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Acid-base balance in aerosol components of the Asia-Pacific region

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ABSTRACT

We have estimated for remote areas the potential extent of neutralization and solubilization of alkaline aerosol by sulfuric acid through atmospheric uptake of acidic sulfur gases by dust particles. Aerosol components were resolved from time sequence measurements of elemental composition in Nuclepore filter samples from 5 locations in the Asia-Pacific region, using factor analysis and multiple linear regression applied to data sets of 66–229 steps of 2.4–4.0 hours each, representing 526 analyses for 7–12 elements. Each component was evaluated for chemical equivalent concentrations of sulfur and alkaline mineral elements. Two or three factors accounted for 87–97% of the variance of each set, consistent with a model of linear mixing of components for most observed variability and resulting in 12 components that may represent a broad range of aging, from recently generated soil dust to particles exposed to trace SO_2 or other sulfur gases for a week or longer. Virtually no aerosol sulfur was found without being associated with soil elements. All 12 components contained statistically significant amounts of both sulfur and alkaline elements in relative proportions that suggest two rate limitations on acidic gas uptake: neutralization of rapidly reacting bases, mainly $CaCO_3$, and gradual neutralization of slowly reacting bases, mainly clay minerals, by H_2SO_4 after SO_2 uptake. After each stage of titration in the atmosphere, further gas uptake may be inhibited by an acidic particle surface. The resolved aerosol components show cases approaching both stoichiometric limits, but no case of excess sulfur beyond the second limit, consistent with these being practical limits in the remote areas investigated. If mineral aerosols are solubilized by strongly acidic surface solutions at ambient relative humidities, as suggested by these results, subsequent deposition to ocean, fresh water, or land surfaces may be more important inputs of nutrient or toxic metal ions than deposition of insoluble mineral particles or of wet or dry deposition of acids followed by dissolution of particles in seawater or leaching of soils.

1. The problem

The residence time of sulfur in the atmosphere may be much longer as an aerosol than as a reactive trace gas. In this paper we inquire into aerosol alkalinity properties that may enhance the uptake of sulfur by particles and thereby increase its residence time and transport distance, as well as modify the chemical characteristics of the aerosol.

In many areas gaseous sulfur is mainly SO_2 released from combustion of fuels, whereas in pristine areas natural organic compounds of sulfur occur that become oxidized to SO_2. In either case, aerosol H_2SO_4 or sulfate may be formed by further oxidation at rates competitive with the deposition of SO_2 directly to the surface. In remote areas, aerosol sulfur concentrations, because of slower deposition, may exceed those of reactive sulfur gases, concentrations that may be of climatic importance (Nguyen et al., 1983; Charlson et al., 1987). Moreover, much of the international transport of air pollution sulfur is as an aerosol, owing to its long residence time before deposition. Indeed, it has been argued that much of the Asian dust reaching Hawaii during spring carries with it some sulfur of air pollution origin (Darzi and Winchester, 1982a).

Considerable attention has been given to the measurement of gaseous sulfur concentrations, and of sulfur in aerosol form, but less to determining all constituents in the aerosol that may affect its ability to accumulate sulfur. Since the products formed by oxidizing gaseous sulfur compounds are generally acidic, the base capacity of dust particles may be especially important for retaining sulfur. Soil minerals are generally alkaline and may be efficient accumulators of sulfur, and chemical reaction with sulfuric acid may lead to their dissolution. The analysis of single particles from the Pacific (Andreae et al., 1986) and the Arctic (Sheridan, 1988), showing internal mixing of sulfur and soil mineral elements, indicates that this may be important in remote areas even far from land.

In this investigation we have tried to estimate acid-base characteristics in aerosols found in widely separated parts of the Asia-Pacific region and measured over long enough periods of time to be considered representative of the nonurban troposphere in this part of the world. We recognize that the atmospheric aerosol is an external mixture of weakly interacting components, but we wish to examine the internal chemical mixture in each. Thus, it is necessary to identify the composition of components present by resolving them from the external mixture. Our approach has been to perform the component resolution statistically by factor analysis of five data sets representing more than 500 quantitative analyses for a dozen chemical elements that could be indicative of the components. Although statistical analysis proves only numerical relationships in the data, and not physical cause and effect relationships, it can summarize large amounts of data and help one to recognize patterns that, with additional information, intuition, or imagination, may be interpreted physically.

2. The data bases

We have based our study on data from ground level sampling programs in Hawaii (Darzi and Winchester, 1982a, 1982b), Japan (Hashimoto et al., 1984), Xinjiang (Sinkiang) (Wang et al., 1987), and Xizang (Tibet) during 1979–1980. Linear Nuclepore filter strips were employed in "streaker" samplers (Nelson, 1977) that collected continuous streaks of particulate matter by a sliding sucking orifice over 1–2 weeks on a single filter. (For sampling coarse and fine aerosol fractions separately a 2-stage streaker is now available, although not when the samples for this study were collected.) In steps along the filter corresponding to 2.4 to 4.0 hour sampling intervals, analysis for up to 12 elements from Mg to Pb in atomic number was performed by PIXE (Johansson et al., 1970, 1975) at Florida State University (Hawaii and Japan samples), Element Analysis Corporation, Tallahassee FL (Xinjiang samples), and Fudan University, Shanghai (Xizang samples). Elements included in the present study were those measured well above detection limit in the great majority of sample steps, so as to minimize the contribution of analytical error to variance in the data. Sampling locations, dates, numbers of steps analyzed, and the elements used for factor analysis are summarized in Table 1.

