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The elemental signature of transported Asian dust at Mauna Loa observatory

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ABSTRACT

Dust storms in Asia's interior deserts loft immense quantities of continental crust that are blown over the North Pacific Ocean every year. The transported mineral aerosol is first lofted and then experiences mixing and fallout during the transport. Its elemental signature is no longer that of bulk soil. The concentration for many elements is greater in transported crust compared to bulk soil due to a difference in mineralogy of the small crustal particle. Small particles are defined as those below 100 μm in diameter. The elements Al, Mg, Ca and Na do not experience an internal concentration change with particle size. Many of the elements in the MLO mineral aerosol have concentrations that are greater than 1.5 times that of bulk soil. Iron, an important biological agent, has twice the concentration in the MLO mineral aerosol than in bulk soil. The elemental to Al concentration ratios observed are consistent, implying that the transported crustal material is below 20 μm in diameter.

1. Introduction

Crustal material that is lofted into the atmosphere over semi-arid and arid regions can be transported long distances in the atmosphere (Prospero et al., 1983). This pathway is a significant source of nutrients to the remote oceans' surfaces (Duce, 1989). Schütz and Rahn (1982) determined that crustal particles below 100 μm in diameter contained increased amounts of micas, clay minerals and some types of feldspar, which caused an increase in internal concentration of many elements compared to bulk soil in this smaller size range. The internal concentration increase for these elements was found to level off in particles approximately 10–20 μm in diameter and below. Lofting and atmospheric transport of crustal particles are not well understood; however, a particle's sedimentation velocity is a function of particle size (Schneider et al., 1990). Thus the mineral aerosol that has been lofted and undergone long distance transport should have a signature more representative of the smaller crustal particles than the bulk soil.

Every year, the North Pacific receives continental crust transported in the atmosphere from Asia. Several researchers estimate the amount of mineral aerosol delivered to the North Pacific by this mechanism each year to be greater than 10×10^{13} g (Uematsu et al., 1985; Holmes, 1993). Asian dust storms are immense meteorological events that affect much of Asia's deserts every year (Gao et al., 1992). The lofted continental material is transported over the North Pacific where it affects an area of 43×10^6 km^2 (Uematsu et al., 1985; Arimoto et al., 1989). The crustal material over the Pacific has been observed to increase by as much as 91% during the dust episodes (Duce et al., 1983).

Mauna Loa Observatory (MLO), on the island of Hawaii, is at an altitude of 3400 m, making it a unique site for collecting remote aerosol. The

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altitude places it far above the marine boundary layer that generally is below 2000 m in the Pacific region (Andreae et al., 1988). The Hawaiian location makes it remote relative to continental and anthropogenic sources. Mauna Loa is a volcano composed primarily of dark basalt. The sunlight heating the basalt causes a diurnal effect creating upslope (Southerly) winds during the day and downslope (Northerly) winds during the night at the observatory. The night winds represent air parcels from the free to mid troposphere (Parrington and Zoller, 1984). Thus night time air sampling allows for ground collection of remote free tropospheric aerosol.

2. Experimental

Since 1974, Asian dust at MLO has been observed as an increased particle count from late winter through mid summer (Bodhaine, 1983). Aerosol collection for chemical analysis of particles began in February of 1979. Weekly samples were collected on open face particle filters. Originally, only time of day was used as criterion to collect for remote tropospheric aerosol in order to take advantage of the local diurnal wind patterns. In 1980 a sector controller was installed to control sampling protocol based on time of day, wind speed, wind direction and particle count. This insures that night time samples represented remote, free to mid tropospheric air (Parrington, 1983; Parrington and Zoller, 1984). These samples were collected on either Nuclepore or Teflon filters and analyzed consistently until June 1991. This allows for a twelve year record at MLO which can be used to determine the elemental signature of the dust transported to the North Pacific.

