METEOROLOGICAL AND CHEMICAL CONTROLS ON THE VERTICAL DISTRIBUTION OF BEIJING SUMMER COARSE AND FINE AEROSOLS

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ABSTRACT

   Vertical profiles of fine and coarse aerosol particles were determined by cascade impactors at the meteorological tower in Beijing for three days and one night, July 18–23, 1980. Coarse mode aerosols showed a maximum concentration at 47 m when there was an inversion at about 140 m height, and a rather uniform distribution when there was no inversion. This may indicate a two-component origin of coarse particles at the tower site, one being surface dust and the other being tall stack emissions. Fine mode aerosols showed more complex vertical profiles. Median particle size distributions of most metals were bimodal, indicating distinct coarse particle dispersion and fine accumulation mode processes. A chemical thermodynamic calculation indicates that fine mode Si can result from the reduction of silica to volatile SiO during coal combustion with limited air supply, a process which should release substantial amounts of carbon monoxide to the atmosphere.

I. INTRODUCTION

   As the atmosphere is a superfluid, air pollutants may be transported to remote areas. Airborne particles which have been carried over long distances, even intercontinental[1], have been extensively studied. Previous studies have focused on the horizontal movement of the aerosols, and relatively few measurements have been made on the vertical distribution and vertical movement. There have been some measurements of the vertical profiles of number concentrations[2] and elemental mass concentrations[3], but the limited literature on vertical profiles of chemical constituents of aerosols is due to difficulties in making such measurements. However, the measurement of vertical transport of aerosols in the atmospheric boundary layer is important for understanding, not only dynamic meteorological processes, but also processes for the formation and transport of air pollutants on a regional scale.

   Elemental analysis of aerosol samples has been carried out in this study by particle induced X-ray emission (PIXE), a technique with high sensitivity suitable for samples of a few mm^2 area collected from 0.1 m^3 of air or less[4]. Therefore, small samplers may be used[5] and be readily placed at different heights on a tower for vertical profile measurements.

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II. EXPERIMENTAL

Single round orifice cascade impactors were used to obtain aerosol samples in 7 particle size fractions. They were operated at about 0.8 L min^{-1} air flow rate; impactor stages 0–6 correspond to aerosol particle size fractions of <0.25, 0.25—0.5, 0.5—1, 1—2, 2—4, 4—8, and >8 μm aerodynamic diameter (μmad), respectively[5]. The four tower levels at 15, 47, 140, and 320 meters were selected to provide reasonably representative vertical profiles with a few samplers.

Previous investigations of meteorology at the Beijing tower site indicate that summer nighttime temperature inversions may occur at about 100 m. Samples were collected for three approximately 6-hour daytime periods, July 18, 21, and 23, 1980, when the air was unstable and well mixed to the top of the tower. During one approximately 10-hour nighttime period, July 22–23, samples were collected when an inversion at about 140 m was well developed throughout the entire sampling period. Specific sampling information is given in Table 1.

PIXE analysis of the samples was carried out at the Element Analysis Corporation, Tallahassee. Florida, U. S. A., using a General Ionex Tandetron accelerator with 2.58 MeV proton beam. Bombardments, each lasting about 5 minutes, were in two steps which simulated the commonly used X-ray absorber with hole (funny filter)[6]. Of the 32 elements detected, concentrations of 22 were sufficiently above detection limits to provide good analytical accuracy. These form the basis for the following discussion.

Table 1. Sampling Conditions at Beijing Tower Site

Date, July 1980		A 18	B 21	C 22—23	D 23
				Sampling Period	
320 m, Start		1130	0915	1926	0932
Stop	(LST)	1635	1505	0550	1523
Air Vol., m^{-3}		0.198	0.224	0.437	0.246
140 m, Start		1130	0953	2003	1005
Stop	(LST)	1717	1534	0645	1550
Air Vol., m^{-3}		0.243	0.187	0.461	0.242
47 m, Start		1130	1010	2120	1055
Stop	(LST)	1737	1552	0645	1608
Air Vol., m^{-3}		0.330	0.281	0.479	0.266
15 m, Start		1130	1055	2108	1100
Stop	(LST)	1805	1605	0656	1615
Air Vol., m^{-3}		0.237	0.248	0.470	0.252

