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MORI, IKUKO

森　育子

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NAGOYA UNIVERSITY
名古屋大学

要旨

黄砂エアロゾルは、反応性に富んだ性質をもち、他の大気成分との物理的および化学的相互作用によって変質しながら、自由大気中を輸送されていることが、これまでの研究で示唆されてきた。しかしながら、自由大気中の黄砂エアロゾルの観測例は、地表付近のエアロゾルの観測と比較して観測が困難なため、限られている。特に、化学的データの観測例はほとんどない。それゆえ、自由大気中のエアロゾルの直接観測が待たれていた。

本研究では、日本海沿岸上空2 kmと4 kmにおいて、航空機に搭載したエアロゾルサンプラーを用いてエアロゾル試料を採取し、その水溶性成分の分析結果から、黄砂エアロゾルの大気化学的振る舞いを明らかにした。

航空機観測によって以下のような知見が得られた：

1. 日本海沿岸の自由大気中のエアロゾルは、粗大粒子の個数濃度や粗大粒子中の水溶性カルシウム濃度が高いことが多かった。粗大粒子中の水溶性カルシウム濃度が高いエアロゾル試料は、アジア大陸や日本で砂塵嵐や黄砂現象が観測された24時間前後に採取されたものである。エアロゾル中のSr^{2+}/Ca^{2+}は、日本の土壌中よりも黄砂エアロゾルの発生源地付近の表層土中のSr^{2+}/Ca^{2+}に近い値だった。これらの結果は、日本海沿岸の自由大気中に黄砂エアロゾルが飛来していたことを強く示唆している。
2. 自由大気中で粒径別に採取されたエアロゾル中の水溶性成分の存在比から、黄砂エアロゾルが、他のタイプのエアロゾル（例えば硫酸アンモニウムエアロゾル）と混合した状態で存在していることが示唆された。
3. 粗大粒子中に含まれる硝酸イオン濃度は、カルシウムイオンが検出されなかったときより、検出されたときの方が高かった。硝酸イオンとカルシウムイオンの粒径分布はどちらも粗大粒子領域にピークがあり、硝酸イオンがアルカリ性の性質をもつ黄砂エアロゾル表面に存在していたことが示唆された。

従来の研究では、黄砂エアロゾルとともに見いだされる硝酸塩や硫酸塩の起源は明らかにされていなかったが、本研究により、地表付近でなく、自由大気中を輸送されているとき、既に黄砂エアロゾル表面に硝酸塩が存在していたことが示唆された。自由大気中の黄砂エアロゾルは、地表付近のものと比較して、長距離輸送されやすいため、窒素成分の長距離輸送の担い手になっているとみなすことができる。

航空機観測は時間的な制約が大きく、地上で行われているような長時間の試料採取は不可能であるため、得られる試料の量はいきおい少量とならざるを得ない。さらに加えて、目視で明らかな大規模な黄砂エアロゾルの飛来だけでなく、目視での判定が困難な小規模な黄砂エアロゾルの飛来にも関心が寄せられるようになってきている。それゆえ、少量の試料にも適用できる黄砂エアロゾル飛来の指標をつくることが、今後の研究にきわめて有用である。本研究を進める中で、黄砂エアロゾルが混じっているエアロゾルは以下のような化学的特

徴をもち、その特徴が黄砂エアロゾル飛来の指標として使えることが示された。

4. 黄砂エアロゾルが混じっているときのエアロゾル中の水溶性カルシウムや水溶性ストロンチウム濃度が高い。
5. エアロゾル中の非海塩性 Ca に対する非海塩性 Sr の比の値が黄砂エアロゾル発生源地付近の表層土中の Sr^{2+}/Ca^{2+} の値（0.0052±0.0011）に近い。

黄砂エアロゾルは自由大気中を単独で輸送されるのではなく、他のタイプのエアロゾルと混合した状態で輸送されている。黄砂エアロゾルが大気中を輸送される途中で粒子同士の衝突があるとすると、その相手としてもっとも可能性の高いのは、大気エアロゾルの主要成分のひとつである硫酸アンモニウムを主成分とするエアロゾルであろう。このようなエアロゾル同士の衝突も黄砂エアロゾルの変質の一端を担っていると思われる。上空で粒子同士の衝突を直接観測するのは不可能であるが、モデル実験によって以下の結果を得た。