Although the sampling and analysis was consistent, there were some slight changes in the protocol. The analyses were moved from the University of Maryland to the University of Washington in May of 1985. The particle filters were also changed from 0.4 μm pore size Nuclepore to 1.0 μm pore size Teflon filters. Teflon filters are woven to allow for efficient collection of particles down to 0.3 μm diameter (Gelman Sciences, 1991). The entire data set is composed of remote, free tropospheric particles down to sizes of sub micrometer diameter (Holmes, 1993). One half of each particle filter was analyzed for elemental concentrations via instrumental neutron activation analysis (INAA). The researchers at U M used the INAA facilities at the National Institute of Standards and Technology (NIST) described by Germani et al. (1980). The researchers at U W used the facilities at Los Alamos National Laboratory Omega West Reactor (LANL-OWR) described by Bunker et al. (1986). The LANL-OWR has a lower thermal neutron flux than the NIST reactor, which caused the detection limits of many elements to be raised.

3. Results and discussion

The MLO aerosol data record reveals a very distinct seasonal Asian dust pattern that dominates the data (Parrington et al., 1983; Parrington and Zoller, 1984; Zieman et al., 1995; Holmes, 1993). In January or February of every year, many elements associated with continental crust experience an increase in the mass observed in the weekly samples. The aerosol concentration of crustal elements remains elevated until June or July (Parrington et al., 1983; Zieman et al., 1995; Holmes, 1993). This results in a dust season from late winter to mid summer each year. Previous papers have reported this seasonal event, as well as given overall data records. This paper differs in that the chemical signature of the mineral aerosol collected is discussed and described in detail. Aluminum and Sc are both excellent crustal tracers as they have no other known significant sources to the remote Pacific free troposphere. Figures 1a and b show monthly average Al and Sc concentrations for February 1979 to June 1991. The dust season is evident in both. It should be noted that there is an increase in Sc in 1989 that is not due to dust and Al does not show a similar concentration increase.

Harris and Kahl (1990) presented composites of ten day isobaric back trajectories to MLO from 1981 to 1988. These revealed that 500 hPa and 700 hPa air parcels at MLO are dominated by westerly transport from October through to June. Merrill (1989) pointed out that air parcels travel isentropically rather than isobarically. However, he reached similar conclusions to Harris and Kahl (1990). Asian dust transport patterns dominate the North Pacific wind flow from late fall to summer. The Asian dust however, is not lofted until the snow in Asia starts to melt in late winter and

spring (Gao et al., 1992). The global circulation and weather patterns thus enable the Asian dust season in the North Pacific.

Many of the elements detected in the MLO aerosol have a continental component (Parrington and Zoller, 1984; Parrington et al., 1983; Zieman et al., 1995; Holmes, 1993). Thus the weekly concentration means of these elements are higher in the dust than in the non dust season (Table 1). The standard deviation is a measure of the natural variation found in aerosol concentrations from week to week. The standard deviation is greater for elements that have a variable source or different sources. An example of this would be Al and I. Al has an overall average of 41 ± 70 ng/m^3 yielding a relative standard deviation of 170%. Iodine, on the other hand has an overall average of 1.1 ± 1.1 ng/m^3 giving it a relative standard deviation of 100%. Aluminum has a crustal source and varies greatly during the year due to the influx of Asian dust. Iodine does not have a significant crustal source and does not vary with Asian dust events. The relative standard deviation for Al and I is more similar and close to 100% when the dust season and non-dust season averages are taken into account. The difference in standard deviation and elemental signatures between the dust and non-dust season will be discussed further later. In 1989, an odd event from June to October resulted in increased concentration of several elements including V, As, Br, Cl, Co, Eu, Fe, I, Mn, Na, Sb, and W. Vanadium experiences the most dramatic increase, an indication of heavy oil or crude burning (Zoller et al., 1973). This episode is considered to be a result of the ocean barge incinerators used during the Exxon Valdez oil spill clean-up (Holmes, 1993). These samples are therefore excluded from further discussion here, leaving only four samples from the 1989 dust season.

