frame of the tower, the sampler was installed on the most windward side of the tower.

The sampler was connected to a high volume pump (GAST Manufacturing Inc. Model 1023), mounted at the base of the tower using PVC hoses, and valves (Fig. 3). A gas meter (American Meter Company Model# AL425) was used to record the total volume of air

that had passed through the system during each deployment period. Although at this site the predominant winds are the NE Trades, which come directly from the open Pacific Ocean, an automated sector control system controlled by a 21 \times data logger (Campbell Scientific), was used to stop the pump, and prevent sample collection whenever the wind was either outside the open water window between 10° and 120°T , or if the wind speed fell below 3 m s^{-1} .

Potential air leaks in the sampling system were detected and eliminated by observing the rate of pressure increase after a vacuum was developed in the sealed system and the pump was stopped. In its final configuration it was estimated that the amount of air leaking into the tubing system below the sampler was less than 5.5% of the total air mass going through the flow meter at the mean flow rate (80 L/min), of this sampling system. While this leak may result in a potential $\sim 5\%$ underestimate of the dust concentration in the atmosphere, it does not have any affect on the calculations of the fractional solubility of Al.

Clarke et al. (2003) have shown that sea spray aerosol created by the shore break at this site doesn't reach the top of 20 m sampling tower where the sampler was installed. However, another potential source of local aerosol is sea spray created by the reef 1.7 km offshore which can also produce aerosols that might reach the top of the tower. While it is impossible to eliminate the possibility of this local source, such an input would be unlikely to cause major Al contamination of the filter samples since Al concentrations in surface seawater around Hawaii are generally low compared to those found in atmospheric dust (Measures et al., 2005). The lack of Al contamination from all sources was confirmed by the results of the Al blank test (see 2.4 below) that show little Al on filters that were exposed without pumping, at the top of the sampling tower for 7 days.

2.2. Aerosol handling procedures

In order to avoid Al contamination of the filters and samples, the handling procedures employed used protocols similar to those we employ for low-level trace element determinations in oceanic water samples. All filter and sample handling was conducted in a class-100 laminar flow bench and plastic gloves were used during all handling stages. Before filter holders were loaded, all plastic materials and silicone O-rings were acid leached in a sub-boiled 0.5 N hydrochloric acid (HCl) bath at room temperature overnight. Millipore polycarbonate filters were acid leached in the same acid in an oven at 60°C overnight. All acid leached materials were rinsed with deionized (DI) water five times and dried in the class 100 flow bench. Once dried, the filters were mounted in the open-faced sample holders using Teflon forceps, and the holders were then placed on the Plexiglass frame and covered with another piece of Plexiglass. This assembled aerosol sampler was then left in a flow bench until the next sampler changeover. The sampler was carried in a clean plastic container between the laboratory and the sampling tower. For convenience, filter samples were identified by their position number (1–10; Fig. 2). Filter # 6 was always a blank filter used to determine handling blanks for ion chromatography determinations. It was deployed with the other filters, but its holder base was sealed to prevent air being pumped through and its surface was covered with an acid cleaned cover to prevent gravitational settling of particles on to the filter.

After deployment for about one week, each sampler was removed from the tower, and was brought back to the laboratory. Each filter sample was unloaded from its holder and placed in a clean Petri dish, using a NRD static master (500 μCi Po^{210} , Model# IU400) to neutralize static electric charges. To avoid losing aerosol particles, filters were carefully folded twice using Teflon bars and forceps, and were stored in a refrigerator at 4°C until analyzed. Filter #1 was used for the analysis of major cations and anions by ion chromatography (IC) and filter #6 was used for the IC handling blank.

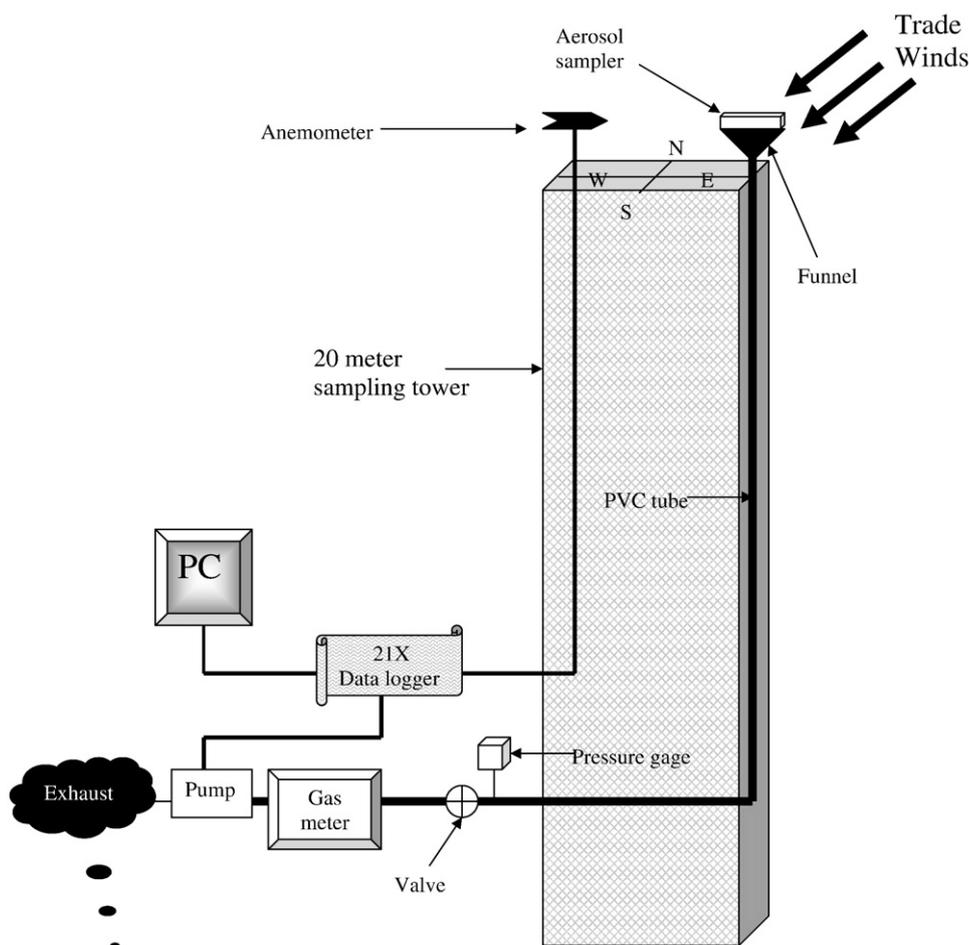


Fig. 3. Tower and aerosol sampler layout.