III. METEOROLOGICAL BACKGROUND

During the study period, July 18—23, 1980, the Far East high was stable, while the subtropic high was weak and located further south than normal. Therefore, the weather in North China during the period was generally cloudy with low wind speed and high relative humidity. However, there was no strong weather system or rainfall at any time in the
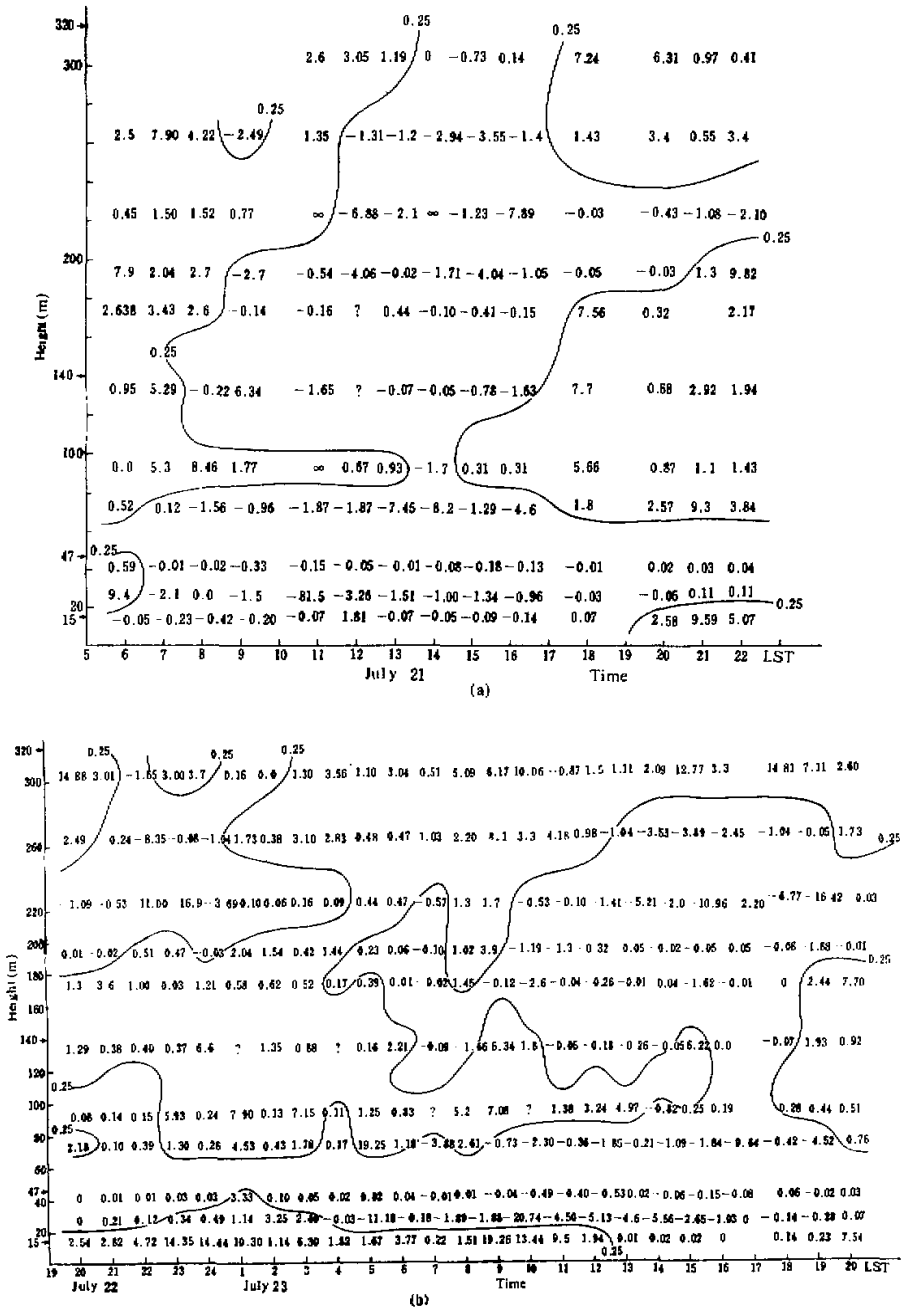
Fig. 1. Richardson numbers Ri in the boundary layer showing atmospheric stability. (a) for sampling period B; (b) for sampling periods C and D.