Enrichment factors (EF) express to what extent an element can be accounted for by a known source (Zoller et al., 1974). This is done by nor-

Table 1. *Average seasonal concentration with standard deviation (SD) from 1979 to 1991 without 1989 anomaly; total number of samples that could be used for each element is also given*

		Overall (Feb. 1979–June 1991)			By season (Feb. 1979–June 1991)					
					dust			non-dust		
element	conc.	ave	SD	# samples	ave	SD	# samples	ave	SD	# samples
Na	ng m(exp(−3))	30	93	556	36	42	265	22	110	277
Mg	ng m(exp(−3))	21	32	337	35	38	178	5	6	151
Al	ng m(exp(−3))	41	70	560	75	88	265	9	8	280
Cl	ng m(exp(−3))	9	14	435	8	11	213	9	15	208
K	ng m(exp(−3))	21	67	525	30	32	256	7	31	254
Ca	ng m(exp(−3))	56	100	349	98	121	188	6	5	155
Sc	pg m(exp(−3))	10	18	548	17	24	262	2	5	272
Ti	ng m(exp(−3))	4	6	400	6	8	215	1	1	179
V	pg m(exp(−3))	273	2001	538	183	300	258	245	2472	268
Cr	ng m(exp(−3))	2	8	462	2	4	207	2	3	242
Mn	pg m(exp(−3))	676	2453	543	1232	3439	262	134	157	266
Fe	ng m(exp(−3))	34	71	500	53	75	251	13	59	238
Co	pg m(exp(−3))	32	215	496	29	43	245	14	64	238
As	pg m(exp(−3))	78	224	470	113	260	226	34	99	231
Se	pg m(exp(−3))	39	84	401	53	110	192	27	47	204
Br	ng m(exp(−3))	3	8	549	3	11	262	3	4	274
Sb	pg m(exp(−3))	19	194	513	10	11	247	22	261	252
I	ng m(exp(−3))	1	1	528	1	1	254	1	1	265
Cs	pg m(exp(−3))	15	57	375	20	33	215	2	3	153
Ia	pg m(exp(−3))	39	122	502	63	129	251	6	6	239
Ce	pg m(exp(−3))	68	102	342	112	118	190	13	12	148
Sm	pg m(exp(−3))	5	7	468	8	9	228	1	2	227

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malizing the concentration of an element [X] to that of a reference element [RE] in the sample. The sample ratio is then normalized to a reference material ratio. The following equation is used:

$$EF = \left(\frac{\left(\frac{[X]}{[RE]} \right)_{sample}}{\left(\frac{[X]}{[RE]} \right)_{ref}} \right). \quad (1)$$

Crustal enrichment factors are commonly calculated using Al as the reference element with crustal averages (Taylor and McLennan, 1985) as the reference material. Elements with an EF near one are considered crustal in this paper. The discussion here considers all elements with dust season EFs closer to 1 than 100 to be crustal (Table 2). This includes: Na, Mg, K, Ca, Sc, Ti, V, Mn, Fe, Co, Cs, La, Ce, Sm and, of course, Al.

An elemental signature of crustal material could be determined by using a concentration ratio of the individual element to a crustal tracer. Continental crust is by far the most dominant source for Al in the remote Pacific. And Al is observed in virtually every sample. Aluminum will be used as the crustal tracer in determining the crustal material's elemental signature. Table 3 shows the average of the individual crustal element to Al ratios ([X]/[Al]) for both the dust and non dust season. The ratio and EF are very similar. However, the EF is normalized to a known source, in this case Taylor and McLennan crustal averages. Thus EFs imply that the signature of the mineral aerosol is the same as that of bulk crustal averages. A ratio is not normalized and therefore no assumption about the chemical composition is made. Thus, ratios are used rather than the EF to describe the mineral aerosol composition observed at MLO. The ratio is slightly higher for most elements for the non dust season with a larger standard deviation than that observed for the dust season. Three elements; Ca, Cs, and La have a slightly lower EF in the nondust season. This would imply that the non Asian dust has a more similar chemical signature to Taylor and McLennan (1985) bulk crustal averages than the Asian dust. However, with such slight differences in EF values, it is difficult to make strong conclusions. The higher standard deviation is because non crustal sources are influencing the [X]/[Al] average during the non dust season (Holmes,