3. Aerosol component resolution

For resolving aerosol components in the data sets and determining their relative elemental compositions, a sequence of steps in multivariate statistical analysis was followed, mainly using Statgraphics Version 2.6 (STSC, 1987) software in a microcomputer. Elemental concentrations in the sample steps of each data set were first organized in a spreadsheet. An additional zero concentration sample was added as step 0, for reasons described below, and absolute principal components analysis (APCA) (Thurston and Spengler, 1985) was carried out with varimax rotation. In this procedure, each variable is standardized by subtracting its mean and dividing by its standard deviation, so that the resulting factor scores for each sample average to zero. In Table 1 the percent variance explained by only 2 or 3 factors is seen to be 87–97%. If other evidence supports the interpretation of the factors as representing physically real components, a linear mixing model of these components of fixed composition explains the data variance quite well.

Two examples of factor analysis results are presented in Tables 2, 3. The number of factors chosen to be retained was verified to be significant after rotation by each having a sum of

Table 1. *Streaker samples evaluated in this study by factor analysis*[a)]

ID	Location	Dates	Steps analyzed	Hours per step	Elements	% variance F1	F2	F3	sum
XJ	Xinjiang China	1980 8–24 Aug	86	4.0	12	58	37	—	94
XZ	Xizang (Tibet)	1980 26 Apr–7 May	66	4.0	9	68	19	–	87
KN	Niigata Japan	1980 19–25 Apr	59	2.4	9	70	14	12	97
ML	Mauna Loa Observatory	1979 23 Apr–6 May	86	3.68	7	79	18	–	97
HV	Hawaiian Volcano Observatory	1979 18–28 Mar and 23 Apr–18 May	229	3.68	8	55	28	13	96

[a)] Elements included in factor analyses: XJ, Mg Al Si P S Cl K Ca Ti Mn Fe Zn. XZ, Al Si S K Ca Ti Mn Fe Zn. KN, Al Si S Cl K Ca Ti Mn Fe. ML, Al Si S K Ca Ti Fe. HV, Al Si S Cl K Ca Ti Fe.

Table 2. *Aerosol component resolution by factor analysis and varimax rotation, Niigata during kosa dust storm*

Element	Concentration ($\mu g\ m^{-3}$) Avg.	SD	Communality	Factor Loadings, r KNF1	KNF2	KNF3	Factor concentration ($\mu g\ m^{-3}$) KNF1	SD	KNF2	SD	KNF3	SD
S	0.842	0.862	0.9985	0.147	0.035	0.988	0.019	0.001	0.007	0.001	0.817	0.004
Al	2.196	0.954	0.9901	0.957	0.265	0.066	1.183	0.016	0.485	0.024	0.529	0.107
Si	6.311	2.680	0.9927	0.955	0.269	0.091	3.203	0.038	1.337	0.057	1.976	0.248
Ti	0.186	0.089	0.9899	0.953	0.269	0.092	0.089	0.001	0.037	0.002	0.056	0.008
Fe	1.681	0.729	0.9932	0.961	0.247	0.092	0.833	0.010	0.317	0.014	0.519	0.062
K	0.897	0.416	0.9882	0.953	0.258	0.114	0.430	0.007	0.173	0.010	0.334	0.043
Ca	1.571	0.731	0.8866	0.895	0.226	0.184	0.655	0.033	0.245	0.049	0.876	0.214
Mn	0.039	0.025	0.8650	0.908	0.107	0.172	0.014	0.001	0.002	0.001	0.017	0.005
Cl	0.750	0.535	0.9965	0.333	0.940	0.039	0.123	0.003	0.514	0.004	0.093	0.019
r^2 sum	8.70	6.327	1.290	1.083								
r^2 %	96.67	70.30	14.33	12.04								

Table 3. *Aerosol component resolution by factor analysis and varimax rotation, Mauna Loa during spring dust season*

Element	Concentration ($\mu g\ m^{-3}$) Avg.	SD	Communality	Factor loadings, r MLF1	MLF2	Factor concentration ($\mu g\ m^{-3}$) MLF1	SD	MLF2	SD
S	0.506	0.842	0.9999	0.225	0.974	0.262	0.001	0.244	0.000
Al	0.572	0.445	0.9811	0.960	0.245	0.590	0.009	0.032	0.002
Si	1.597	1.098	0.9921	0.965	0.247	1.463	0.015	0.081	0.003
Ti	0.034	0.026	0.9108	0.933	0.201	0.034	0.001	0.002	0.000
Fe	0.470	0.310	0.9910	0.967	0.238	0.414	0.004	0.022	0.001
K	0.204	0.151	0.9703	0.962	0.210	0.200	0.004	0.009	0.001
Ca	0.766	0.540	0.9635	0.962	0.197	0.717	0.016	0.032	0.003
r^2 sum	6.81	5.559	1.250						
r^2 %	97.27	79.41	17.86						

squares of factor loadings greater than unity ($\sum R^2 > 1$). The factor loadings after rotation show distinctive elemental compositions of the components by high or low values of the correlation coefficients between elements and factors, and the communalities show that the 2 or 3 factor models for these examples account very well for variabilities of all the elements.

Following Thurston and Spengler (1985), the step 0 factor scores are subtracted from those of all steps, and non-zero mean factor scores of the measured steps result. Then multiple linear regression analysis (MLRA) is carried out for each element. Its concentration is expressed as a linear combination of the factor scores, e.g. for the example of Table 2,

$$\mathrm{Al} = \text{const.} + a_1 \mathrm{FS}_1 + a_2 \mathrm{FS}_2 + a_3 \mathrm{FS}_3$$

a series of equations for all sample steps, where FS_1, FS_2, FS_3 are factor scores and a_1, a_2, a_3 are regression coefficients calculated with standard deviations. The products $a_1\mathrm{FS}_1$, $a_2\mathrm{FS}_2$, $a_3\mathrm{FS}_3$ are then computed using the mean factor score values to determine the mean concentration of the element (e.g. Al) in each factor. In Tables 2, 3 these are given for the two examples with standard deviations (S.D.) from the regression equations. The small SD and the agreement between sums of factor concentrations and measured average concentrations indicate good fits of the elements to the factors with only small constant amounts left unexplained.

