

On the study of aerosol composition at the Great Wall Station, South Pole

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(Received October 5, 1988)

Abstract—The South pole area offers one of the best locations on the Earth for studying the composition of the background aerosol. For this purpose, aerosol samples were collected in particle size fractions by 8 stages cascade impactors. Aerosol sampling was begun in Jan. and finished in Dec. 1986 at the St. Great Wall, South Pole. The samples were analyzed by Proton Induced X-ray Emission (PIXE) method. In order to learn the enrichment factors of various elements all the results were separated into two groups: coarse ($> 10\mu\text{m}$) and fine ($< 10\mu\text{m}$) particles. The correlation coefficients of elements of both coarse and fine particles were discussed. The aerosol levels measured at St. Great Wall were compared to those recently measured at some other locations. It can be concluded the South Pole is a good background area on the Earth.

Keywords: South Pole; aerosol; PIXE method.

Atmospheric pollutant is not only directly harmful to human health in source regions, it can also be transported through the atmosphere over great distances. Atmospheric particles, especially submicron aerosol particles, which have long atmospheric residence times, have led to the contamination of many non-urban areas. Baseline atmospheric measurements should help us make clear the source, dispersion, concentration, degree of transportation and enrichment factors of these pollutants. The South Pole area offers one of the best locations on the Earth for studying the composition of the background aerosol since it is isolated both geographically and meteorologically from the major sources of anthropogenic emission. For this purpose, some aerosol samples were collected from Station Great Wall at the South Pole in 1986 and the composition was analyzed by Proton Induced X-ray Emission (PIXE) method (Winchester, 1981; Ma Ciguang, 1987).

SAMPLE COLLECTION

The aerosol samples were collected by cascade impactors designed and constructed by our Res. Center. Each sample provided eight particle size fractions in the normal aerodynamic diameter ranges (μm) as shown in Table 1.

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Table 1 Particle size fractions

Stage	Size range, μm
1	greater than 11
2	7.7-11
3	5.0-7.7
4	3.5-5.0
5	2.3-3.5
6	1.2-2.3
7	0.7-1.2
8	smaller than 0.7

From the first stage to the 7th stage, Mylar film in 3 μm thickness were used. Nucleopore film with 0.40 μm of pore diameter was used in the last stage. The samplers were operated at two liters per minute. The samples have been collected in 1986. The sampling conditions for these samples are summarized in Table 2.

Table 2 Conditions of aerosol sampling

Sample number	sampling date, MO/Da/YR	Volumeos samples, m^3 STP
1	012986-013186	3.06
2	021086-021186	4.92
3	022286-022386	5.76
4	051886-062486	10.237
5	070186-072386	10.904
6	072486-081986	8.788
7	090786-092486	10.012
8	092886-102086	8.70
9	102086-110186	9.00
10	110186-120286	13.83

PIXE ANALYSIS SYSTEM

A $2 \times 1.7\text{MV}$ Tandetron accelerator (General Ionex Corp., U.S.A.) in the Institute of physics, Academia Sinica, Beijing, China, is used for PIXE analysis. The negative ion H^- is produced by bombarding a hydrogen absorbed on a Ti target with Cs^+ beam. The H^- ion beam is injected into the tandem accelerator. The proton beam from the acceleration tube with MeV energy passed through the quadrupole lens and magnetic switch into the PIXE beam line. For analysis of non-uniformly distributed sample, a homogeneous beam density is required. This is obtained by using the quadrupole lens to defocus the proton beam or diffusion foil made of high purity aluminum foil of 1.6 mg/cm^2 thick. The diffused proton beam is collimated by three or four collimators made of high purity graphite before impacting into the sample. The X-rays produced from the sample are detected in an 80 mm^2 (collimated to an effective area of 48 mm^2 by high purity graphite tube) Si (Li) Canberra detector with an energy resolution of 185 eV at 5.9 KeV, through 10 μm thick Mylar chamber window. The target to detector distance is 40mm. The X-ray spectrum enhancer, ADC(ND-580) and a multichannel analyzer (ND-76) with PDP 11/23 computer are used as a data acquisition and analysis system.