Table 2. *Average enrichment factor with standard deviation (SD) for overall 79–91 and seasonal without 1989 anomaly; total number of samples that could be used for each element is also given*

	Overall (Feb. 1979–June 1991)			By season (Feb. 1979–June 1991)					
				dust			non-dust		
element	ave	SD	# samples	ave	SD	# samples	ave	SD	# samples
Na	7	47	556	3	5	265	11	64	277
Mg	35	41	338	26	17	179	40	25	151
K	3	14	525	2	4	256	3	6	254
Ca	2	2	349	3	2	188	2	1	155
Sc	2	3	548	2	2	262	2	3	272
Ti	3	2	401	2	1	216	4	2	179
V	56	553	538	24	239	258	74	731	268
Cr	694	1840	463	158	443	208	1003	1673	242
Mn	2	2	543	2	1	262	2	3	266
Fe	3	11	500	2	5	251	4	14	238
Co	17	137	497	5	11	246	16	39	238
As	364	1525	470	259	1524	226	391	1305	231
Se	5671	14064	401	2572	6181	192	8640	18314	204
Sb	470	2967	513	152	716	247	595	2929	252
Cs	10	90	375	6	4	215	5	6	153
La	3	19	503	3	12	252	2	2	239
Ce	2	2	342	2	1	190	2	3	148
Sm	3	4	469	2	3	229	3	6	227

Table 3. *Average element concentration to Al concentration ratio (ave) for overall and by season with standard deviation (SD); total number of samples that could be used for each element is also given; note the larger standard deviation for the non-dust samples*

	Overall ratio average (Feb. 1979–June 1991)			Ratio average by season (Feb. 1979–June 1991)					
				dust			non-dust		
element	ave	SD	# samples	ave	SD	# samples	ave	SD	# samples
Na	2.4	16	558	0.84	1.3	264	3.7	23	277
Mg	0.56	0.66	338	0.45	0.30	195	0.65	0.40	142
K	0.72	1.26	527	0.55	0.50	255	0.71	1.08	254
Ca	0.92	0.64	349	0.99	0.71	206	0.83	0.52	143
Sc	0.00027	0.00028	550	0.00023	0.000088	261	0.00026	0.00022	272
Ti	0.13	0.086	400	0.092	0.042	227	0.17	0.086	172
V	0.026	0.18	540	0.0040	0.021	259	0.0048	0.0094	264
Mn	0.015	0.014	545	0.014	0.0083	266	0.015	0.0069	269
Fe	1.20	2.87	501	0.73	0.47	251	1.2	1.2	237
Co	0.0014	0.0037	499	0.00051	0.00060	248	0.0018	0.0046	241
As	0.0061	0.026	472	0.0042	0.022	230	0.0051	0.0090	226
Se	0.0035	0.0087	401	0.0015	0.0036	196	0.0053	0.011	203
Sb	0.00094	0.0053	515	0.00028	0.00043	248	0.0013	0.0071	251
Cs	0.00027	0.00029	376	0.00026	0.00017	227	0.00025	0.00026	148
La	0.00096	0.0033	504	0.00084	0.00093	252	0.00073	0.00074	243
Ce	0.0016	0.0015	342	0.0014	0.00063	197	0.0018	0.0022	145
Sm	0.00014	0.00017	470	0.00011	0.000048	234	0.00013	0.00014	220

1993). The lower crustal content allows other influences, such as anthropogenic activity, to become more significant increasing the variance or standard deviation. Also, during the non dust season wind patterns to MLO tend to come more frequently from the East rather than the North or West (Harris and Kahl, 1990; Merrill, 1989). The non dust season [X]/[Al] average is thus less representative of the crustal component and will not be discussed further.