2.3. Dissolved Al determinations

Dissolved Al in both the digested filter samples and the fractional solubility experiments, was determined using a direct injection version of the Flow Injection Analysis (FIA) method of Resing and Measures (1994). In this mode the pre-concentration column was replaced by a 1.6 m sample loop made of Teflon tubing (i.d., 0.508 mm) with an internal volume of 324 μL . In this mode the pH of both sample and carrier solutions need to be matched (at 1.5) to ensure that the pH of the effluent was 5.7, within the optimal reaction pH range of the method. In this mode the sample volume required for a single Al analysis was 5 mL and the detection limit was 0.5 nM. Typical precision of this method for an 8.3 nM Al sample was 1.8% ($n=8$).

2.4. Total aerosol digestion

The total amount of Al on the aerosol filter samples was determined by digesting one complete filter, using a CEM Model MDS-2100 microwave acid digestion system. First, the filter sample and 7 mL of nitric acid (HNO_3) were placed in a high-pressure CEM Teflon digestion vessel to digest organic matter using the time and pressure settings (Table 1). After releasing the pressure built up during this process, 1 mL of HCl and 50 μL of hydrofluoric acid (HF) were added to the HNO_3 solution and the contents microwaved again to digest the mineral material. Lastly, to remove excess fluorine in the solution, 10 mL of saturated boric acid (H_3BO_3) was added to the mixed acid solution and the mixture heated again. The digested filter solution was placed into an acid leached Nalgene high-density

polyethylene (HDPE) translucent 60 mL bottle. The inside of the digestion bomb was rinsed 4 times with sub-boiled 0.048 N HCl solution, and the rinse solution was also added to the bottle to ensure complete recovery of the digested material. The dilution factor was calculated from the mass of the final solution. For the Al FIA determinations, an aliquot of the composite digested filter solution was diluted 100 times volumetrically.

To ensure that the digestion acids did not introduce chemical interferences into the FIA method, an Al standard was carried through the entire digestion procedure. The recovery of the Al spike was found to be $100 \pm 1.4\%$ ($n=6$) relative to an undigested Al standard sample. This result also indicated that the digestion procedure resulted in no loss of Al.

Table 1
Microwave acid digestion settings.

Purpose	Step 1			Step 2	Step 3
	Digest millipore polycarbonate filters			Digest aerosol minerals	Remove excess free fluorine
Acids used	HNO_3 15.4 M (7 mL)			HCl 6 M (1 mL) HF 50% (50 μL)	H_3BO_3 (10 mL)
Microwave settings	Stage 1	Stage 2	Stage 3	Stage 1	Stage 1
Power (%)	90	100	100	100	100
Maximum pressure (psi)	90	95	100	100	50
Time (min)	10	10	10	30	15
TAP (min)	5	5	5	30	10

Note: TAP = time at maximum pressure.

In order to check the recovery of the digestion method for mineral materials, a standard reference material, AGV-1, was digested using different times at pressure.

The results indicated that the concentration of dissolved Al did not increase significantly beyond a 30 min digestion time which was then adopted for the aerosol digestions. The recovery of Al from AGV-1 was $92.2 \pm 2.4\%$ ($n=7$) of its 17.15% certificate value (Flanagan, 1967; Govindaraju, 1989). The aerosol numbers have not been corrected for this apparent low recovery since it is believed that this results from the presence of augite, in AGV-1, a refractory volcanic mineral that is unlikely to be found in aerosols.

Since the digestion, partial dissolution process and ion chromatography determinations each use complete filters, it was necessary to ensure that the filters in the different positions in the aerosol sampler were reasonable replicates of each other. This was achieved by digesting an entire set of filter samples that had been exposed for seven days between 5 and 12 December, 2001. The results (Table 2) showed that filters were identical within a standard error of 11% (1sigma), ($n=9$), suggesting that it is reasonable to compare the dissolvable Al from one filter to the total Al on another filter.

The Al blank from the filters and handling was also estimated by exposing an entire set of filter samples (10) on the top of sampling tower for one week without pumping air. After digestion the Al content was found to be below the FIA detection limit.

2.5. Determination of fractional solubility

The fractional solubility of Al from the mineral aerosols was determined in filtered (0.2 μm Pall Gelman, Cat#4260) surface seawater from Station Aloha (22.75°N, 158°W). A weighed amount of filtered surface seawater (average 60 g) was added to an acid leached 60 mL HDPE bottle and the aerosol filter sample and a Teflon-coated stirring bar were added using Teflon forceps. The sample was stirred for 5 min and then left in the flow bench at room temperature (24 °C) until the first dissolved Al determination was made. At appropriate intervals, a 10 mL sub-sample of the solution was pumped out of the sample bottle using a peristaltic pump through an acid leached Pall Gelman 25 mm 0.2 μm in-line filter into another container. Filtration of the sub-sample is required to avoid possible Al dissolution artifacts when samples are acidified prior to FIA determination. After collection, the sub-sample was immediately acidified with sub-boiled 6 N HCl to 0.048 N and was injected into the FIA system for Al determination. Sub-samples were withdrawn at 24 h intervals for four days.

Since during the dissolution experiments, the solution is not acidified, the potential loss of Al by adsorption on to the walls of 60 mL HDPE bottles was also examined. The potential for Al adsorption was evaluated by observing the change in Al concentration over a 4-day period in both a spiked (198 nM) and unspiked (1.4 nM) sample of filtered surface water. These concentrations were selected to cover the range of Al concentrations seen in the fractional solubility experiments. The results (Table 3) indicate no significant loss of Al over this period of time and thus wall loss of dissolved Al was unlikely to be a significant error in the assessment of the mineral solubility over a 4-day period.

Table 2
Replication of filters.