The mean values of the factor scores for all 12 aerosol components resolved from the five data sets in this study are summarized in Table 4. These components are arranged in increasing order of relative amounts of S and alkaline elements, as discussed further below. Also presented for each component are the mean concentrations and SD of two key elements, S and Al.

4. Temporal variability and composition of components

A sense of the physical significance of the components may be gained by examining their temporal trends. Figs. 1–5 present them for each site in turn, starting with the step 0 factor score. When the trend follows the zero ordinate, the component has zero concentration. Mean scores for the components as well as S and Al mean concentrations are given in Table 4, and mean element ratios are given in Table 5. The absolute concentration for an element in a component at any high peak time can be determined by multiplying the mean element concentration given in Table 4, or by combining Tables 4 and 5, by the ratio of peak score to mean factor score. (The total mass concentration of a component would require knowledge of additional elements not measured here). In the following descriptions, reference will be made to relative elemental compositions of the components. These can be

Table 4. *Mean values in aerosol components*

Aerosol component	Mean F score	Mean concentration ($\mu g\ m^{-3}$)			
		S	SD	Al	SD
KNF2	0.730	0.0066	0.0010	0.4853	0.0243
KNF1	0.492	0.0188	0.0007	1.1830	0.0164
HVF1	0.751	0.0066	0.0008	0.1179	0.0022
XJF2	1.425	0.1480	0.0407	2.1789	0.0618
XZF1	1.938	0.0216	0.0039	0.2630	0.0163
HVF2	0.294	0.0053	0.0003	0.0158	0.0009
MLF1	1.382	0.2619	0.0012	0.5900	0.0092
XJF1	0.508	0.5731	0.0145	1.5241	0.0221
KNF3	3.197	0.8165	0.0042	0.5290	0.1065
XZF2	1.801	0.0566	0.0036	−0.0184	0.0152
MLF2	0.298	0.2445	0.0003	0.0324	0.0020
HVF3	1.017	0.2166	0.0011	0.0211	0.0030

Table 5. *Element weight ratios in aerosol components*

Weight Ratio[a]	Component from factor analysis[b]											
	KNF2	KNF1	HVF1	XJF2	XZF1	HVF2	MLF1	XJF1	KNF3	XZF2[c]	MLF2	HVF3
Si/Al	2.75	2.71	2.54	2.97	2.21	3.50	2.48	2.93	3.74		2.49	2.59
% S.E.	6.6	1.8	2.2	2.8	6.6	6.0	1.9	2.0	24		7.3	16
EF E.C.	0.81	0.79	0.75	0.87	0.65	1.03	0.73	0.86	1.10		0.73	0.76
Fe/Al	0.652	0.704	1.445	0.616	0.518	1.187	0.702	0.091	0.981		0.679	
% S.E.	6.7	1.8	2.1	3.6	6.5	6.5	1.9	7.6	23		7.5	
EF E.C.	1.06	1.14	2.35	1.00	0.84	1.93	1.14	0.15	1.60		1.10	
Ti/Fe	0.117	0.107	0.189	0.105	0.117	0.066	0.082	0.185	0.108		0.049	
% S.E.	8.0	2.0	2.5	5.0	5.0	14	4.0	10	24		17	
EF E.C.	1.33	1.22	2.15	1.19	1.33	0.75	0.93	2.10	1.23		0.90	
K/Al	0.356	0.364	0.158	0.316	0.403	0.864	0.340	0.331	0.632		0.291	0.563
% S.E.	7.5	2.1	4.0	3.7	8.2	5.8	2.5	1.9	24		11	16
EF E.C.	1.12	1.14	0.50	0.99	1.26	2.71	1.07	1.04	1.98		0.91	1.77
Mg/Al				0.313				0.329				
% S.E.				5.1				2.5				
EF E.C.				1.22				1.28				
Ca/Al	0.504	0.553	0.976	0.822	0.736	1.836	1.215	0.652	1.655		0.975	0.804
% S.E.	20	5.2	2.5	4.2	10	6.0	2.7	2.5	32		12	20
EF E.C.	1.13	1.24	2.19	1.84	1.65	4.11	2.72	1.46	3.71		2.18	1.80
Mg/Ca				0.381				0.504				
% S.E.				6.0				3.0				
EF E.C.				0.66				0.88				
Mn/Al	0.0050	0.0118		0.0159	0.0130			0.0022	0.0325			
% S.E.	46	5.6		3.4	7.9			7.2	35			
EF E.C.	0.43	1.01		1.36	1.11			0.19	2.78			
Zn/Al				0.0030				0.0004				
% S.E.				7.9				30				
EF E.C.				3.48				0.46				
S/Al	0.0137	0.0159	0.0561	0.0680	0.0821	0.336	0.444	0.376	1.544		7.541	10.27
% S.E.	15	3.7	12	28	19	8.0	1.6	2.9	20		6.1	14
EF E.C.	4.28	4.97	17.5	21.3	25.7	105	139	118	482	9	2357	3209
Cl/Al	1.060	0.104	0.647	0.014		8.13		0.0323	0.176			
% S.E.	5.1	2.8	6.2	12		5.6		2.9	29			
EF E.C.	660	65.0	404	8.7		5083		20.2	110			
P/Al				0.028				0.047				
% S.E.				13				4.1				
EF E.C.				2.13				3.6				

[a] Element ratio in each component, its standard error from linear regression, and the ratio normalized to average earth crust (Mason and Moore, 1982), the "enrichment factor". Some elements were not determined in all samples; may be estimated from earth crust composition.

[b] Components are arranged in increasing order of apparent aging.

[c] Only 4 elements were detected, in weight ratios K/S = 0.735, Zn/S = 0.128, Mn/S = 0.0112.

verified by referring to element weight ratios in Table 5 and enrichment factors EF relative to the composition of earth crust given in Table 6 (Mason and Moore, 1982).