6. 凝集した黄砂粒子と硫酸アンモニウム粒子が化学反応し、中間物質の koktaite $[(NH_4)_2Ca(SO_4)_2\cdot H_2O]$を経て、最終的には gypsum $(CaSO_4\cdot 2H_2O)$が生じることが確認された。この化学反応は、比較的低湿度の条件下で、日オーダーで起きた。

本研究により、自由大気中を輸送されている黄砂エアロゾルが大気中のガスやエアロゾルと活発な化学的相互作用により変質している様子が明らかになった。今後、さらなる観測やモデル実験データの積み重ねによって、自由大気中における黄砂エアロゾルと他の大気成分との化学的相互作用が定量化されることが期待される。それにより、黄砂エアロゾルの変質が、地球化学的物質循環や気候変動モデルに与える影響の大きさも明らかになるであろう。

Abstract

Aerosol particles in the free troposphere over the Japan Sea coast were collected with a nine stage cascade impactor mounted on an aircraft and concentrations of water soluble components in the aerosol particulate matter were measured. Number size distributions of aerosols were also measured by use of an optical particle counter mounted on the aircraft. On the basis of these results, I discuss the transport and chemical modification of the *kosa* aerosol in the free troposphere.

High number concentrations of coarse size particles and high concentrations of water soluble Ca in the coarse size aerosols were observed in the free troposphere. The concentrations of Ca^{2+} in aerosols in the free troposphere increased when dust events were observed. The mean Sr^{2+}/Ca^{2+} values were closer to those of desert soil in China than the Japanese soil value. These results strongly suggest the transport of the *kosa* aerosol to the free troposphere over the Japan Sea coast.

The concentrations of nitrate in coarse particles were higher in samples in which Ca^{2+} was detected than in those in which it was not. The size distribution pattern of nitrate showed good correspondence with that of Ca^{2+}. These results suggest that nitrate was formed on the surface of *kosa* particles.

Concentrations of sulphate and ammonium in fine particles at 2 km when Ca^{2+} was detected were higher than those when it was not. It is suggested that *kosa* aerosols were transported with other types of aerosols, such as ammonium sulphate, ammonium nitrate, etc. aerosols.

The possibility of chemical reaction, when the *kosa* aerosol collided and coagulated with ammonium sulphate, was investigated by a series of the model experiments. The results show that a chemical reaction during the

coagulation of *kosa* and ammonium sulphate aerosols actually occurred, at a rate measured in days, to yield koktaite [$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$] as an intermediate product and, finally, gypsum ($CaSO_4 \cdot 2H_2O$).

Additionally, a new discrimination method of the transport of the *kosa* aerosol, which could be applied to small amounts of aerosol sample such as collected by use of an aerosol sampler mounted on an aircraft, was developed. Chemical characteristics of aerosol samples which possibly contain *kosa* aerosols are: concentrations of water soluble Ca and Sr are high; the ratio of non sea salt strontium to calcium in the aerosol is around 0.0052.

Contents

1. Introduction

1.1. *Kosa* Aerosol in East Asia and the North Pacific

Mineral dust aerosol cannot be neglected in global change studies, because the effects of mineral dust aerosols on the radiation budget are important relative to those of other types of aerosols, such as sulphate and black carbon particles, due to widespread distribution and large optical depth (Duce, 1995; Li et al., 1996; Sokolik and Toon, 1996; Tegen et al., 1996; Bergametti and Dulac, 1998). The desert and loess areas on the Asian continent is one of the major source regions of mineral dust aerosol. Surface soil particles in the desert and loess areas on the Asian continent are arise by strong winds created by travelling cyclone with a cold front then transported to the Korean Peninsula, Japan, and the North Pacific by the westerly winds. Increases of aerosol concentration by mineral dust aerosols were reported found in long-term aerosol monitoring in China (Gao et al., 1992; Sekine et al., 1992), over the North Yellow Sea (Zhang et al., 1993), in Korea (Hashimoto et al., 1990), in Japan (Kadowaki, 1979; Mukai et al., 1990), and over the North Pacific (Duce et al., 1980; Parrington et al., 1983; Tsunogai et al., 1985). These particles in the atmosphere are called *kosa* aerosols. It is estimated that $6\text{-}12 \times 10^6$ tons of *kosa* aerosol are transported annually to the central North Pacific (Uematsu et al., 1983).