Filter	1	2	3	4	5	*7	8	9	10	Average
Al, nM	40.65	38.50	44.34	51.33	45.87	36.39	39.43	41.50	39.53	41.94 (10.8%)

* Note sample #6 was lost during transfer process.

Table 3
Al absorption test results.

Time (day)	0	4	Al change in samples (nM)
Sample1	3.73	3.95	+ 0.22 < FIA detection limit
Low in Al (nM)	± 0.0047 ($n=2$)	± 0.0029 ($n=2$)	
Sample2	195.07	195.02	- 0.05 < FIA detection limit
High in Al (nM)	± 0.0049 ($n=1$)	± 0.0049 ($n=2$)	

2.6. Inorganic ions

Concentrations of the DI water dissolvable fraction of chloride (Cl^-), sulphate (SO_4^{2-}), oxalate ($\text{C}_2\text{O}_4\text{H}^-$), nitrate (NO_3^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) on the filters were determined using ion chromatography (IC) (Huebert et al., 1996). The detection limits for these ions were 0.0042, 0.0031, 0.0034, 0.0048, 0.0708, 0.0077, 0.0123, 0.011 ($\mu\text{moles}/\text{filter}$), respectively. Ammonium was not determined on these aerosol samples due to sodium interference.

2.7. Air mass trajectories

The sources of the air masses sampled and residence time of the particles in the air was estimated using the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT backward trajectory model (Draxler and Hess, 1997). The trajectories were calculated for each sampling day (total 102 days).

3. Results

3.1. Atmospheric sampling

Aerosol sampling was conducted at the Bellows aerosol sampling site between January and June, 2002, this period includes both high and low dust seasons. Individual sampling periods generally lasted one week although during the high dust season they were shorter (Table 4). In cases where sector control limited pump operation to less than 15% of the total collection period, samples were not used. These samples have relatively small quantities of dust and produce excessive analytical uncertainties in the Al fractional solubility results. Application of these criteria led to the rejection of 4 out of 20 samples (Table 4).

The amount of particulate mineral material on each of the filters is presented in Table 4 and Fig. 4. Since Al is a relatively constant component of mineral aerosol material (8% Al by mass Taylor, 1964; Wedepohl, 1995; Li, 2001), total Al determined by the digestion process has been converted to an atmospheric mineral dust load using this ratio.

The minimum and maximum dust concentrations observed were $0.02 \mu\text{g}/\text{m}^3$ (Sample #21; 20–26 February) and $0.70 \mu\text{g}/\text{m}^3$ (Sample #32; 17–23 April), respectively. These values are at the low end of the atmospheric dust concentrations previously observed on Oahu, Hawaii by Uematsu et al. (1983), who found a range of 0.02 to $4.6 \mu\text{g}/\text{m}^3$ during their January 1981 and March 1982 sampling (Table 5).

Dramatic variations in mineral dust load are exemplified by the contrast between samples #24 and #25. The more than one order of magnitude increase in atmospheric mineral dust concentration observed during the sampling period 18–24 March (sample #25) was coincident with an intense dust storm that began in China on March 16, as observed by the Total Ozone Mapping Spectrometer operated by National Aeronautic Space Administration (NASA). Back trajectory calculations using HYSPLIT suggest that this air mass arrived at Bellows, during the deployment of sample #25. However it is important to note that the uncertainties in HYSPLIT model

Table 4
Aerosol filter samples.

Sample#	Sampling start date	Sampling period (days)	Active sampling time (%)	Volume of air sampled (m ³)	Total Al (nmole/m ³)	Dust ♥ (ng/m ³)	Al solubility (%)
19	6-Feb-02	7	69	637.16	0.0508	17.1	6.45
20	13-Feb-02	7	59	559.52	0.185	62.3	0.090
21	20-Feb-02	7	86	707.08	0.0447	15.1	6.20
22	27-Feb-02	7	58	639.79	0.101	34.0	2.10
23	6-Mar-02	7	45	360.76	0.120	40.3	3.01
24	13-Mar-02	5	37	274.84	0.107	36.2	13.6
25	18-Mar-02	7	64	544.05	1.15	387	1.39
26	25-Mar-02	3	62	208.16	0.532	180	1.15
27	28-Mar-02	4	2.4♦	15.12	–	–	–
28	1-Apr-02	4	49	268.98	0.708	239	2.01
29	4-Apr-02	5	9.8♦	75.13	–	–	–
30	8-Apr-02	5	8♦	63.49	–	–	–
31	12-Apr-02	6	51	315.45	1.14	383	0.476
32	17-Apr-02	7	58	351.92	2.08	701	0.297
33	24-Apr-02	7	64	399.61	0.204	68.8	6.47
34	1-May-02	7	70	436.51	0.298	100	3.72
35	8-May-02	7	56	332.24	0.363	122	3.32
36	15-May-02	7	72	520.69	0.128	43.2	6.48
37	22-May-02	7	13♦	139.86	–	–	–
38	29-May-02	7	83	612.72	0.386	130	1.10

♦ Samples were rejected because of small amount of air sampled by filter.

♥ Calculated assuming mineral aerosol are 8% Al by mass.

calculations increase by 50% for each 24 h of hindcasting, and are not usually considered reliable beyond 5 days. Thus the majority of our Pacific trajectories which often exceed 5 days since the air mass was above land, should be considered only as indirect evidence of aerosol origin.

Nevertheless, the changes in the material making up the aerosol mass are apparent in SEM images (not shown) where typical low dust samples (e.g. #19) are predominantly composed of sea salt particles while a typical high dust season sample (e.g. #25) contains a large number of aggregate dust particles as well as sea salt.