period. Under such weather conditions the vertical transport of air pollutants is governed mainly by turbulent diffusion.

To describe the strength of the turbulent diffusion, the Richardson number Ri has been calculated according to the definition

$$Ri = (g/T)(\Delta T/\Delta z + \gamma_d)/(\Delta u/\Delta z)^2, \tag{1}$$

where g is the acceleration of gravity, z the altitude of the air parcel studied, T the absolute temperature of air, u the horizontal component of wind speed, and γ_d the dry adiabatic lapse rate. When $Ri > 0.25$, the air is stable, and the turbulent diffusion develops only to a limited extent, and the air pollutants will not easily be transported vertically. On the other hand, when $Ri < 0.25$, the air is unstable, and the turbulent diffusion and vertical transport of air pollutants will be active.

Shown in Fig. 1 are Richardson numbers for 15 levels of the tower for three of the sampling periods B, C, and D. Contours in Fig. 1 are equiscalar lines of $Ri = 0.25$ showing regions of stable and unstable air. Weather conditions were similar for the daytime sampling periods A and B, i. e. cloudy with gentle wind and high relative humidity and unstable boundary layer air, as shown in Fig. 1a by the low Richardson numbers. For the nighttime period C, there was a continuous temperature inversion at an average height of 140 m throughout the entire sampling period. High Richardson numbers were found in layers of 0—50 m and 70—140 m, where the air was very stable, as shown in Fig. 1b. For the daytime period D, following period C, the temperature inversion has gradually weakened, the high Richardson numbers were found only in a thin layer of 80—140 m, until 1500 LST, the end of the sampling period. The regions below and above this layer were unstable with low Richardson numbers; high Richardson numbers were also found in the layer above 260 m. Thus, we may expect that during this study period the air below 260 m was well mixed.

IV. AEROSOL SIZE DISTRIBUTIONS AND COARSE MODE PROFILES

The distributions of most elemental concentrations with particle size show two distinct modes, one being a fine mode with the maximum mass concentration in the 0.5—1 μmad fraction and the other being a coarse mode with the highest concentrations in the 4—8 μmad fraction. For period C the median concentrations of the elements for the four tower heights are shown in Fig. 2.

Coarse particles are generated from the dispersion of wind-blown and industrial dust, composed mainly of elements in earth crustal proportions, and of mechanically dispersed coal fly ash or other dusts from combustion, often of similar composition. Fine particles can result from vaporization of elements at elevated temperature, such as in combustion, followed by condensation in the atmosphere to solid or liquid particles.

As discussed further below, several metals may be volatilized during coal combustion as chlorides and recondense into fine particles. Silicon is of special interest because of its remarkably high concentration in ultrafine particles, < 0.25 μmad, possibly from the reduction of silica during combustion in limited air supply, its vaporization, followed by nucleation of very fine particles.