The counts of the most significant X-ray lines of element is proportional to the content of the element in samples for thin target in principle. The standard samples of various elements were prepared for calibration. At the same time some vacuum-evaporated standard targets produced by an independent laboratory (Micromatter Inc., U.S.A) are used for parallel reference study. The counts of the most significant X-ray lines vs. the concentrations of elements in standard sample are shown in Fig. 1. The linear curve is obtained by least square fitting.

The sensitivity of the X-ray detection system $S(Z)$ is defined as, $S(Z) = N_x(Z)/(N_p(M(Z)))$

$/As)$), where $M(Z)/As$ is area mass density, As is irradiation area of target, Np is the number of projectiles in μC , so the sensitivity S unit is counts of X-ray ($\mu C \cdot Mg / cm^2$) Fig.2 is the sensitivity curve for the K lines in the PIXE system. The reliability and reproducibility of the results were checked in the next.

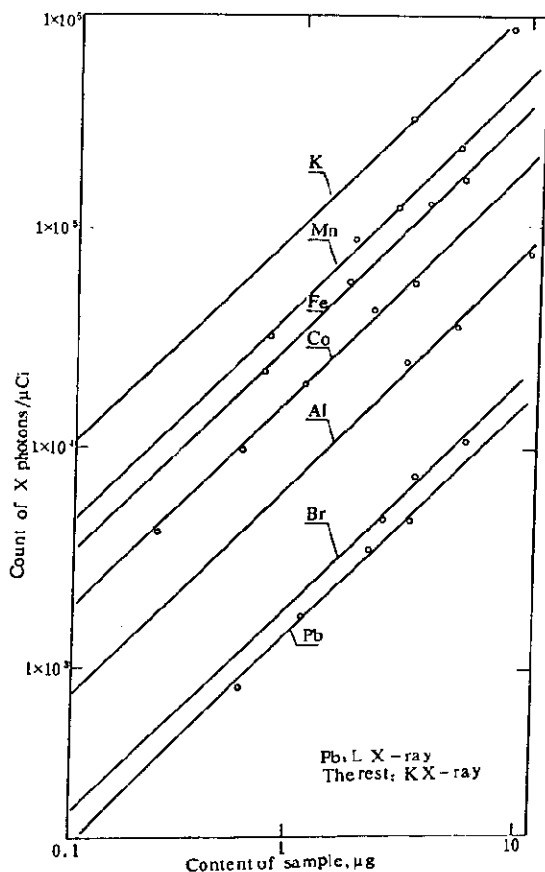


Fig.1 The counts vs. the element concentration

The minimum detection limits are defined as $3(Nb)/(S \cdot Np)$ in this paper, where Nb is background counts within an interval of two full width at half maximum around the X-ray peak. If $Nb < 11$, then $3(Nb)$ is set to ten. For comparing the detection limits of various kind of target backing the number of projectiles in μC will be taken in accounting. Fig. 3 shows the minimum detection limits of various elements of some films for collection of aerosol samples using K line for $6\mu C$ proton beam integration. In that the minimum detection limits of V, Cr, Mn, Fe, Co, Ni, Cu and Zn in our system are better than 1 ng/cm^2 . The absolute detection limits for those elements will be 0.1 ng for irradiation area used for aerosol sample.

Aerosol samples on the films with the plastic rings were put into a target holding frame driven by a stepping motor to change samples. Counting rates are normally limited to 2000 counts per second by changing proton beam current (3-15 nA).