3.2. Fractional solubility

Results of the Al fractional solubility experiments are presented in Table 4. The fractional solubility ranges from 0.087 to 14.3% with a mean value of 4.6%. Results from time course experiments (Fig. 5) demonstrate that within the first 24 h, aerosol Al dissolved relatively quickly (first stage dissolution), then continued dissolving slowly for the next 3 days (second stage dissolution). Additional results, while the analytical protocol was being developed, indicated that most of the initial dissolution occurred extremely rapidly, within the first

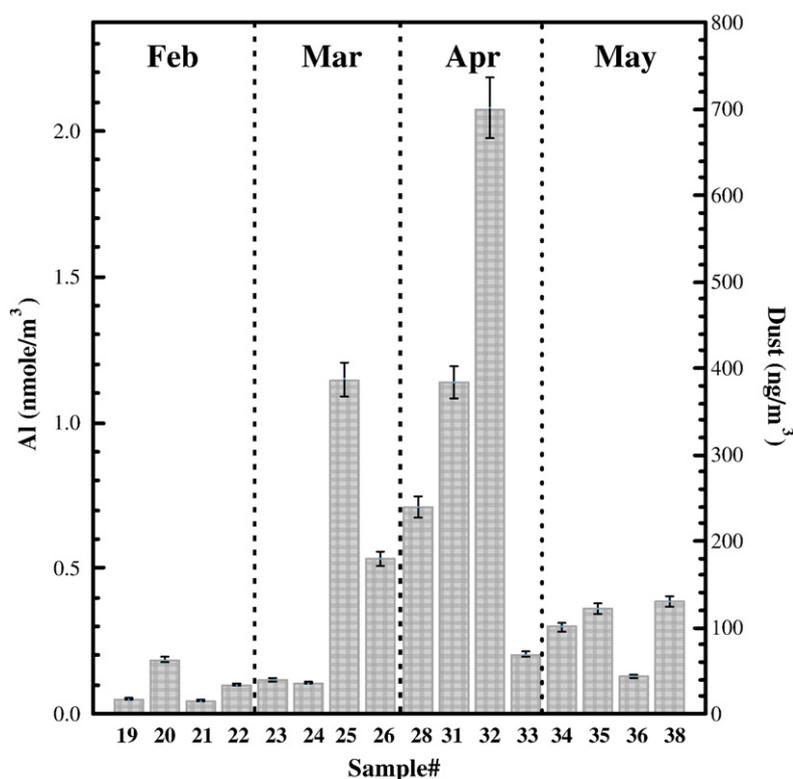
**Fig. 4.** Al and dust concentration in the aerosol samples.

Table 5
Range of atmospheric concentrations of mineral aerosol in Hawaii.

	Entire period		Low dust period		High dust period	
	Range	Mean	Range	Mean	Range	Mean
Feb (1981)–Mar (1982) ♥	0.02–4.6	0.65	0.02–0.93	0.19	0.29–4.6	1.3
Feb–Jun (2002)	0.015–0.700	0.160	0.015–0.062	0.034	0.043–0.700	0.235

Note1: Concentrations in $\mu\text{g}/\text{m}^3$.

Note2: Assuming 8% of mineral aerosol is Al.

♥ Uematsu et al. (1985)'s data.

20 min. This work was not repeated though, and is thus not reported here, since we subsequently focused on establishing a daily sampling protocol. This two-stage dissolution process qualitatively agrees with the Al solubility results reported by Maring and Duce (1987). Their results also indicated that approximately 5–6% of the Al in atmospheric dust dissolved within 0.6 h, and an additional 3–4% dissolved within 60 h. A plot of fractional solubility after one day vs. that after four days shows a good correlation between the first and second mode fractional solubility with the second mode being about 20% of the first mode.

3.3. Concentration and ionic charge balance of the major ions

Table 6 shows the concentration of the major ions and their charge balance in the DI soluble fraction of the aerosol particles for each filter sample. Although ammonium was not determined, the charge balance agreement between the total major cations and anions (99.9%) indicates that the major anions and cations are accounted for.

Since we will interpret our data in terms of the magnitude of sulphur and nitrogen containing atmospheric acids it is necessary to correct our filter sample results for the presence of seawater sulphate (all nitrate on filters is assumed to be atmospheric, since surface seawater nitrate levels around Hawaii are extremely low). We have corrected for the sea salt component using the Na content of the leaches and assuming that all Na originates from sea salt and applying the Na:SO₄ ratio in seawater. While Na is also a significant component of crustal material and could also arise in our leaches from that material we estimate that this source would contribute at a maximum from 0–4.6% (average $1 \pm 1.1\%$) of the Na we see in leaches. This estimate, which is based on an average upper crust concentration of 1.09 mmole Na/g dust is very much a maximum estimate since it assumes that all the Na contained within the particles would come into solution during a DI leach. Thus the error in using Na is comparable to, or less than, the analytical precision of the Na determination (~2%), and thus will not adversely affect the interpretation of our data sets. The results, Table 7, shows that the non sea salt (nss) SO₄²⁻ concentration on filters varied by approximately one order of magnitude from 0.07 to 0.92 $\mu\text{moles}/\text{filter}$.

4. Discussion

4.1. The role of atmospheric acid in promoting mineral aerosol solubility

Before dust particles are deposited on the sea surface or are removed from the atmosphere by precipitation, they may have passed through many wetting and drying cycles during the cloud formation and evaporation (Junge, 1964). During these processes, the dust particles are subject to a very low pH environment, during which the chemical bonds in the mineral lattice are attacked and broken by atmospheric acids deriving from sulphur and nitrogen species. Consequently, some of the Al in dust particles is in a “ready to dissolve” form before the dust deposits on the sea surface. In other words the process of mineral dissolution in the ocean, is largely

determined by atmospheric processes, the ocean merely serves as a receptor for the dissolved material, and only exerts an influence when elemental solubility levels are exceeded in this high pH matrix. Spokes et al. (1994) through a series of elegant laboratory experiments showed that the solubility of Al in Saharan dust was indeed increased by repetitive cycling of this material through a series of low pH acid vapour cycles. Thus the amount of dust that dissolves is largely dependent on the past chemical history of the dust particles in the atmosphere. Such a process implies that the longer the residence time of the dust particles in the atmosphere is, the more Al will be in a “ready to dissolve” form. However, as has been reported for SEAREX data, the initial transport of Asian dust is in the cold, dry, free troposphere where such cloud cycling would not occur. It is probably when this dust descends into the marine boundary layer and is transported to Hawaii in the NE Trades, that cloud cycling is likely. A cloud cycling process is consistent with the extremely rapid first stage dissolution that we observe in our aerosol samples when they are suspended in seawater, and also seen by others. Whether the ultimate source of this rapidly dissolving material is from the lattice of the crustal materials or from the release of trace elements adsorbed onto the surface of the particles before atmospheric transport, is beyond the scope of this work. Also, the role that particle size distribution and how the role of surface area to volume interacts with acid concentrations would have important consequences for fluxes. This leaves the question of the process that leads to the slower second stage dissolution. It is feasible that removal of the outer coating of “ready to dissolve” materials, could leave fresh unweathered mineral surfaces that would then release materials slowly as they equilibrate with the alkaline environment of ocean water.