Fig. 1, Xinjiang, 2–23 August, 1980. Samples were taken on a high mountain ridge in the Tian Shan range that bisects this far northwest province of China. The sampling site, remote from the city of Urumqi, overlooked the Dzungarian Plain to the north. Diurnal winds brought air from the plain upslope by day and from the surrounding forested mountains downslope by night. Factor 2 displays diurnal daytime maxima and is considered to be representative of the regional aerosol over the plain. Its composition resembles earth crust composition, is low in S, Cl, and P, and may be typical of desert soil composition. Factor 1 occurs sporadically during a 4-day period and is a local dust, low in Fe, high in S.

Fig. 2, Xizang (Tibet), 26 April to 7 May, 1980. Samples were taken on the high Tibetan Plateau, 4950 meters altitude, at Yongbu Temple in Dingyi County, 28°13′N, 86°49′E, a sparsely populated region near Nepal some 500 km WSW of Lhasa. Factor 1 fluctuates moderately about its mean throughout the two weeks of sampling and may be representative of the regional aerosol. It resembles earth crust composition and Xinjiang factor 2, although its S and Al concentrations (Table 4, XZF1) are nearly an order of magnitude lower. Factor 2, composed of S with equivalent

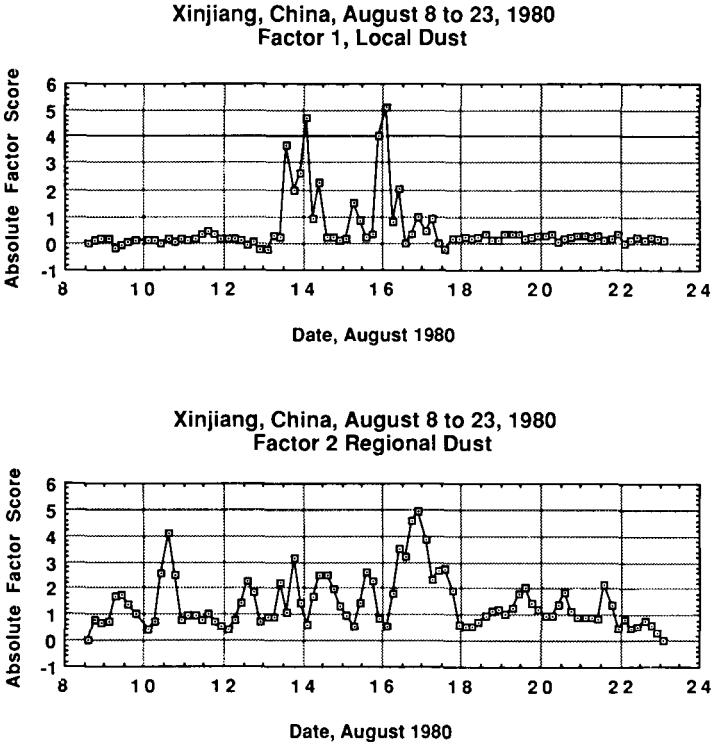

Fig. 1. Xinjiang (Sinkiang). Time variation of absolute factor scores in two factors (aerosol components), in order of variance explained, resolved from time sequence aerosol composition measurements. The few short pulses of factor 1 suggest a local dust, whereas the diurnal fluctuations of factor 2 throughout two weeks of sampling suggest a regional dust. A zero factor score represents the absence of the component. An element concentration at any peak is its mean concentration in the component (from Tables 4, 5) multiplied by the ratio peak score/mean factor score (from Table 4).

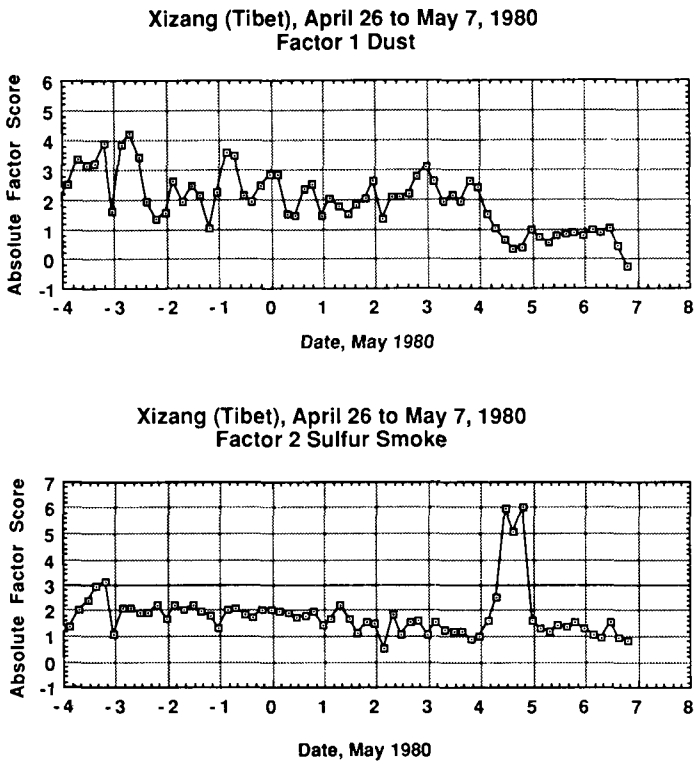

Fig. 2. Xizang (Tibet). (See caption to Fig. 1). Dates −4 to 0 represent April 26 to 30. The fluctuations of factor 1 throughout the 1.5 weeks of sampling suggest a regional dust, whereas the few short pulses of factor 2 suggest a local dust, in this case resembling smoke in composition.

amounts of K, Zn, and Mn, may be smoke from fuel burning in the region. It is also low in concentration, although a pulse at night on 4–5 May reaches 3 times the mean.