Sulfur is a common pollutant which occurs in fine particles after the oxidation of gaseous sulfur dioxide from fossil fuel combustion, but it may also occur as coarse particles if the oxidation occurs on dust particle surfaces or if finer sized sulfate coagulates with coarse dust. For research on surface catalyzed oxidation of SO_2 in the atmosphere our finding
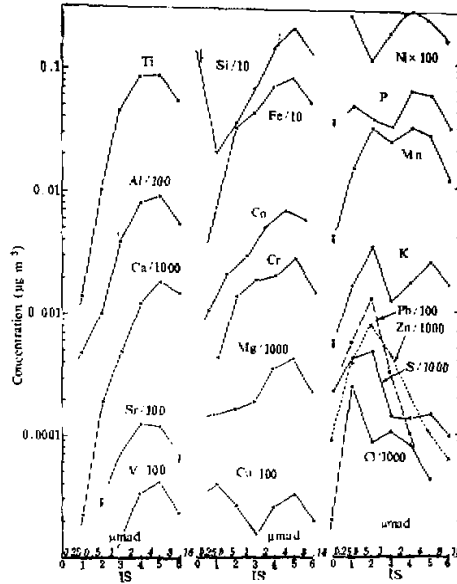
Fig. 2.   Median particle size distributions of 19 elements for sampling
          period C, arranged in increasing order of prominence of
          the fine mode. IS—Impactor Stage.

of coarse particle S may be important.   Surface oxidation of SO_2 to sulfuric acid may also occur on materials and cause the deterioration of marble building stone in Beijing, even though rainwater, which is not unusually acidic[7], should not cause this deterioration.

Vertical distributions of coarse mode aerosol concentration are shown in Fig. 3, averaged for 16 elements.   A few important fine mode elemental concentration profiles are also shown.   Generally the daytime coarse aerosol profiles show little concentration variation with height, whereas the nighttime period C shows low concentrations at 320 m with their maximum at 47 m.   These profiles can be examined in relation to boundary layer stability information.

The coarse mode aerosol concentrations are most uniform with height for the daytime periods A and B.   The small increasing trend with height for A and small maximum at 140 m for B are probably within experimental uncertainty.   These results are consistent with the good vertical mixing expected from the Richardson numbers of Fig. 1.

In contrast, at night during period C, when there was a continuous temperature inversion at 140 m from 1900 LST July 22 to 0600 LST July 23, the coarse mode showed a maximum concentration at 47 m.   A maximum in the stable air below the inversion could result from coarse particle deposition at the surface without turbulent diffusion from above, and direct emission from elevated smoke stacks would also lead to a polluted stratified layer without vertical mixing downward or upward.

Period D, which followed C without delay, showed coarse aerosol concentrations at the top two levels significantly greater than nearer the ground.   Particles may be well mixed below 80 m and may penetrate the thin stable 80—120 m layer to overlying air, and may

accumulate there owing to a stable column above 260 m.

The coarse mode aerosols at the tower site have two types of sources, surface dust and emission from tall smoke stacks. The latter may be more important during the time of this study. Smoke stacks from coal fired combustion units in Beijing average 30 m height. Under normal atmospheric conditions, i. e. with no passage of strong weather systems, plumes of smoke released from these stacks may first rise to 50 m height, then travel downwind while turbulent diffusion and gravitational settling cause vertical dispersion of aerosol particles. Different vertical concentration profiles may result according to categories of atmospheric stability. When the atmosphere is stable, e. g. at night during period C, there may be negligible vertical movement of aerosols, and the coarse mode aerosols should have maximum concentration at about 50 m. When the atmosphere is unstable, e. g. daytime as in period B, the vertical movement during transport may make the air well mixed in the mixing layer, causing a uniform coarse aerosol concentration profile.

These profiles of coarse mode aerosols due to smoke stack plumes are further modified by surface dust. In summer in Beijing the earth's surface is wet and the land is well covered with vegetation, so that the surface dust is expected to be less. Therefore, the concentrations of the lowest tower level are usually lower than at the levels above.

Fine mode elemental concentration profiles are more complex, undoubtedly reflecting variety in combustion and other sources both near the ground and aloft. Chemical transformations in the atmosphere, e. g. of S, during transport further complicate the profiles.

Coarse mode elemental weight ratios for period A (day) and period C (night) are given in Table 2. Significant differences in the ratios are observed for both sampling periods.