Scandium, as seen in Fig. 1b, is a crustal tracer. However, the 1989 pollution event appears to be a source for Sc. The seasonal [Sc]/[Al] average is plotted by year with standard deviation represented as error bars in Fig. 2. Schütz and Rahn (1982) determined that many elements in the crustal minerals, including Sc, had internal concentrations that increased with decreasing size. This trend stopped, and internal concentrations remained consistent at 20 μm and below diameter. Fig. 3 shows that cobalt has more varied source(s). This is evident by 1986, 1989 and to some extend 1983 having average ratios that fall outside the standard deviation bars of most other years. Most years do fall within the standard deviation of other years so typical yearly ratio values or typical years are evident. The atypical years, where the [Co]/[Al] seasonal average is higher, could be due to sporadic anthropogenic activity, volcanic emissions, or differences in concentrations due to the smaller mineral aerosol observed. Information regarding particle size could yield insight into sources. However, the open face filters used to maximize aerosol collection, do not allow for any type of size information. The fact that typical yearly ratios are evident for crustal elements implies that the majority of the mineral aerosols that reach MLO are in a size range that has consistent internal concentrations. This would be crustal particles in a size range below 20 μm in diameter based on the observations of Schütz and Rahn (1982). This agrees with Schneider et al. (1990) who observed crustal particles averaging 2.0 μm in diameter on Oahu. It supports the data of Clarke and Porter (1991) who measured the difference in crustal aerosol over MLO between the dust and non dust season using CO2 laser backscatter technique. Carbon dioxide laser backscatter can observe particles in the 1 to 5 μm diameter size range.

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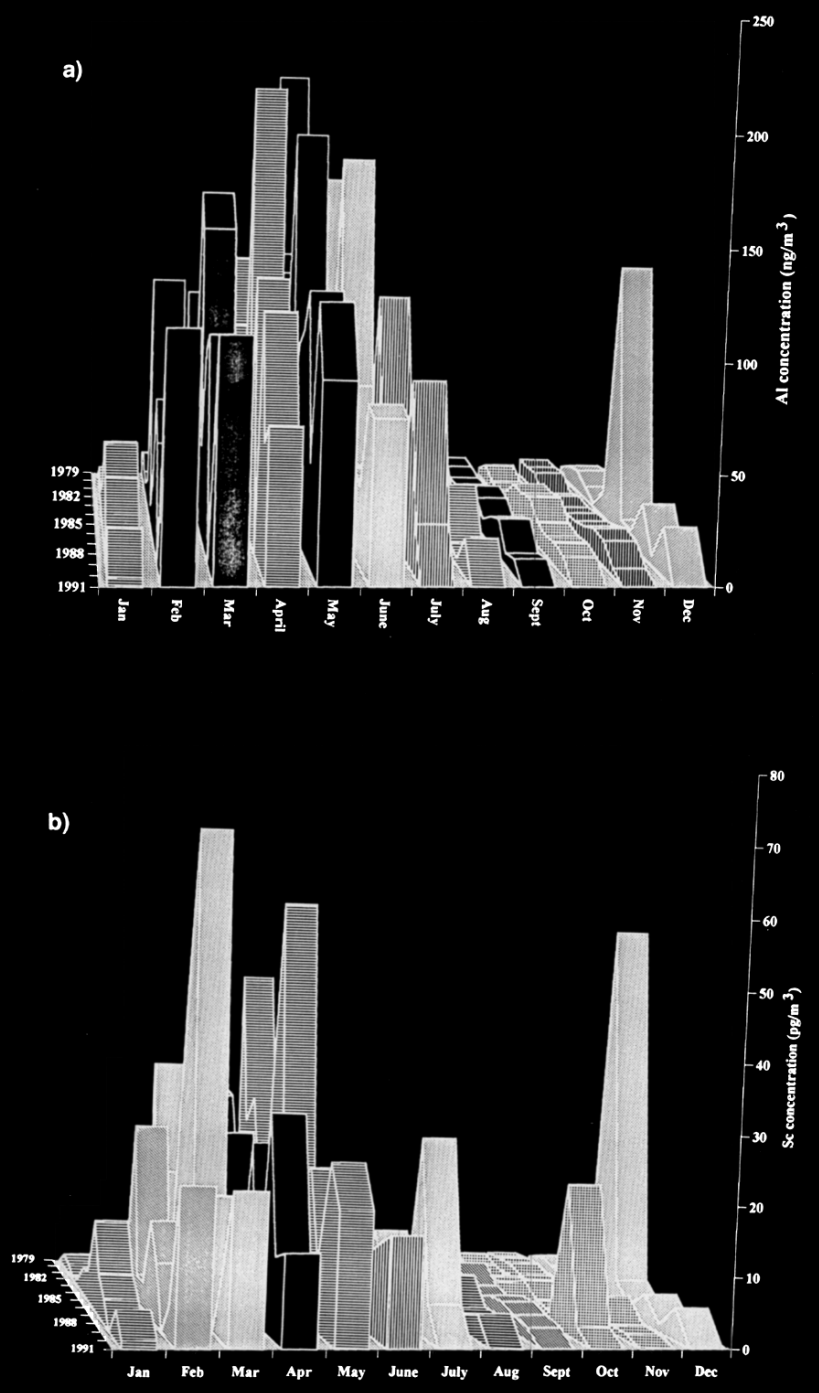