Kosa aerosols deposited on land and / or ocean impact the geochemical cycle of terrestrial materials and the ecosystem. *Kosa* aerosols deposited on land are an important component of surface soils (Naruse and Inoue, 1982; Mizota et al., 1992; Naruse et al., 1997). *Kosa* aerosols deposited on the ocean provide terrestrial materials even in remote oceanic areas where riverine input can be neglected. They are a source of iron and other elements which can control the growth of phytoplankton (Martin et al., 1994; Jickells, 1995). They can also account for much of the non-biogenic portion of deep-sea sediments in the Japan Sea (Mizota and Matsuhisa, 1984) and in the North Pacific region (Blank et al., 1985; Zhang and Huang, 1992).

The *kosa* aerosol also has noticeable impacts before being deposited, that is during transport. Direct forcing by *kosa* aerosols results from the scattering and absorption of solar and terrestrial radiation. Indirect forcing results from their role as ice nuclei (Isono et al., 1958 and 1971). Important parameters to determine the magnitudes of those impacts are concentration, chemical composition, size distribution of the aerosol, and so on. These physical and chemical parameters are not uniform.

For example, particle sizes in the Taklamakan desert soil range between 35-120 μm, that of loess in Lanzhou is 30 μm or less (Murayama, 1984). The mass size distribution of the aerosol particulate matter collected in Japan during *kosa* event had a peak around 4 μm diameter (Ishizaka and Ono, 1982). The mass median diameter of the particulate matter collected at the Mauna Loa Observatory, Hawaii was 1.0 ± 0.3 μm (Braaten and Cahill, 1986).

Chemical characteristics of the *kosa* aerosol apparently reflect its source. Surface soils of desert and loess areas in the Asian continent where *kosa* aerosol originates contain crustal elements (Inoue and Yoshida, 1978; Tanaka et al., 1986 a; Nishikawa et al., 1991 a) and abound in carbonate carbon (Quan et al., 1994). Chemical characteristics of the aerosol particulate matter collected during *kosa* phenomena are: concentrations of crustal elements such as aluminium, iron, and calcium in the aerosol increase (Tanaka et al., 1986 b and 1989; Okada et al., 1990; Fan et al., 1996); the ratio of Ca to Al in the aerosol approaches that of Chinese desert surface soils (Tanaka et al., 1989); the concentration of carbonate in the aerosol increases (Hayakawa and Sakamaoto, 1989).

There is also a possibility of modification of *kosa* aerosol during transport. Iwasaka et al. (1988) found soil particles coated by water or solution containing sulphate at altitude 4400 m over Japan, suggesting that such particles absorb various atmospheric gases. Okada et al. (1990) found that *kosa* particles were present as mixed particles (internal mixture of water soluble and insoluble material) by use of an electron microscope equipped with an energy-dispersive X-ray analyser. *Kosa* particles mixed internally with sea salt were present to the extent of 16-100% among analysed dust particles in Nagasaki, Japan (Niimura et al., 1998). Wu and Okada (1994) found that nitrate existed on the surface of dust particles during the *kosa* phenomenon. Nishikawa et al. (1991 a) collected *kosa* aerosols at Yaku Island, Japan and found high correlation coefficients between nitrate, and non-sea-salt sulphate, with total surface area of aerosol particles for all size fractions of the coarse fraction, indicating that these ions are deposited on and transported with the *kosa* aerosol. Mori et al. (1998) showed evidence for the chemical reaction during the coagulation between *kosa* and ammonium sulphate particles by a series of model experiments. Dentener et al. (1996) indicated the importance of the role of mineral dust aerosols particles on tropospheric chemistry, especially in Asia, by use of a global three-dimensional model of the troposphere which coupled mineral dust processes with photochemistry and the nitrogen and sulphur cycles. Their results suggested: O_3 decrease caused by interactions of N_2O_5, O_3, and HO_2-radicals with mineral dust in and near dust source areas; association and / or neutralisation of HNO_3 with mineral dust aerosols over large parts of the globe; and reaction of SO_2 on mineral dust aerosols especially in Asia. This reaction will change the size distribution of sulphate, and that may diminish the local cooling effect of the sulphate aerosol.

Sulphate associated with mineral dust aerosols will enhance the ability of dust to act as cloud condensation nuclei.