4.2. Sources of atmospheric acid in the Bellows samples

Given the likely importance of the acid in the aerosol samples it is worth examining the occurrence of the principle acid materials in our samples before we discuss the actual solubility values we report for Al (Section 4.3).

The concentrations of water leachable NO₃⁻ and nssSO₄²⁻ in our samples are shown in Fig. 6. The good correlation ($R^2 = 0.83$) implies that the source of these acids is similar. NO₃⁻ is produced by oxidation of NO_x, which is mainly from fossil fuel burning (Prospero, 1996). We have deliberately avoided reporting HYSPLIT back trajectories beyond 5 days in this work because we realize that the error increases

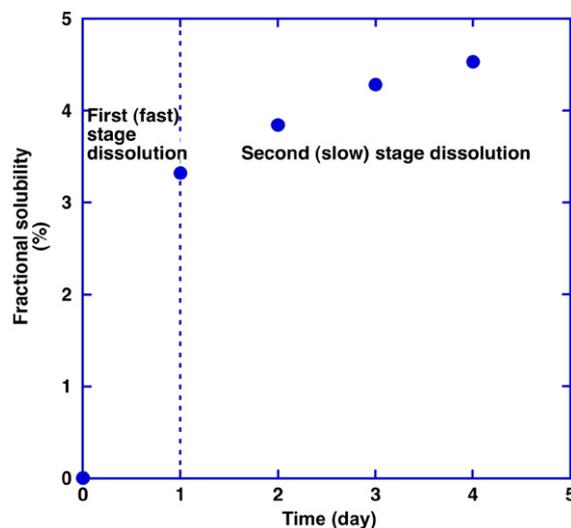


Fig. 5. Typical time course of 2-stage dissolution.

Table 6
Ion chromatography results ($\mu\text{moles}/\text{filter}$).

Element detect. limit ($\mu\text{mole}/\text{filter}$) Sample#	Cl^- 0.0042	SO_4^{2-} 0.0031	Oxalate^- 0.0034	NO_3^- 0.0048	Na^+ 00.78	K^+ 0.0077	Mg^{2+} 0.0123	Ca^{2+} 0.011	Total cations ($\mu\text{eq.}/\text{filter}$)	Total anions ($\mu\text{eq.}/\text{filter}$)
19*	12.77	1.12	0.04	0.18	11.75	0.00	1.41	0.32	15.21	15.23
20*	9.62	0.62	0.06	0.14	8.67	0.00	0.97	0.25	11.11	11.05
21*	14.01	1.00	0.04	0.31	12.15	0.00	1.46	0.34	15.76	16.38
22	9.16	0.68	0.07	0.20	7.60	0.20	0.93	0.22	10.10	10.80
23	7.31	0.56	0.04	0.16	6.48	0.15	0.74	0.19	8.48	8.62
24	5.44	0.40	0.05	0.12	5.16	0.11	0.62	0.15	6.79	6.41
25	10.55	1.52	0.04	0.56	9.99	0.24	1.15	0.72	13.97	14.19
26	4.95	0.33	0.01	0.10	4.34	0.10	0.53	0.12	5.75	5.71
28	2.71	0.50	0.02	0.27	2.84	0.08	0.33	0.16	3.92	4.00
31	5.68	0.44	0.04	0.15	5.19	0.12	0.64	0.16	6.91	6.74
32	6.38	0.49	0.03	0.16	5.76	0.14	0.74	0.20	7.79	7.56
33	6.52	0.56	0.03	0.15	6.10	0.15	0.75	0.21	8.17	7.80
34	6.04	0.50	0.02	0.14	5.54	0.13	0.71	0.20	7.49	7.20
35	5.88	0.76	0.01	0.26	5.87	0.15	0.75	0.22	7.95	7.67
36	8.04	0.80	0.03	0.27	7.74	0.19	1.00	0.24	10.39	9.95
38	5.00	0.59	0.09	0.23	5.08	0.12	0.67	0.23	6.99	6.50

* No blank correction for these samples.

significantly each day of hindcasting and that their use beyond a 5-day period is controversial. However at a remote site such as Hawaii air masses have frequently been out of contact with any land mass for significantly more than 5 days thus making rigorous identification of the source of particulates and acids problematic. We do note nevertheless that the occurrence of the highest levels of acid in our samples was in sample #25 (18–25) March, which was also one of the highest dust loads ($387 \text{ ng}/\text{m}^3$) and was collected after an extremely large dust storm in China had commenced (March 16th, see Section 3.1 above). We also note that high acid levels were also found in samples 28 and 35 which also had high dust loads associated with them. Since this was in the midst of the high dust season that routinely brings large amounts of Asian dust to Hawaii, we take this as lending credence to, if not proof of, that the likely source of NO_3^- and of nss SO_4^{2-} on the filter samples is from fossil fuel combustion in Asia. Although contamination of nss SO_4^{2-} from the volcano on the Island of Hawaii is a possibility, our use of sector control reduces this possibility. In addition, volcanic contamination would contribute nss SO_4^{2-} , but not NO_3^- which is inconsistent with the correlation shown in Fig. 6. We realize of course that natural sources of these materials also exist, from DMS oxidation and nitrogen oxidation, however these appear to be small compared to the anthropogenic signal we encounter. It should also be pointed out, that although the highest acid samples are associated with high dust, samples 31 and 32 (April 12–24) also are

high dust but have relatively low nss SO_4^{2-} and NO_3^- . Whether this is a result of differential trajectories across the Asian continent is beyond the scope of this manuscript.