For the night samples, the elemental weight ratios at 15 and 47 m (below the inversion) are generally very similar, but ratios at 320 m (above the inversion) are different. Local aerosol sources in the city are confined to below the inversion height whereas the aerosol above may reflect regional air mass characteristics. The finding here indicates that the local urban Beijing aerosol, represented by the two lowest tower levels, differs from the North China regional aerosol, seen at the highest level, in the relative mixture of individual
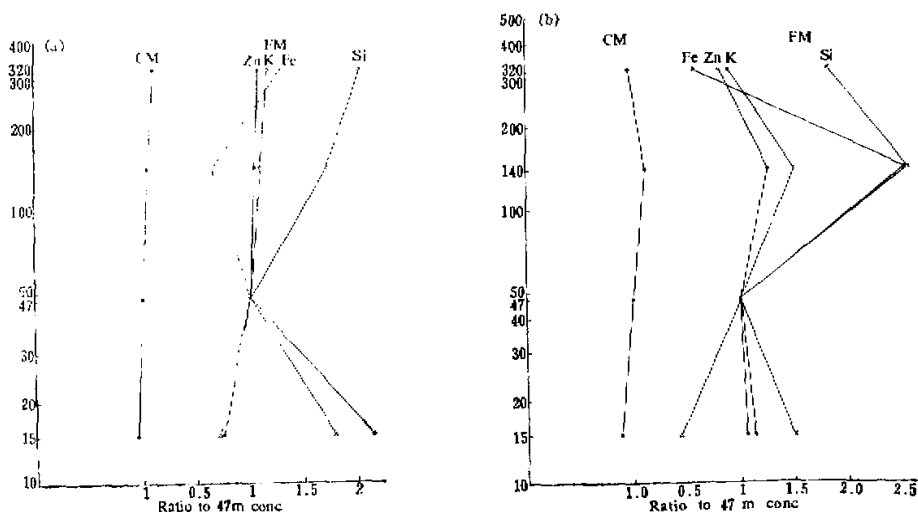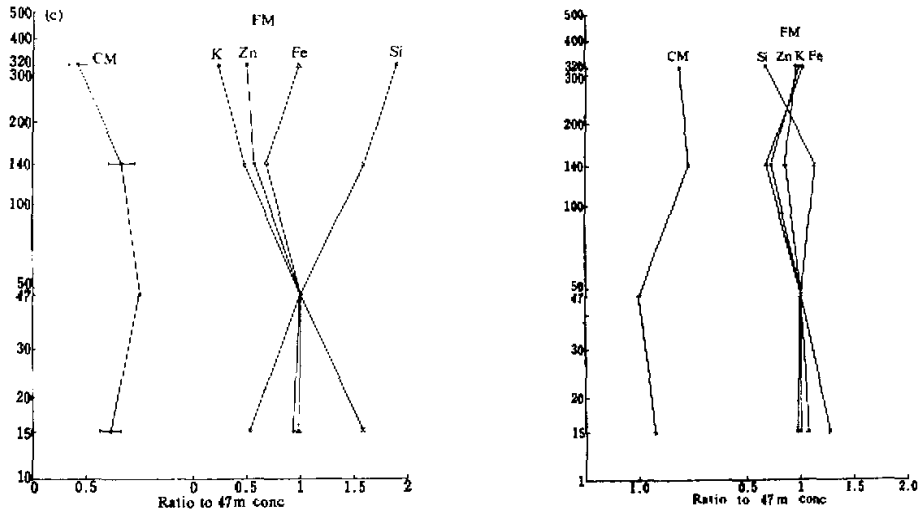
Fig. 3. Vertical profiles of total coarse mode (CM) aerosols and fine mode (FM) concentrations of K, Si Zn, and Fe. (a), (b) and (d, right) show the results of day samples, and (c) shows results of night samples.