Thus, the *kosa* aerosol itself and the reaction of the *kosa* aerosol cannot be neglected in global change studies. However, observationals of aerosols during transport are not enough to evaluate these reactions. Physical and chemical characteristics of *kosa* aerosol in the free troposphere should be measured.

1.2. Observation of *Kosa* Aerosols in the Free Troposphere

It was pointed out that the *kosa* aerosol was transported in the free troposphere when it was transported for long range (Merrill et al., 1985; Iwasaka et al., 1988). Data obtained by use of satellites, lidar, sun-photometers, balloons, and aircraft are useful to understand the behaviour of the free tropospheric aerosols and sometimes suggest transport of the *kosa* aerosol to the free troposphere.

Visible images of geostationary meteorological satellites have been used to understand the spacial distribution and transport path of the *kosa* aerosol (Ishizaka, 1979; Hasegawa, 1980; Iwasaka et al., 1983; Chung and Yoon, 1996). However, it is hard to detect *kosa* aerosol on the basis of a satellite image when the *kosa* event is a small one or when there are clouds around a *kosa* cloud.

Results obtained by sun-photometer have indicated enhancement of aerosol concentration in the spring in the middle and lower troposphere over Japan, suggesting transport of the *kosa* aerosol in the free troposphere (Hayasaka et al., 1990; Shiobara et al., 1991).

A lidar is useful to understand aerosol vertical distribution and temporal variation. Highly concentrated particle layers were frequently found in the range of about 2 to 6 km altitude (Iwasaka et al., 1983 and 1988; Kai et al., 1988). Simultaneous measurements of tropospheric aerosol particles and water vapour by use of a Raman lidar have shown that high concentration of particulate matter appears over Japan in spring, when relative humidity is apparently lower than in August (Kwon et al., 1997). Combined with satellite images, back trajectory analysis, and weather maps, they concluded that those layers likely contained *kosa* aerosols. It is difficult, however, to determine the physical and chemical features of aerosols only from lidar measurements.

Balloon measurements are also useful to understand aerosol vertical distribution and temporal variation. High -altitude balloons with optical particle counters were launched at Laramie, Wyoming from 1971 to 1990 (Hofmann, 1993). The concentration of larger particles ($r > 1\ \mu m$) peaks in spring. He concluded that these are probably *kosa* aerosol transported over long range.

Optical particle counters mounted in aircraft have shown enhancement of the number concentrations of coarse size particles in the lower and middle troposphere around Japan (Ikegami et al., 1993; Iwasaka et al., 1996), suggesting that *kosa* aerosol from the Asian continent contributes to the tropospheric aerosols around Japan.

Combining the results of balloon, aircraft, and lidar measurements of free tropospheric aerosols, Iwasaka et al. (1997) concluded that soil particles frequently diffuse into the free troposphere and are transported over Japan.

Those observations are useful to understand free tropospheric aerosol transport. However, it is hard to determine what chemical reactions of the *kosa* aerosol with other substances in the free troposphere take place only from those observational results, because of the lack of information on chemical characteristics. Chemical analysis of the aerosols in the free troposphere is necessary to understand chemical reactions of the *kosa* aerosol in the free troposphere.

Highly concentrated particle layers which likely contain *kosa* aerosols are frequently found from 2 to 6 km altitude (Iwasaka et al., 1983 and 1988; Kai et al., 1988). An aerosol sampler mounted on an aircraft, which can fly in the range of about 2-6 km altitude for several hours, can collect enough free tropospheric aerosols for chemical analysis.

1.3. Objectives

A large amount of *kosa* aerosol is transported and deposited over East Asia and the North Pacific. The *kosa* aerosol deposited on lands and /or oceans in this region impacts the geochemical cycle of terrestrial material, and the ecosystem. The *kosa* aerosol in the free troposphere (during transport) also impacts tropospheric chemistry and climate forcing. Reaction of *kosa* aerosol with other atmospheric substances may change the magnitude of those impacts, because physical and chemical characteristics of the free tropospheric aerosol will change as a result of chemical reactions. However, observationals of aerosol during transport are not enough to evaluate these reactions, without information on chemical characteristics (Fig. 1.1).

The purpose of this study is to clarify the transport and chemical modification of *kosa* aerosol in the free troposphere by the chemical analysis of aerosol and a series of model experiments. Additionally, a new discrimination method for *kosa* aerosol, which can be applied to small amounts of aerosol collected in the free troposphere, has been developed.