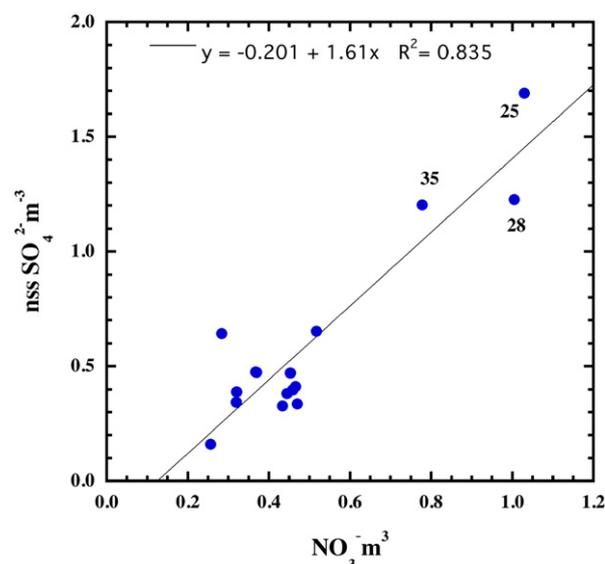
4.3. Relationship between dust solubility, aerosol acidity and mass at Bellows

The data in Table 4 show a wide range in the fractional solubility of the Al from the mineral dust with values ranging from 0.087 to 14.3%, with a mean of 3.61 ± 3.4 (1 sigma). While the average is close to that reported by other researchers, the large range clearly implies difficulties in modeling this process, if the underlying mechanisms behind the solubility process cannot be enumerated. Thus our discussion will focus on elucidating those processes from the data we have at hand.

It is important to bear in mind that our determination of solubility on any particular filter represents the bulk solubility of all the particles on that filter. With a 7 day sampling period it is likely, though hard to determine given the limits of HYSPLIT hindcasting and the travel times of materials to the central Pacific, that some of our filters will contain aerosols of different origin that had been exposed to different

Table 7
Non-sea salt (nss) ions calculated using Na as a reference.

Sample#	nss SO_4^{2-}	nss K^+	nss Mg^{2+}	nss Ca^{2+}
19	0.643	0.0	0.141	0.0942
20	0.161	0.0	-0.0179	0.107
21	0.382	0.0	0.141	0.0990
22	0.344	0.047	0.125	0.0782
23	0.471	0.028	0.0277	0.139
24	0.327	0.0	0.109	0.146
25	1.69	0.037	0.0368	0.919
26	0.336	0.048	0.192	0.144
28	1.23	0.074	0.0372	0.372
31	0.412	0.0	0.190	0.127
32	0.398	0.028	0.284	0.227
33	0.475	0.050	0.150	0.200
34	0.389	0.023	0.206	0.183
35	1.20	0.090	0.271	0.271
36	0.653	0.038	0.250	0.134
38	0.473	0.016	0.163	0.180

Note1: Concentrations in nmole m^{-3} .**Fig. 6.** Non sea salt sulfate vs. nitrate.

acid concentrations in the atmosphere. The possibility of high acid coated particles artificially promoting the solubility of low acid particles on the filters through surface contact is possible, but SEM pictures of even highly loaded filters show little contact between individual particles on the filter. In the case of two distinct particle types on the filter with different solubilities our protocol would determine the average solubility of all the particles. However, this is true even for a homogenous air mass, where particles of different sizes, with different surface to volume ratios might display different fractional solubilities. It is hard to see though how this problem can be avoided until solubility determinations can be made on single particles. Clearly as the work in this field progresses and sampling and analytical protocols are refined identification of potential artefacts and the magnitude of their effect will need to be assessed against the logistical issues of filter changing and the analytical requirements for this kind of work.

Fig. 7 shows there is a clear inverse relationship between the mass of dust collected on the filters and the fractional solubility of that material. During the high dust season, solubilities are lower than during the low dust season. This relationship has been reported before e.g. (Prospero et al., 1987; Baker and Jickells, 2006). However, since fractional solubility is a ratio, it is perhaps not surprising that the fraction of material that dissolves should vary inversely with the amount of material.

Thus it is valuable to investigate the relationship between solubility and the amount of acidic components in the aerosol. Fig. 8 shows the relationship between the amount of acid from NSS plus nitrate correlates well with the amount of Al that dissolves from each filter. The correlation coefficient R^2 is 0.46, However there are three points that do not fall on the general trend line they are samples (# 24, 33 and 34). Exactly why those three data points are anomalous is not clear at this time. Sample #24, which also had the highest fractional solubility of all samples ($13.6\% > 2 \times$ the next highest sample) has a suspicious lack of change of solubility between 1 and 4 days, implying that this sample may be contaminated. However this same evidence of potential Al contamination is not present for the other two samples. The alternative possibility, that the $nss\ SO_4^{2-} + NO_3^-$ are underestimated seems unlikely from charge balance considerations and the presence of other ions (discussed below). We note that without those three anomalous samples (Fig. 8) R^2 is 0.92. That the amount of Al released from the mineral dust on the filter increases with the amount of free acid, is not surprising since this would represent a simple acid

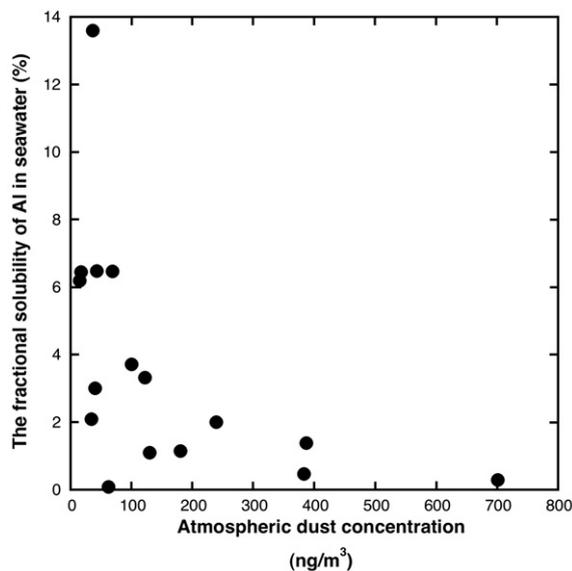


Fig. 7. The fractional solubility of Al vs atmospheric dust concentration. All normalized per m^3 air sampled.