Table 2. Coarse Mode Weight Ratios to Al

Height (m)	15		47		140		320	
	Day Time	Night Time	D	N	D	N	D	N
Mg	0.67	0.44	0.47	0.36	0.53	0.47	0.47	0.52
Si	2.97	2.30	2.33	2.20	2.31	1.60	2.31	2.40
S	0.29	0.15	0.32	0.15	0.27	0.16	0.30	0.22
Cl	0.14	0.084	0.13	0.10	0.16	0.13	0.12	0.12
K	0.36	0.27	0.27	0.23	0.28	0.24	0.29	0.38
Ca	2.33	1.80	2.70	1.80	1.84	1.40	1.84	1.60
Ti	0.12	0.10	0.10	0.10	0.10	0.10	0.10	0.09
Cr	0.004	0.0025	—	0.0035	—	0.0025	0.003	0.004
Mn	0.022	0.026	0.018	0.029	0.019	0.039	0.019	0.034
Fe	1.11	0.77	0.87	0.77	0.93	0.80	0.89	1.30
Co	0.009	0.006	0.008	0.006	0.008	0.006	0.008	0.010

elemental constituents, owing to the different mixing ratios of the various sources in region.

V. CHEMISTRY OF TRACE ELEMENT VOLATILITY IN COMBUSTION

Fine modes of the elements were resolved by a graphical procedure in which typically coarse particle elements were compared with elements containing excess fine particle concentrations. An important difference was found between samples from the night period C and the three day periods: At night the fine mode concentration of Cl relative to S was between 10% and 20%, much greater than found in any of the day samples, in which it was

generally 5% or less. A process which could account for this difference is due to more extensive volatility of HCl during the day by deposition of H_2SO_4 onto the surfaces of initially metal chloride fine aerosol particles.

We may hypothesize that the metals were vaporized as chlorides during coal combustion and condensed in the atmosphere as fine aerosol particles. Subsequent transformation of the SO_2 released in combustion to H_2SO_4 and deposition on these particles would transform the chloride salts to sulfates and release HCl to the atmosphere. If the reaction was less extensive during the night, when the H_2SO_4 production is slower (due to lack of oxidant production without sunlight), the residual Cl in the aerosol would be relatively greater than during daytime.

If the reaction was incomplete, because of limited supply of sulfuric acid at night, a material balance among sulfate, chloride, and the sum of the metal ions should be found and serve as a test of the premises of the hypothesis of chloride volatility during combustion. By day an excess of sulfuric acid may exist, little chloride should remain in the aerosol, and a cation–anion material balance calculation should show an excess of the anions. These may be balanced by hydrogen ion (acidity) or ammonium ion.

The hypothesis of chloride volatility is based on the expected properties of chlorides and

Table 3. Metal Chloride Element Balance, Period C (Night)

Element	neq m⁻³ at height (m)*			
	15	47	140	320
Fe +2	19.0	19.7	13.3	19.3
Co −2	0.098	0.102	0.088	0.085
Cr +2	0.088	0.085	0.077	0.046
Mg +2	23.0	32.9	21.4	5.7
Cu +1	0.112	0.112	0.094	0.065
Ni +2	0.112	0.150	0.068	0.187
Mn +2	2.44	2.44	1.35	1.60
Pb +2	2.31	2.41	2.05	1.25
Zn +2	6.42	7.34	4.16	3.64
K +1	13.30	25.32	12.28	6.01
Na +1	(24.8)	(47.0)	(22.6)	(11.3)
Sum +	91.7	137.6	77.6	49.8
Cl −1	11.85	16.64	6.19	5.64
S −2	70.5	90.4	59.9	39.3
Sum −	82.4	107.0	65.2	44.9
Cl/S	0.168	0.207	0.103	0.143
R −/+	0.90	0.78	0.84	0.90

*Concentrations in nanoequivalents m⁻³ for expected valence of the elements, i. e. nanograms m⁻³/ (atomic weight/charge).