Fig. 3, Niigata, Japan, 19–24 April, 1980. Samples were taken during a kosa ("yellow sand") dust storm, forecast to arrive just after sampling commenced. Factors 1 and 2 have identical elemental composition, except for high Cl in factor 2, exhibit rise and fall 21–23 April that corresponds to the kosa event, and are considered to represent the dust cloud that crossed the Japan Sea. S is somewhat lower, relative to soil elements, than in the Xinjiang and Xizang regional components and may represent natural composition of the soil dust that was raised from the Asian mainland surface by the storm. Factor 3 exhibits a very different temporal pattern. Present throughout the sampling period, including before and after the kosa event, its composition shows very much higher S concentration relative to soil elements. It may represent regional aerosol, derived from soil dust but contaminated with S through aerosol aging in a polluted regional atmosphere.

Fig. 4, Mauna Loa Observatory, 23 April to 6 May, 1979. Samples were taken at 3400 meters altitude during spring when dust was observed by satellite to be crossing the Pacific from Asia. Factor 1 is present throughout the two weeks and exhibits periodicity that averages about 10% shorter that diurnal. Strongly enriched in S compared to the natural soil aerosol components from China and Japan, it may represent soil dust that was raised daily and then aged in polluted Asian air by taking up SO_2, thereafter transported in a nonuniform wind field above the Pacific boundary layer to Hawaii. Factor 2 occurs intermit-

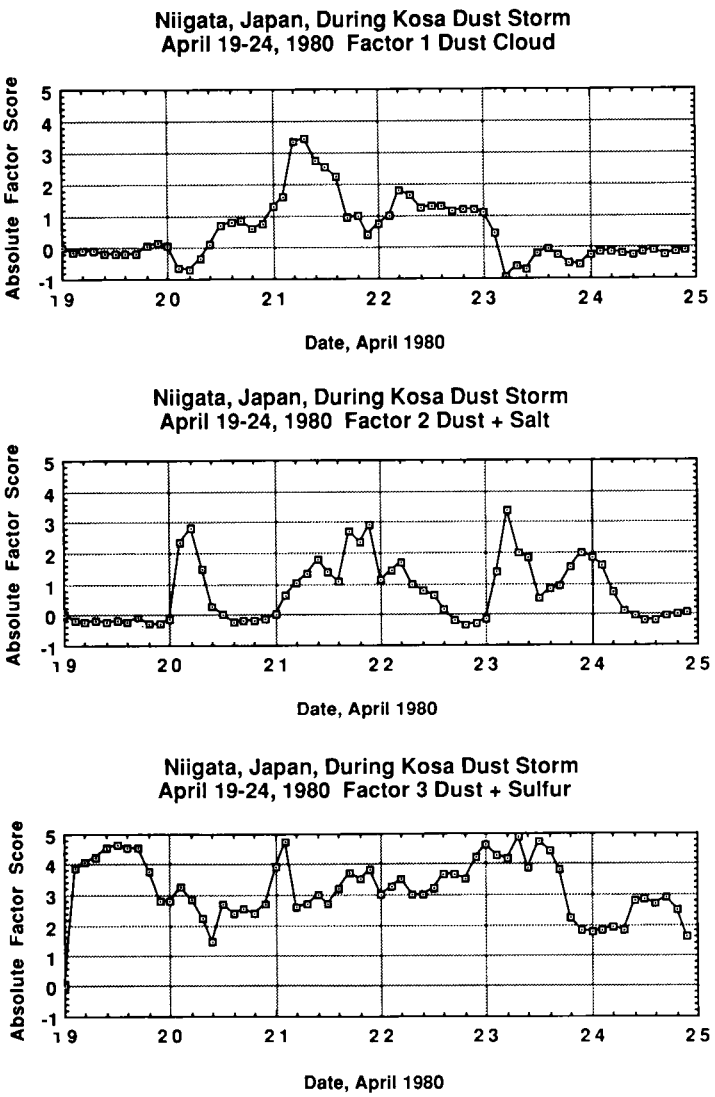

Fig. 3. Niigata in western Japan during an Asian dust storm event. (See caption to Fig. 1.) The broad 3-day presence of factor 1 and the fluctuations of factor 2 bounding this interval correspond to the dust cloud observed to pass the sampling site. Factor 3, present throughout the six days of sampling, represents background sulfur-laden dust unrelated to the storm but typical of the region.

tently. It contains soil elements in average crustal proportions but has S enriched much more strongly than in factor 1. Factor 2 may represent a dust aerosol that is more extremely aged by uptake of atmospheric S.

Fig. 5, Hawaiian Volcano Observatory, 18–28 March and 23 April–18 May, 1979. Samples were taken at 1200 meters altitude. Factor 1 shows strongly diurnal daytime maxima and low relative K concentration, as well as low S, indicative of basaltic soil dust from Hawaii. Factor 2 in its composition resembles continental dust, rather than island basalt, with elevated S approaching that of Mauna Loa factor 1. It occurs as intermit-