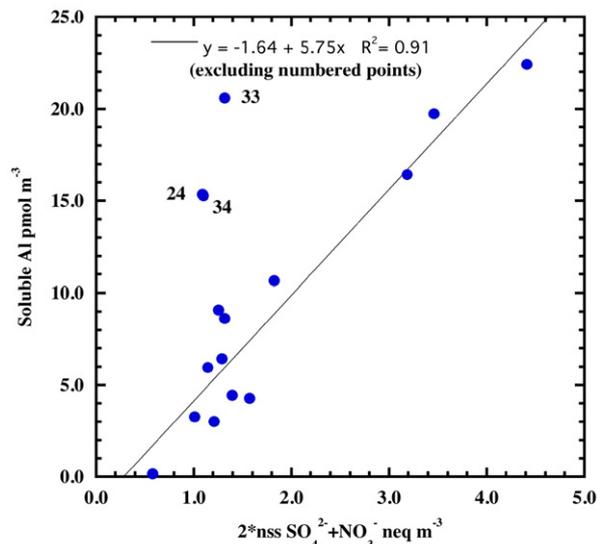


Fig. 8. The amount of dissolved Al vs. equivalents of acidic aerosols. All normalized per m^3 air sampled.

based dissolution of the mineral dust, however the slope of the line 3.9 pM Al/neq acid (which would indicate 11.7 peq Al/neq acid), indicates that attack of the mineral lattice and release of Al by the free acid accounts for only ~1% of the neutralization of the atmospheric acid. Thus with mineral dust containing a high percentage of calcium carbonate it is perhaps not surprising, that the majority of the acid neutralization is occurring via other mechanisms. In fact a plot of the major nss ions that might be also be expected to be released by acid mineral interactions Fig. 9), shows a similarly good correlation with the $nss\ SO_4^{2-} + NO_3^-$ ($R^2 = 0.68$). It should also be noted that the anomalous samples 24, 33 and 34 all fall on the same general trends in this plot as the other data. The slope of the correlation line, 0.32 implies that 32% of the acid is neutralized by minerals releasing these major ions. Since most of this material is in fact Ca and Mg, were one to further assume that these ions originated in Ca and Mg carbonates, the entire amount of $nss\ SO_4^{2-} + NO_3^-$ could be neutralized, leaving only the small observed fraction of acid to release of Fe or other elements from the aluminosilicate matrix. Not considered here, because we

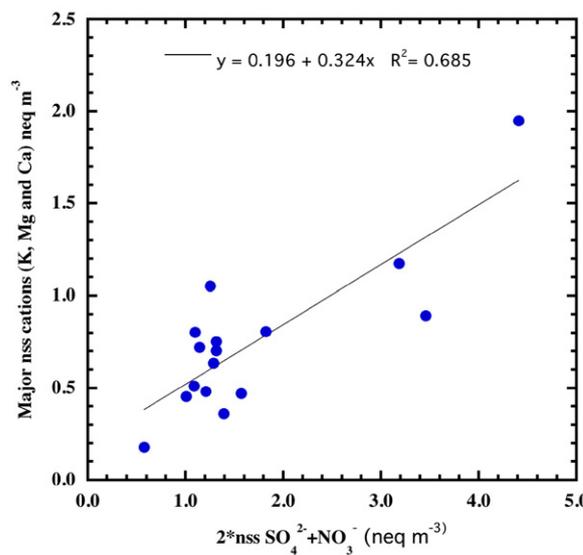


Fig. 9. Equivalents of non sea salt major cations vs. equivalents of acidic aerosols. All normalized per m^3 air sampled.

have no data, is that the amount of ammonia in the sample will also play a role in acid neutralisation and thus will also affect mineral solubility. Quinn et al. (1990) found that the molar ratio of NH_4^+ to nss SO_4^{2-} on particles they collected in the Pacific was 1.5 ± 0.88 , and 0.38 ± 0.064 between $50\text{--}30^\circ\text{N}$, and $29\text{--}15^\circ\text{N}$ respectively. These results suggest that ammonia may also play an important role in neutralising atmospheric acids and modifying mineral dust solubility.

5. Conclusions

Mayewski et al. (1986) reported that the data from an ice core in southern Greenland during the period of 1879 to 1984 shows that atmospheric nss SO_4^{2-} concentration has tripled in this region starting in approximately around 1900 and the nitrate concentration has doubled since approximately 1955. These increases are probably due to the deposition of these chemical species from air masses carrying anthropogenic emissions. In our work we see that the amount of dissolved Al is positively correlated ($R^2 = 0.47\text{--}0.91$) with the amount of acids in the atmosphere. Thus, the dissolvable fraction of aerosol Al may also have increased since 1900. As mentioned in the introduction, the Vostok ice core data show that during glacial periods, there was 15–50 times as much dust flux as today. This however, would not necessarily mean that the dissolved Al flux was 15–50 times as much as today unless atmospheric acid concentration was also 15–50 times as much as today. This Al fractional solubility research implies that the atmospheric acid concentrations of that period are key components in developing an understanding of how much Al (and by extension iron) dissolved in seawater during glacial periods. However, even if the acid concentrations are the driving force behind the solubility, mass of aerosol, surface area and the presence of acid neutralizing materials are all important modifiers of this initial forcing function. In the end the amount of material that dissolves in the ocean from any given dust deposition event will be a complex combination of all these factors. At this stage we understand only a few of these parameters well enough to incorporate them in models. It will be vitally important to develop reproducible protocols to assess mineral dust solubility as well as ensuring that mineral dust samples from a range of different environments are quantified. The high levels and good correlations between the nss SO_4^{2-} and NO_3^- in our samples imply anthropogenic influences. Thus, they may be overstating the role that acids play in this process in pre-anthropogenic times.

Although the work we present has shortcomings in the detail to which we can interpret the data, we think that it sheds light on the processes that lead to dust dissolution in the ocean. It is clear from this initial work that other parameters should be carefully constrained in continued investigations, in particular future work should pay close attention to the availability of all acid neutralizing materials, including carbonates and ammonia.