Fig. 1. Monthly averages at MLO from Feb. 1979 to June 1991. (a) Aluminum concentration (ng/m^3) (b) Scandium concentration (pg/m^3).

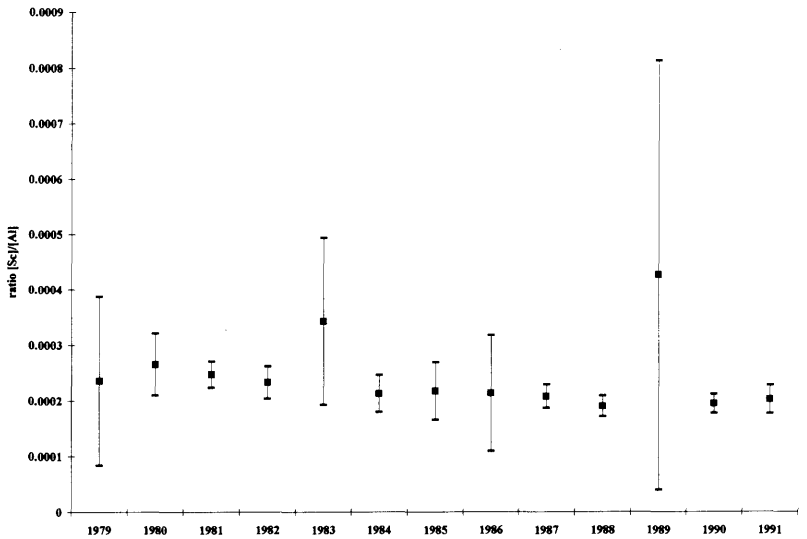

Fig. 2. Seasonal average Scandium to Aluminum ratios for each year with standard deviation represented as error bars.

Table 4 presents [X]/[Al] ratios using different statistical methods used to determine the transported Asian dust signature. Method 1 averages every [X]/[Al] ratio for weekly samples collected in the dust season. In method 2, an alternative way of examining the same data, we average the seasonal averages for all years. In method 3, we eliminate those seasons suspected of being influenced by non crustal sources and only typical seasons are averaged. Typical seasons are defined by the student t test.

Averaging only those samples that have the maximum crustal concentrations would yield results most representative of the crustal aerosol.