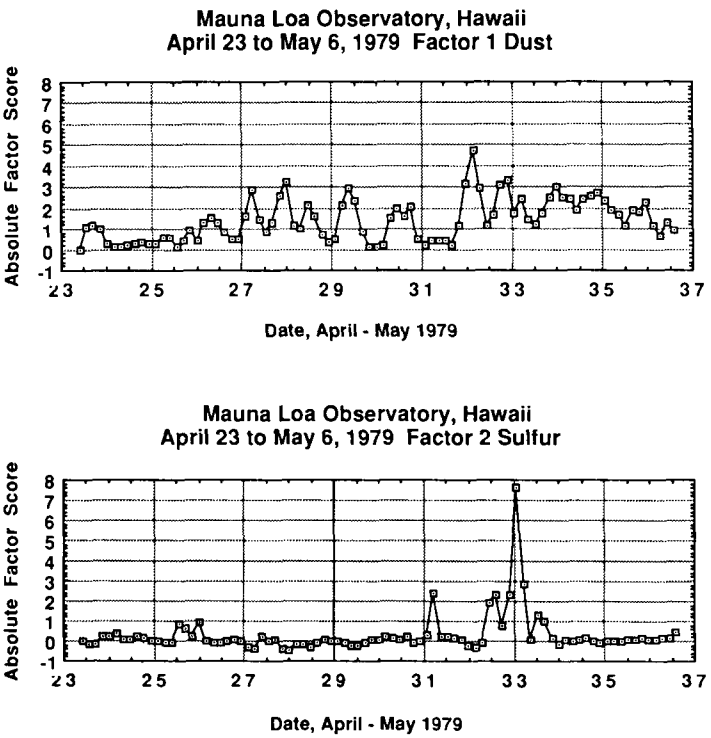

Fig. 4. Mauna Loa Observatory, Hawaii, 3400 meters altitude, during a spring Asian dust season. (See caption to Fig. 1.) Factor 1, attributed to Asian dust, occurs throughout the two weeks of sampling, with maxima averaging about 21 hours separation. Factor 2 occurs sporadically as an atypical aerosol component, with composition of continental dust strongly enriched in sulfur.

tent pulses. A portion of the current spring dust or a resuspension of island loess soil of Asian origin are possible sources. Factor 3, like Mauna Loa factor 2, is short pulses of dust with crustal average composition except for strong S enrichment, suggestive of an extremely aged aerosol by atmospheric S uptake.

5. Estimated acid-base balance as a measure of aerosol aging

At all five sites aerosol components are found in external mixture, each of which contains alkaline mineral elements but with differing amounts of additional sulfur. It is important to realize that these dust-like components account for essentially all the aerosol sulfur measured. We consider that nitric acid vapor is less likely than liquid sulfuric acid to accumulate in an acidified aerosol solution coating, and that other acids may be much less abundant in air. Thus, sulfur may constitute most of the strong acids that could react with alkaline minerals.

Components with the lowest relative S concentrations may represent natural soil dust, with a few-fold enrichment over average crustal abundance that could reflect the segregation of soluble ions at the soil-air interface in semi-arid regions of Asia. Further enrichment of S seems likely to be caused by atmospheric uptake of gaseous SO_2 on alkaline particle surfaces or in their aqueous sulfate salt solution coatings. At ambient relative humidities such solutions may be in the molal concentration range. For example, at 80% relative humidity ammonium sulfate forms a 6 molal saturated solution, and at lower humidities additional sulfuric acid allows

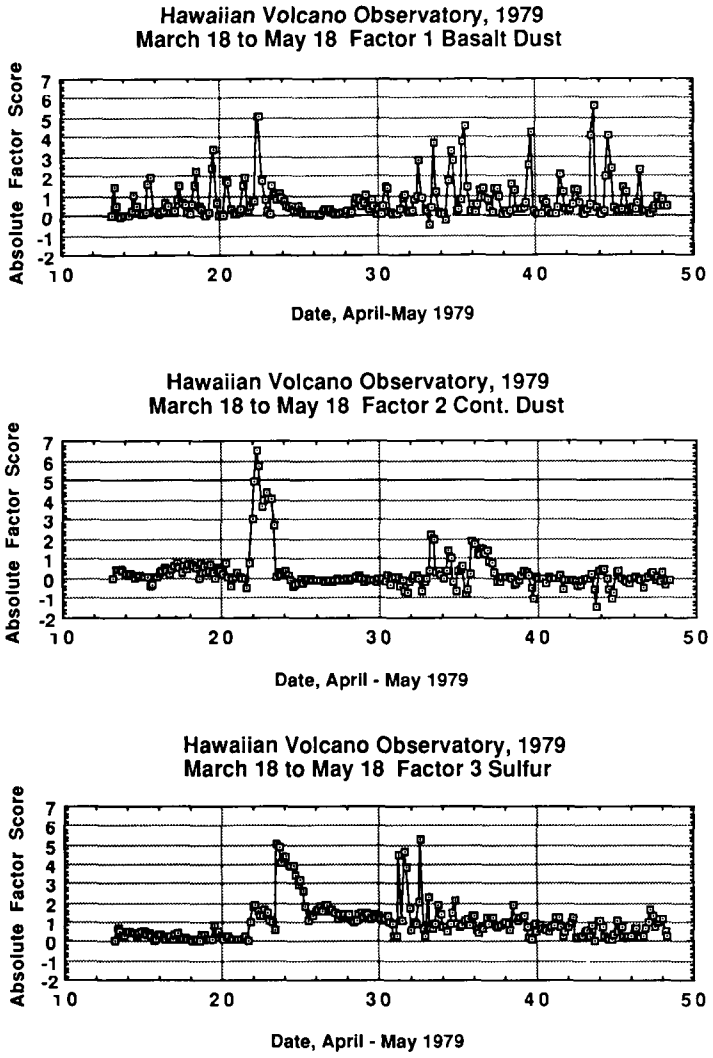

Fig. 5. Hawaiian Volcano Observatory, 1200 m altitude, during a spring Asian dust season. (See caption to Fig. 1). Samples were collected as three sequences, March 18–28 (plotted as dates 13–23), 23 April to 5 May, and 5–18 May (these plotted as dates 23–48). Factor 1 occurs throughout the five weeks of sampling, exhibits strong daytime maxima, and is associated with winds that bring basaltic soil dust to the sampling site. Factor 2 is sporadic and is an atypical component with composition similar to continental soil dust. Factor 3 is also sporadic and atypical and has composition of continental dust strongly enriched in sulfur.

the solution, at even higher molalities, to remain without crystallizing (Tang et al., 1978).

If acidic, molal concentration aerosol solutions may be near pH = 0 (Ferek et al., 1983), a potentially corrosive concentration not only for carbonates but also for clay minerals. A low pH for an aerosol surface solution coating may inhibit further SO_2 uptake, but gradual mineral dissolution should lead to neutralization and pH rise that would enhance SO_2 uptake. In other words, the rate of SO_2 accumulation on dust particles may be regulated by the rate of a

neutralization reaction that also leads to mineral dissolution, an atmospheric titration of particle alkalinity by SO_2. In order to examine its quantitative features, we should examine relative elemental composition on a chemical equivalent basis. For appropriate conversions we use the atomic weights, ionic charges, and equivalent weights given in Table 6.