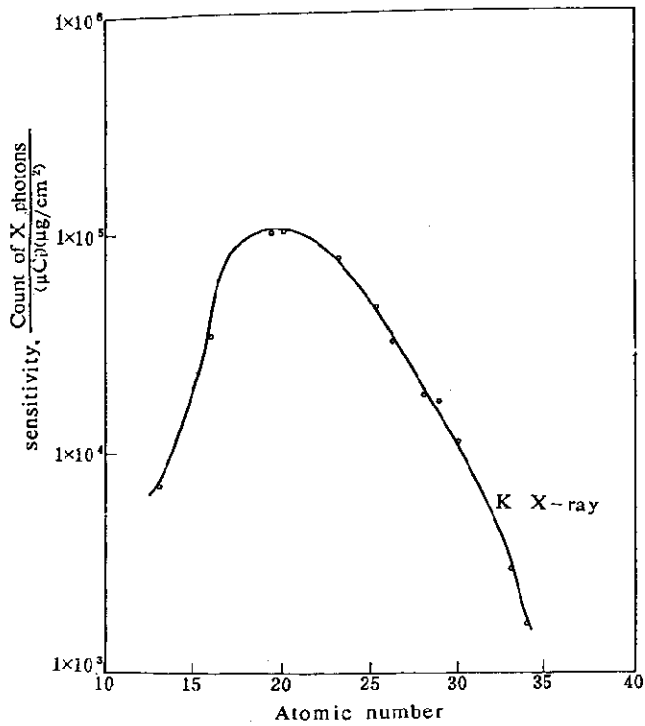


Fig.2 The sensitivity curve

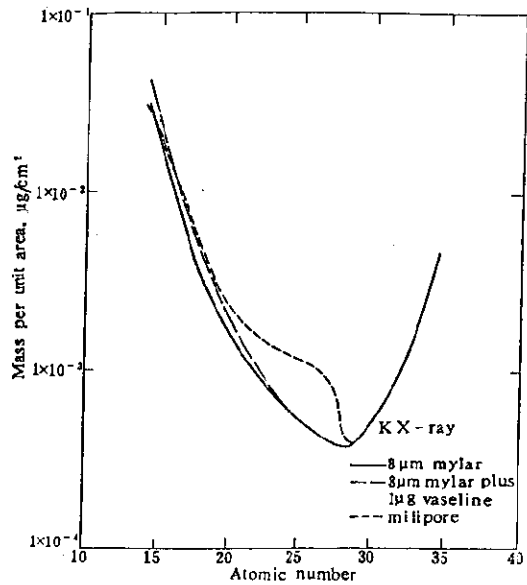


Fig.3 The minimum detection limits

RESULTS AND DISCUSSIONS

The average element concentrations of aerosol samples

Atmospheric sampling was begun in Jan. and finished in Dec. 1986 at Great Wall Station. The samples were analyzed by PIXE method. The X-ray spectra were analyzed by computer, with small peaks checked by manual integration, then the final concentrations were obtained. The data are given in μg per standard cubic meter. The average trace element concentrations of coarse and fine particles for the all sampling periods are presented in Table 3.

Table 3 The average trace element concentrations of aerosol at St. Great Wall ($\mu\text{g}/\text{m}^3$) (a. coarse particles; b. fine particles)

Element	Average conc.	Concentration range	standard deviation
Si	a. .00673	0 - .0340	0.01042
	b. nd	nd	nd
S	a. .00727	0 - .0340	0.01362
	b. .02550	0.0588	0.01632
Cl	a. .00454	0 - .0409	0.01285
	b. .30763	0 - .6378	0.23290
K	a. .00937	0 - .0415	0.01258
	b. .01128	0 - .0412	0.01216
Ca	a. .05106	0 - .2670	0.07976
	b. .00005	0 - .00052	0.00016
Ti	a. .00750	0 - .0279	0.00828
	b. .00281	0 - .0136	0.00472
V	a. .00056	0 - .00220	0.00080
	b. .00049	0 - .00261	0.00086
Cr	a. .00005	0 - .00046	0.00014
	b. .00156	0 - .00610	0.00181
Mn	a. .00204	0 - .00560	0.00180
	b. .00405	0 - .00579	0.00128
Fe	a. .07051	0 - .2221	0.07465
	b. .01898	0 - .0990	0.03174
Pb	a. .00031	0 - .00123	0.00046
	b. .00216	0 - 0.00597	0.00188

The enrichment factors and the correlation coefficients of elements in coarse particles