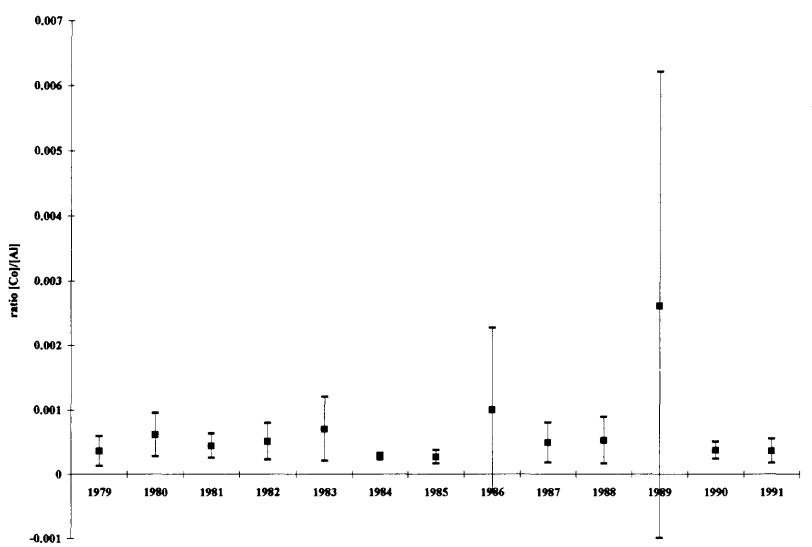

Fig. 3. Seasonal average Cobalt to Aluminum ratios for each year with standard deviation represented as error bars. Note that the signature is not as consistent as found for Sc. This is probably due to Co's having other sources besides crust.

Table 4. *Element to aluminum ratio for crustal material in MLO aerosol determined by various statistical methods; Taylor and McLennan (1985) bulk crystal averages and Tanaka et al. (1986) are listed for comparison*

Element	Bulk crust[a] ratio to Al	Asian desert[b] ratio to Al	Method 1 ratio to Al	Method 2 ratio to Al	Method 3 ratio to Al	Method 4 ratio to Al	# samples (of 42)	Method 5 ratio to Al	Samples used by %
Na	0.36	0.25	0.84	0.87	0.87	0.31	42	0.33	39
Mg	0.17	0.46	0.45	0.41	0.41	0.35	39	0.38	66
Al	1	1	1	1	1	1	42	1	100
K	0.35	0.25	0.55	0.63	0.63	0.38	42	0.39	65
Ca	0.37	0.82	0.99	0.89	0.89	0.92	40	0.94	64
Sc	0.00014	0.00011	0.00023	0.00025	0.00025	0.00021	41	0.00022	88
Ti	0.037	0.040	0.092	0.091	0.091	0.069	39	0.076	62
V	0.00075	0.00085	0.0040	0.0045	0.0045	0.0022	42	0.0018	66
Mn	0.0075	0.0074	0.014	0.014	0.014	0.016	42	0.013	90
Fe	0.44	0.32	0.73	0.69	0.69	0.63	40	0.71	71
Co	0.00012	0.00013	0.00051	0.00068	0.00068	0.00031	40	0.00032	54
Cs	0.000046	0.000059	0.00026	0.00027	0.00027	0.00024	39	0.00025	39
La	0.00037	0.00049	0.00084	0.00095	0.00095	0.00099	41	0.00082	38
Ce	0.00080	0.00078	0.0014	0.0015	0.0015	0.0013	35	0.0014	75
Sm	0.000056	0.000056	0.00011	0.00012	0.00012	0.00010	38	0.000099	80

[a] Taylor and MacLennan (1985).
[b] Tanaka et al. (1986).

However, this can also be influenced by weeks that might have experienced larger crustal particles (Betzer et al., 1988). The Lucite shelter that houses the open faced filter packs generally restricts particles of greater than 50 μm in diameter from being impacted on the particle filters, considering the shelter's angle and the typical collection flow rate determined to be 0.2 m^3/min. [STP]. Weeks with maximum crustal concentration are defined as the three samples with the highest Al concentration of each dust season (except 1989) as well as other dust season samples with Al concentrations above 200 ng/m^3. This yields 42 samples from a possible 207 collected during the dust season at MLO since the sector controller was installed. The [X]/[Al] average for this method (called method 4) is lower than other ratios for most elements. This result is not surprising considering Al, the denominator, is chosen to be at a maximum. Table 4 also lists the actual number of samples that had detectable quantities of the individual elements and were thus able to be included in the ratio's average for method 4.