Acknowledgements

We would like to acknowledge the financial support of the NSF for this work through OCE grant # 0082317. We would also like to thank 2 anonymous reviewers and the associate editor Bill Landing for their comments which have helped strengthen the manuscript. We would like to thank Eric De Carlo and Chuck Fraley for their help with the digestion methodology, Liangzhong "John" Zhuang for the major ion determinations, and Kristen Mailheau for help in filter changing. This is contribution number 7621 of the School of Ocean Earth Science and Technology of the University of Hawaii.

References

- Baker, A.R., Jickells, T.D., 2006. Mineral particle size as a control on aerosol iron solubility. *Geophysical Research Letters* 33, L17608. doi:10.1029/2006GL026557.
- Clarke, A., Kapustin, V., Howell, S., Moore, K., Lienert, B., Masonis, S., Anderson, T., Covert, D., 2003. Sea-salt size distributions from breaking waves: implications for marine aerosol production and optical extinction measurements during SEAS. *J. Atmos. Ocean. Technol.* 20, 1362–1374.
- Duce, R.A., et al., 1991. The atmospheric input of trace species to the world ocean. *Global Biogeochemical Cycles* 5, 193–259.
- Draxler, R.R., Hess, G.D., 1997. Description of the HYSPLIT_4 modeling system, NOAA technical memorandum ERL ARL/224, Silver Spring, Md.: U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, Environmental Research Laboratories, Air Resources Laboratory.
- Flanagan, F.J., 1967. U.S. Geological Survey silicate rock standards. *Geochimica et Cosmochimica Acta* 31, 289–308.
- Govindaraju, K., 1989. Compilation of working values and sample description for 272 geostandards. *Geostandards Newsletter* 13, 1–113.
- Hodge, V., Johnson, S.R., Goldberg, E.D., 1978. Influence of atmospherically transported aerosols on surface water composition. *Geochemical Journal* 12, 7–20.
- Hoffman, G.L., Duce, R.A., 1972. Consideration of the chemical fractionation of alkali and alkaline earth metals in the Hawaiian marine atmosphere. *J. Geophys. Res.* 77, 5161–5169.
- Huebert, B.J., Zhuang, L., Howell, S., Noone, K., Noone, B., 1996. Sulfate, nitrate, methanesulfonate, chloride, ammonium, and sodium measurements from ship, island and aircraft during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol Gas Exchange. *Journal of Geophysical Research* 101, 4413–4423.
- Junge, C.E., 1964. The modification of aerosol size distribution in the atmosphere, Final Technology Report Contract-Da 91-591-EVC 2979, U.S. Army.
- Li, Y.H., 2001. *Compendium of Geochemistry*. Princeton University Press.
- Maring, H.B., Duce, R.A., 1987. The impact of atmospheric aerosols on trace metal chemistry in open ocean surface seawater, 1. Aluminum. *Earth Planet. Sci. Lett.* 84, 381–392.
- Martin, J.H., 1990. Glacial-interglacial CO_2 change: the iron hypothesis. *Paleoceanography* 5, 1–13.
- Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the north-east subarctic Pacific. *Nature* 331, 341–343.
- Mayewski, P.A., Lyons, W.B., Spencer, M.J., Twickler, M., Dansgaard, W., Koci, B., Davidson, C.I., Honrath, R.E., 1986. Sulfate and nitrate concentrations from a south Greenland ice core. *Science* 232, 975–977.
- Measures, C.I., Brown, E.T., 1996. Estimating dust input to the Atlantic Ocean using surface water Al concentrations. In: Guerzoni, Chester (Eds.), *The Impact of African Dust across the Mediterranean*. Kluwer. 389pp.
- Measures, C.I., Vink, S., 2000. On the use of dissolved aluminum in the surface water to estimate dust deposition to the ocean. *Global Biogeochemical Cycles* 14, 317–327.
- Measures, C.I., Brown, M.T., Vink, S., 2005. Dust deposition to the surface waters of the western and central North Pacific inferred from surface water dissolved aluminum concentrations. *Geochem. Geophys. Geosyst.* 6, Q09M03. doi:10.1029/2005GC000922.
- Petit, J.R., Jouzel, J., Raynaud, D., Barkov, N.I., Barnola, J.M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V.M., Legrand, M., Lipenkov, V.Y., Lorius, C., Pepin, L., Ritz, C., Saltzman, E., Stievenard, M., 1999. Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. *Nature* 399, 429–436.
- Prospero, J.M., 1996. Saharan dust transport over the North Atlantic Ocean and Mediterranean: an overview. In: Guerzoni, Chester (Eds.), *The Impact of African Dust Across the Mediterranean*. Kluwer. 389pp.
- Prospero, J.M., Ruby, T.N., Uematsu, M., 1987. Deposition rate of particulate and dissolved aluminum derived from Saharan dust in precipitation at Miami, Florida. *Journal of Geophysical Research* 92, 14723–14731.
- Quinn, P.K., Bares, T.S., Johnson, J.E., Covert, D.S., Charlson, R.J., 1990. Interactions between the reduced sulfur and reduced nitrogen cycles over the central Pacific Ocean. *J. Geophys. Res.* 95, 16405–16416.
- Resing, J., Measures, C.I., 1994. Fluorimetric determination of Al in seawater by FIA with in-line preconcentration. *Analytical Chemistry* 66, 4105–4111.
- Sato, T., Determining the fractional solubility in seawater of aluminium derived from atmospheric aerosols MS thesis, University of Hawaii, 2002.
- Spokes, L.J., Jickells, T.D., Lim, B., 1994. Solubilisation of aerosol trace metals by cloud processing: a laboratory study. *Geochimica et Cosmochimica Acta* 58, 3281–3287.
- Taylor, S.R., 1964. Abundance of chemical elements in the continental crust: A new table. *Geochimica et Cosmochimica Acta* 28, 1273–1285.
- Uematsu, M., Duce, R.A., Prospero, J.M., Chen, L., Merrill, J.T., McDonald, R.L., 1983. The transport of mineral aerosol from Asia over the North Pacific Ocean. *Journal of Geophysical Research* 88, 5343–5352.
- Uematsu, M., Duce, R.A., Prospero, J.M., 1985. Deposition of atmospheric particles in the North Pacific Ocean. *Journal of Atmospheric Chemistry* 3, 123–138.
- Wedepohl, K.H., 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59, 1217–1232.