Table 6. *Earth crust concentrations of elements and chemical equivalent weights*

Element	EC (ppm)	Atomic weight	Ionic charge	Equivalent weight
S	260	32.06	2−	16.03
Al	81,300	26.98154	3+	8.994
Si	277,200	28.086	4+	7.022
Ti	4,400	47.90	4+	11.975
Fe	50,000	55.847	3+	18.616
K	25,900	39.098	1+	39.098
Mg	20,900	24.305	2+	12.152
Ca	36,300	40.08	2+	20.04
Mn	950	54.9380	2+	27.469
Zn	70	65.38	2+	32.69
Cl	130	35.453	1−	35.453
P	1,050	30.97376	3−	10.325

Table 7. *Summary of aerosol aging categories*

Component	Equivalent ratios		
	$S/\sum$	S/Ca	$EF_{Al}(S)$
KNF2	0.0014	0.034	4
KNF1	0.0017	0.036	5
HVF1	0.0055	0.072	18
XJF2	0.0069	0.103	21
XZF1	0.0095	0.139	26
Unaged	0.001–0.01	0.03–0.14	4–26
HVF2	0.0236	0.229	105
MLF1	0.0463	0.457	139
XJF1	0.0389	0.719	118
KNF3	0.1166	1.166	482
XZF2	—	[a]	—
Semiaged	0.02–0.12	0.2–1.2	105–482
MLF2	0.8045	9.709	2357
HVF3	1.079	15.873	3209
Aged	0.8–1.1	10–16	2300–3200

[a] S/(K + Zn + Mn) = 1.144.

At risk of oversimplification, let us divide the measured elements into two groups, one typical of clay minerals that react slowly with concentrated acids, the other contained in cabonates or oxides that react rapidly. The slowly reacting group contains Al, Si, Ti, and Fe, and the rapidly reacting group contains Ca and, in some aerosols, K, Mn, Zn, and other elements. Assuming the usual ionic charges given in Table 6, for any measured composition we can compute the total equivalents of base capacity, or alkalinity, and thus the acid needed to neutralize either or both of these two groups. In practice, most of the slow group alkalinity is due to Al and Si whereas of the rapid group is mainly due to Ca, as may be seen by close examination of the element ratios of the components shown in Table 5.

The result of the acid-base equivalent calculation for each of the 12 aerosol components is shown in Table 7 and plotted in Fig. 6. In equivalent units, the ratio $S/\sum$ is between S and the sum of all alkaline elements for both slow and rapid groups. The ratio S/Ca is between S and Ca, the most abundant element in the rapid group. The components are arranged in order of increasing values of these ratios. The "enrichment factors" of S to earth crust composition with Al as a reference element $(S/Al)_{aerosol}/(S/Al)_{crust}$, are also shown as $EF_{Al}(S)$.

The ratios span a range from low to high, but there seem to be three principal ranges. The lowest "unaged" range may represent natural soil composition. The second "semi-aged" range seems to approach the ratio S/Ca = 1, a stoichiometric endpoint for SO_2 titration of the rapid group, i.e., H_2SO_4 neutralization by $CaCO_3$. (The singular Xizang factor 2 smoke aerosol also has a sulfate equivalence with oxides of K, Zn, and Mn.) The third "aged" range consists of two cases approximating a ratio $S/\sum = 1$, a stoichiometric endpoint for SO_2 titration of the slow group, i.e. H_2SO_4 neutralization by clay minerals that should lead to their dissolution. In principle, of course, further addition of S to the aerosol by some "superaging" process may be possible. However, in these data sets no evidence for it is found, and such a process would need a stronger driving force than acid-base neutralization by minerals.

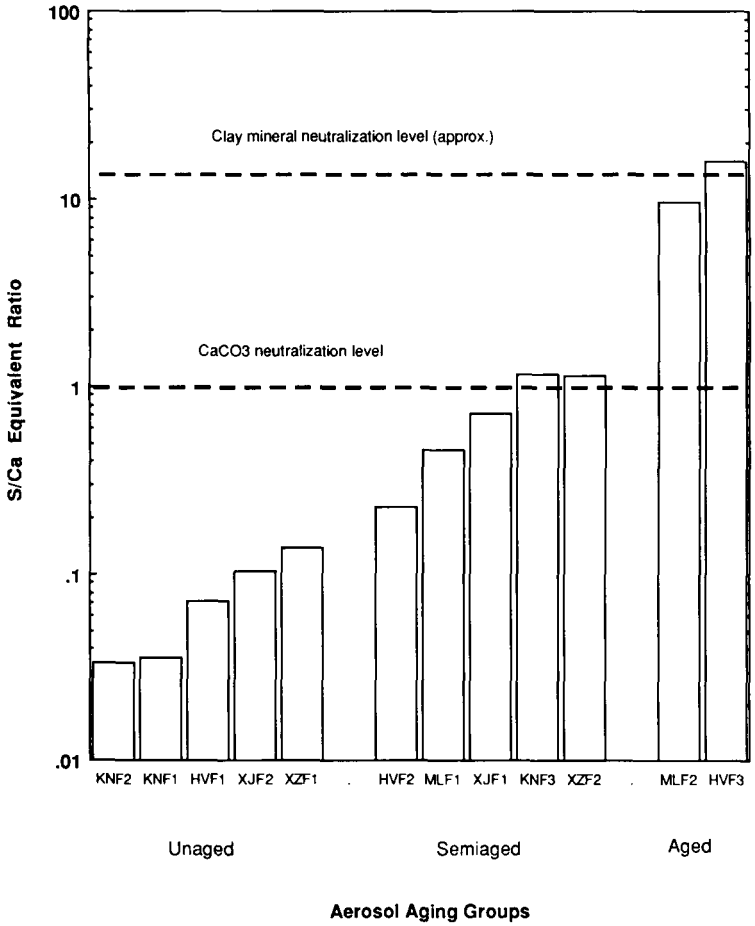

Fig. 6. Chemical equivalent ratios of sulfur to calcium in aerosol components, arranged in increasing order of the ratios, as indication of increasing state of apparent aerosol aging. Values of the ratios correpond to the components in Table 7. Complete conversion of $CaCO_3$ to $CaSO_4$ is indicated by S/Ca = 1 and of all alkaline elements in clay minerals approximately by S/Ca = 12 based on average earth crust abundances relative to Ca.