Method 5 attempts to include only the crustal component by averaging only those weeks where at least 70% of the mass of the elements is explained by the crustal component. Method 5 also includes the percentage of each element's samples in which crustal material was able to explain at least 70% of the individual element's mass. Mineral aerosol is able to describe nearly all of Na's mass in 39% of the samples. This is most likely due to sodium's marine component. Although marine sodium at MLO is low, in fact, it is comparable to the South Pole (Holmes, 1993). In other words, a significant portion of the sodium observed at MLO is due to mineral aerosol and not of marine origin.

Table 4 lists the results for all methods. The bulk soil (Taylor and McLennan, 1985) ratios and bulk Asian desert soil (Tanaka et al., 1986) ratios are listed for comparison. The higher values seen for many of the [X]/[Al] averages as compared to bulk soil are due to the mineralogy of the small crustal particles that comprise the majority of transported mineral aerosol. Calcium and Mg have ratios similar to that seen in bulk Asian desert soil. Schütz and Rahn (1982) found that Ca, Mg and Al concentrations did not vary internally in crustal particles from 1 to 100 μm in diameter. It appears that Al is depleted in the MLO transported crustal aerosol. However, this is probably due to the source soil and not a size effect. Asian desert crustal material has about 6.8% Al (Tanaka

et al., 1986) compared to 8% in the bulk global crustal averages (Taylor and McLennan, 1985). This depletion, however, does not account for the increase in element to Al ratios observed in MLO crustal aerosol over bulk soil averages.

On the basis of method 5, which discriminates based on both the crustal component and individual element criteria, Sc, V, Fe, Co and Cs have concentrations greater than or equal to twice that found in bulk Asian desert soil. This is due to the mineralogy of the size range of the transported crustal particles (Schütz and Rahn, 1982) and is not simply a result of non crustal sources. The crustal component was able to describe the elemental mass in greater than 50% of the samples for Sc, V, Fe and Co. Iron is an important nutrient (Duce, 1986; Young et al., 1991; Martin, 1992). Lofting and long range transport of continental crustal material is considered the primary source of Fe to the remote North Pacific (Zhaung et al., 1990). It appears the transported crust is enriched in this biologically important element.

The elements K, Ti, Mn, La and Sm have ratios greater than 1.5 times bulk soil, based on method 5. This is consistent with the mineralogy associated with crustal particles below 20 μm diameter (Schütz and Rahn, 1982). Sodium, Mg and Ca have ratios very similar to that found in bulk soil.

4. Conclusions

The transport of Asian dust over the North Pacific is complex. Asian dust is transported long distances from the desert regions of Asia to the North Pacific each year (Gao et al., 1992). This occurs from late winter to summer when there are dust storms over Asia and the Asian dust transport pattern dominates the MLO air flow (Merrill, 1989; Harris and Kahl, 1990). The surface conditions control the lofting of the crustal material and can be quite variable. Crustal particles below 100 μm in diameter have a more variable mineralogy containing more feldspar and micas than the bulk soil. The elemental internal concentrations increase with decreasing particle size due to the mineralogy difference. The increase is found to level off at 20 μm diameter and remains stable down to 1 μm diameter (Schütz and Rahn, 1982). The MLO data record reveals a typical transported dust signature implying that the majority of the Asian dust particles' masses are below 20 μm in diameter. Also, the chemical signature of that transported mineral aerosol is different than that of bulk soil or crustal averages.

The size of the transported mineral aerosol results in many elements having a greater crustal aerosol concentration than that expected based on bulk soil. Iron, an important nutrient, experiences a concentration nearly twice that expected from bulk soil in transported mineral aerosol. The concentration of many elements increases to 1.5–2 times that of bulk soil in the transported crustal material. The elements Na, Mg, Al and Ca have crustal components that do not vary with size. Apparently, the crustal size can explain the slight enrichment observed in many crustal elements. However, it does not explain the anomalous enrichment of greater than two orders of magnitude. This anomalous enrichment is due to other sources, such as anthropogenic activity or biological emissions.

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