Table 4. Metal Chloride Element Balance, Periods A, B, D (Day), Summary

Element	neq m^{-3} at height (m)											
	15			47			140			320		
Period	A	B	C	A	B	C	A	B	C	A	B	C
Sum +	94.7	140.5	168.3	122.0	125.1	161.8	128.8	192.5	101.0	136.4	118.4	163.0
Cl −1	6.21	7.70	6.21	24.82	27.36	6.21	22.57	48.80	10.15	30.74	26.23	16.64
S −2	483.4	402.7	262.6	573.2	412.5	247.6	669.9	796.5	258.2	710.5	484.7	246.4
Sum −	489.6	410.4	268.8	598.0	439.9	253.8	692.5	845.3	268.4	741.2	510.9	263.0
Cl/S	0.013	0.019	0.024	0.043	0.053	0.025	0.034	0.061	0.039	0.043	0.054	0.067
R −/+	5.17	2.92	1.60	4.90	3.52	1.57	5.38	4.39	2.66	5.43	4.32	1.61

oxides at the high temperatures of combustion[9]. The chemical properties of elements show that those metals with chloride boiling points less than about 1500°C, and refractory (non-volatile) oxides, are found with fine modes. Na and K also have volatile hydroxides at high temperature. At combustion temperatures the vaporization of these metals as chloride salts is expected, limited by the supply of Cl in the fuel.

In Tables 3 and 4 the cation–anion balances for the four sampling periods are presented. By use of atomic weights, the concentrations of the elements in air were converted to ionic charge concentrations, in nanoequivalents, for the expected oxidation states of the metals in chloride salts expected to be formed in combustion. In night period C, the anion/cation ratio was slightly less than unity and is expected to be close to unity if nitrate ion would have been measured. Thus the material balance is good, consistent with the hypothesis of chloride volatility of the metals during combustion.

In the three day periods, anion concentrations were found several times greater than cation, an imbalance which indicates large amounts of sulfuric acid reaction with the aerosol. The excess acidity may be present in the aerosol, or neutralization could have occurred by ammonia absorption. Extensive sulfuric acid production during daytime is suggested. A direct measurement of aerosol acidity and ammonium ion in the aerosol should be carried out in future studies of acidic air pollution in Beijing.

Ultrafine particle silicon is an anomaly which requires special explanation. In all samples, the fraction < 0.25 μmad contains several micrograms of Si per cubic meter, approaching the concentration of coarse particle Si in dust, and no other element was found in the ultrafine fraction. These high concentrations may present a health risk by deposition in the respiratory tract when inhaled. Reaction of SiO_2 with C may produce a high temperature vapor of SiO during incomplete combustion of coal in a limited supply of air, a process which also should produce considerable carbon monoxide.

Chemical thermodynamic data[10] can be used to calculate the high temperature equilibrium between gaseous silicon monoxide (SiO) and CO which form from the reduction of silica (SiO_2) by elemental carbon (C) in coal. Fig. 4 is a plot of the equilibrium constant between 1000 K and 1900 K, a range which includes various stages of the combustion process. In a limited air supply, CO will form in preference to CO_2 and may be several percent or more of the combustion gases in the high temperature zone. Fig. 4 shows that, in such

conditions, the partial pressure of SiO is about 10^{-4} atm. at 1500 K.

With a drop in temperature of the exhaust gases, and exposure to air containing oxygen, this vapor will rapidly condense into a very fine aerosol of silica. This process appears to account for the occurrence of the concentrations of ultrafine Si observed. The chemical reaction should produce equal amount of CO and SiO. A confirmation of the reaction could be achieved by measurements of both gaseous CO and ultrafine Si under controlled combustion conditions.
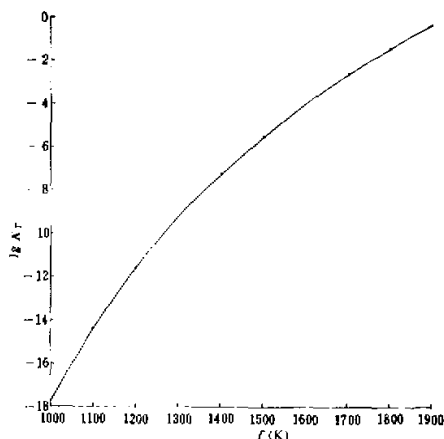
Fig. 4. Logarithm of the equilibrium constant, K_T, of the reaction
SiO_2 (quartz)$+C$ (graphite)$=SiO$(gas)$+CO$(gas) according to
thermodynamic data. In the presence of both solids, $K_T = P_{SiO} \cdot P_{CO}$.

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