6. Discussion

In this study we have resolved aerosol components based on correlations between elemental concentrations in samples collected by filters without particle size selection. It is likely that the different components differ in average particle size, in distribution of particle concentration with size, and even in variation of particle composition with size, although these features cannot be demonstrated here. Future studies could be improved by size selective aerosol sampling, but this by itself cannot define the particle size distribution of a component: Both a "fine mode" and a "coarse mode" include some particles of any size.

Implicit in our analysis is the assumption that physically distinct components of fixed composition in an external mixture, whether they appear to be fine or coarse particle "modes", are not likely to covary in time, owing to their probably different sources and transport paths through the atmosphere. They are therefore not likely to be assigned statistically to a single factor or principal component. In fact, the statistical approach used here to interpret composition as it

varies in a set of unfractionated aerosol samples may lead to a more precise resolution of components than particle size selective sampling without a statistical analysis of composition variations.

There are not many reports in the literature of aerosol composition measurements with which our findings may be compared. One difficulty is the strategy of long sample averaging times that investigators often follow, so that data sets have much of the variance smoothed over, and multivariate analysis is made insensitive to resolve external mixtures of aerosol components of very different aging histories. The frequently rather few samples analyzed also make a variance approach insensitive, and other studies are shorter "snapshots" of aerosol composition that do not indicate what may be typical or average conditions.

But two small data sets deserve mention here, both summarized in Table 8. The first consists of coarse particles selectively sampled by aircraft over the Arctic in late winter during the 1983 Arctic gas and aerosol sampling project, AGASP (Winchester et al., 1984, 1985). The ratios approach S/Ca = 1, suggesting a mostly "semiaged" condition. Sources of gaseous sulfur from fuel combustion or marine biological activity, for uptake on dust particles, were probably more remote from the Arctic sampling area than the likely continental sources of dust, thus making a more advanced state of aerosol aging not to be expected.

The second consists of three samples collected from shipboard over the equatorial Pacific during July 1982 (Andreae et al., 1986). The ratios approach $S/\sum = 1$, suggesting a mostly "aged" condition similar to that seen in two components found on Hawaii. Sources of gaseous sulfur in central Pacific surface water may have led to an advanced degree of "aging" of a limited supply of terrestrial dust, as it circulated over the ocean, by S absorption up to a saturation limit by clay mineral dissolution.

The work of Sheridan (1988) also provides evidence for the interaction of acidic sulfur compounds with dust particles in remote regions. Individual particle analysis by electron microscopy was applied to Arctic samples collected by aircraft. A variety of particle types was found, including sulfuric acid, aluminosilicate dust, and soot carbon. Many particles contained liquid sulfuric acid coatings on solid aluminosilicate cores. X-ray analysis by high resolution electron beam of coating and core separately indicated the presence of crustal mineral elements in the liquid coating. The core may represent the residual mineral after incomplete dissolution by surficial sulfuric acid.

The circumstantial evidence in this study points to alkaline aerosol particles playing an active role in acidic trace sulfur gas scavenging. The relative fluxes of gaseous sulfur and soil dust aerosol through the troposphere may control the approach to a saturation limit in this natural SO_2 titration of alkaline mineral particles. The components resolved here indicate that this limit can be reached, with the result that even clay minerals may become solubilized in the atmosphere.

If, as has been suggested, the source of soluble Al measured in surface waters of the Pacific is from the atmosphere (Orians and Bruland, 1986), the predissolution of dust by low pH H_2SO_4

Table 8. *Comparison with other aerosol data*

Sample	Equivalent ratios		$EF_{Al}(S)$	Aging category
	$S/\sum$	S/Ca		
AGASP[a]				
A101	0.0179	0.097	31	slight
A109	0.0230	0.169	43	semi
A105	0.0170	0.225	34	semi
A107	0.0264	0.439	31	semi
A111	0.0252	0.500	37	semi
A110	0.0379	0.855	48	semi
Pacific[b]				
C15	0.144	—	329	semi
C06	0.503	—	1181	aged
C11	0.867	—	2509	aged

[a] AGASP, March-April 1983: Winchester et al. (1984, 1985).

$S/\sum$ used $\geq$ Al + Si + Ti + Fe + Mn + K + Mg + Ca; Mg & Mn estimated.

[b] Equatorial Pacific, July 1982: Andreae et al. (1986).

$S/\sum$ used $\geq$ (Al + Si + Fe)/0.84 as estimate.

aerosol coatings may be more effective than dissolution of mineral grains in seawater at pH = 8. The enrichment of Fe in surface ocean waters compared to deeper waters (Landing and Bruland, 1987) may also be explained by atmospheric deposition of presolubilized mineral Fe and may account for the observation that atmospheric Fe input to Pacific surface waters can stimulate biological productivity (Martin and Gordon, 1988).

In general, the deposition of soluble Al, Fe, and other mineral elements to oceanic or terrestrial surfaces may be of greater biological importance than the deposition of the same elements in an insoluble mineral form. In areas impacted by acid rain, much of the soluble Al and other metals in fresh waters may result from atmospheric deposition of presolubilized aerosols, not only the leaching of soils. The direct measurement of these elements as water soluble ions in suitable atmospheric samples should be a priority for future research.

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