In order to learn the enrichment factors of various elements we separated the results to two groups: coarse and fine particles. Coarse mode ($> 10\mu\text{m}$) concentrations may be compared with the composition of the earth's crust. Aerosol crust enrichment factors ($E.F.$) were calculated for all elements (X) according to the equation:

$$E.F.(X) = \frac{(\text{Conc. } X / \text{Conc. Fe})_{\text{aerosol}}}{(\text{Conc. } X / \text{Conc. Fe})_{\text{crust rock}}}$$

The average composition of crust rock (Mason, 1966) is used. Table 4 shows that for the majority of the elements the $E.F.$ are close to the values of 1.0. Si is the most important soil derived element. Its low $E.F.$ indicates that Si in the particles come from rather remote locations. The occasional deviation from 1.0 reflect the general crust air fraction and differences in regional geochemical composition of crust rock. S and Pb are apparently present in fine particles in concentrations too high to be explained in terms of normal crustal weathering processes. In coarse particles S generally presents in form of SO_4^{2-} as we found in the samples collected from other clean places, the so-called aged aerosol component. Perhaps they appear to have marine source in these samples.

Table 4 Enrichment factors of elements of coarse particles

No.	Si	S	K	Ca	Ti	V	Cr	Mn	Fe	Pb
1		11.70		.472				1.104	1.0	
2								0.123	1.0	
3			.173					0.925	1.0	
4	.0152	26.35	.267	1.033	.898			0.914	1.0	
5	.0245		.558	.750	1.831	3.431		0.053	1.0	
6	.0218		.317	.840	.986	2.578	3.316	1.362	1.0	17.73
7	.0209		2.179		3.43				1.0	
8	.0280		.539	1.680	1.434	3.605		1.008	1.0	
9					8.650	46.50		12.719	1.0	304.8

Table 5 shows the correlation coefficients for the elements in coarse particles. Some elements such the correlation coefficients for the elements in coarse particles. Some elements such as Ca, K and Si are positively correlated to each other. This can be explained by the fact that these elements come from natural sources.

Table 5 The correlation coefficients of elements in coarse particles

Element	K	Ca	Ti	V	Mn	Fe	Pb
Si	.954	.964	.961	.100	.400	.986	
S		.998	.998	.998		.998	
K		.934	.956	.994	.907	.924	
Ca			.856	.987	.988	.163	
Ti				.952	.830	.951	.988
V					.919	.085	.189
Mn						.914	.887
Fe							.998

The enrichment factors and the correlation coefficients of element in fine particles

The fine mode of elements shows large relative enrichments. S and Pb are apparently present in the atmospheric fine particles in *E.F.* too high to be explained in terms of normal weathering processes. They may come by remote transportation from continent. At St. Great Wall, the northwest and southeast wind blow frequently due to the transport of pollution aerosols from the west coast of South America (Table 6).

Table 6 Enrichment factors of elements in fine particles

No.	S	K	V	Cr	Mn	Fe	Pb
1	33.94		11.71		1.104	1.0	
2	231.01	12.62	69.52			1.0	
3						1.0	
4	4.22	0.022	2.64		0.914	1.0	32.9
5	53.13	5.21		3.315	0.053	1.0	716
6	511.9		18.52		1.362	1.0	1176
7	396.7	5.47				1.0	555
8					1.01	1.0	
9	903.9	15.93			27.62	1.0	1770

Table 7 shows the correlation coefficients for the elements in fine particles. Because of remote transportation, the sources of elements in fine particles were rather complicated.

Table 7 The correlation coefficients of elements in fine particles

Elements	Cl	K	Ti	V	Cr	Mn	Fe	Pb
S	.285	-.136	.135	.423	.191	.290	-.546	-.008
Cl		-.250	.417	-6.71	.053	.417	-.882	.026
K			.713		-.281	-.841	-.742	.343
Ti				.897	-.251	-.119	.331	-.203
V					-.777	-.905	-.203	
Cr						.056	-.266	-.468
Mn							-.201	.446
Fe								-.128

Comparison of aerosol levels of St. Great Wall with other locations

In order to assess the aerosol levels measured at St. Great Wall in Table 8 we have compared to some other locations measured recently. It can be concluded that the background values of elements at St. Great Wall from Table 3 are better than others.

Table 8 Comparison of aerosol levels of St. Great Wall with other locations ($\mu\text{g}/\text{m}^3$)

Location	Si	S	Cl	K	Ca	Ti	Mn	Fe
Tian An Men, Beijing	12.77	28.84	5.92	3.96	5.36	.216	.145	1.959
Mt. Baihua, Beijing*	25.28	1.92	1.63	0.66	2.80	.147	.041	1.602
Zhangjiajie, Hunan**	6.64	0.68	2.22	0.21	0.53	.002	.002	.537
Namjagbarwa Mt., Tibet*	3.68	0.57	4.15	0.34	0.29	0.30	0.13	.302
Chacaltaya Mt., Bolivia***	2.34	2.00	0.13	0.128	0.11	.030	.005	.284
Great Wall, South Pole	.0067	.033	0.31	0.021	0.051	.01	.0061	.090

Location	Cu	Zn	Pb	As	Ni	Br	Cr	V
TianAnMen, Beijing	.034	.166	.185		.008	.013	.035	
Mt. Baihua, Beijing*	.132	.023	.016		< .001		.038	
Zhangjiajie, Hunan**	.049	.035	< .010	< .010	.027	< .005	< .001	
Namjagbarwa Mt., Tibet*	.070	.056	.076	< .01	< .0001	< .005	< .001	
Chacaltaya Mt., Bolivia***	.026	.036	.120	.025	.041	.023	.001	
Great Wall, South Pole	< .0001	< .00001	.003	< .001	< .0001	< .001	.0016	.0011

* Ma Ciguang, 1986; ** Ma Ciguang, 1988; *** Adams, 1977

Table 9 shows the aerosols measured at South Pole (Zoller, 1979; Duce, 1974). The aerosols at the South Pole at Amunsen-Scott or South Pole Station at 90° S, 2800m above sea levels were collected and measured. Nakaya has published the results measured at St. Showa (Nakaya, 1983). Our samples were collected in particle size fractions by 8 stages cascade impactors, while Nakaya's samples were collected by single stage high volume air samplers. Because of the differences of sampling locations and analytical methods, the results show somewhat discrepancy.

Table 9 The elemental concentrations of aerosols measured at South Pole ($\mu\text{g}/\text{m}^3$)

Location Element	Si	S	Cl	K	Ca	Al	Cr	Fe
Amundsen-Scott U. S. A.*				.0003	.0005	.00057	.000005	.0008
Amundsen-Scott U. S. A.**		.49	.0026	.0007	.0051	.00081	.00011	.00062
St. Showa, Japan***				.017	.014	.47		.95
St. Great Wall,	.0067	.033	.31	.021	.051	< .01	.0016	.090
Location Element	Cu	Zn	Ti	Mn	Br	As	Pb	V
Amundsen-Scott U. S. A.*	.000036	.000031		.00011	.00063		.00063	
Amundsen-Scott U. S. A.**	.000029	.000033	.00011	.000013	.0014	.0000071		
St. Showa, Japan***	.033	.037		.0057				
St. Great Wall	< .0001	< .00001	.01	.0061	< .001	< .001	.0030	.0011

* Zoller, 1974; ** Duce, 1975; *** Nakaya, 1983

CONCLUSION

It can be concluded that the South Pole is a good background area on the Earth. The low content of S in the samples from Amundsen-Scott shows the absence of sulfur pollution. We, therefore, suggest that Amundsen-Scott is the best clean place in this area. These measurements of atmospheric chemical composition are valuable in order to establish concentration baselines with which polluted air may be compared. They also give an opportunity to investigate the physical and chemical characteristics of the atmosphere without anthropogenic influences (Wang Mingxing, 1978).

Acknowledgements—Our thanks to Mr. Shen Ji for useful advice in data analyses.

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