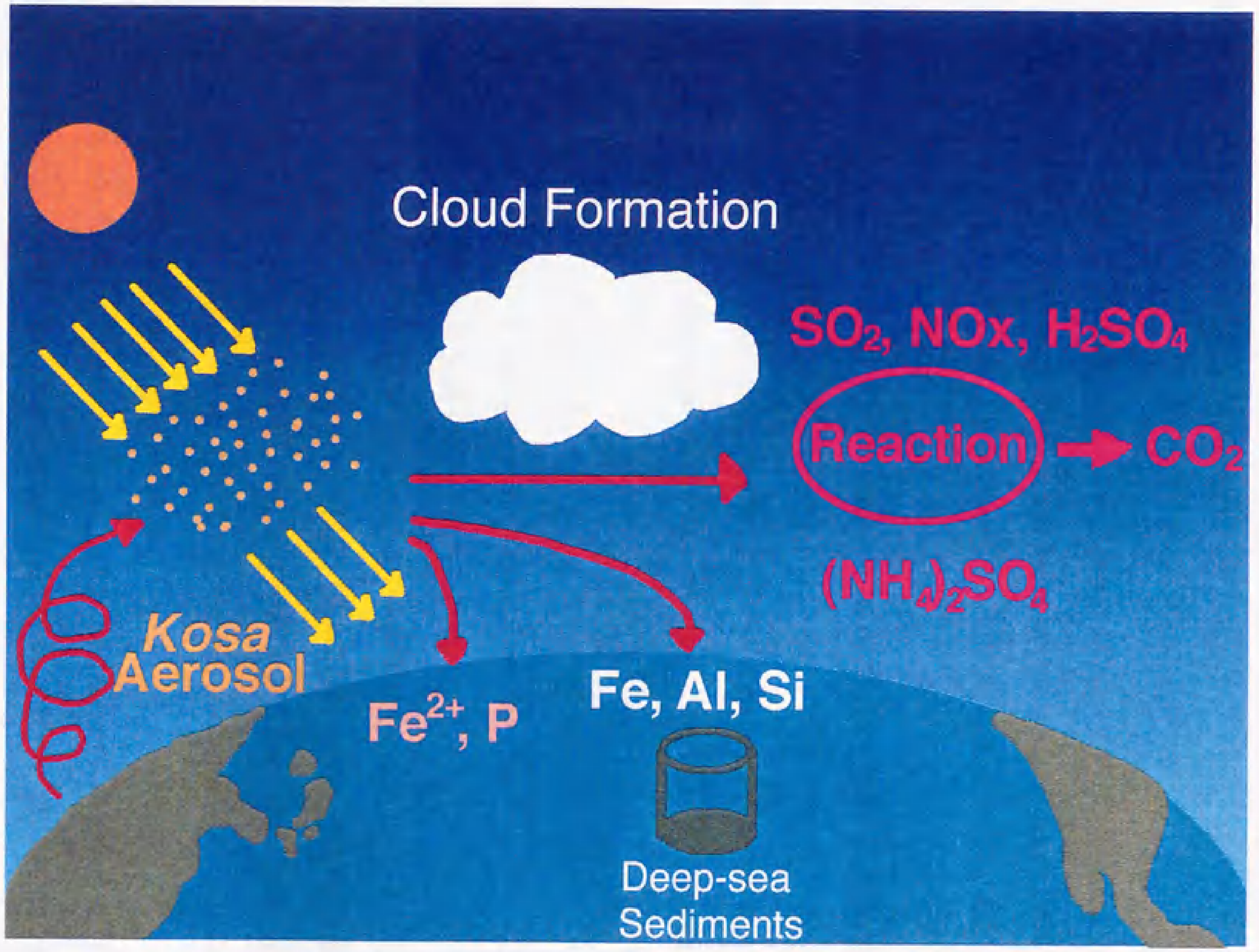

Figure 1.1 Schematic diagram of effects of the chemical reaction of the *kosa* aerosol on the global environment.

2. Chemical Indicators for *Kosa* Aerosol

2.1. Necessity for a New Discrimination Method

From past studies several chemical characteristics of *kosa* aerosol have been reported. These include:

1. Concentrations of crustal elements such as aluminium, iron, and calcium in the aerosol collected during *kosa* event are higher than those collected during non-*kosa* event. (Tanaka et al., 1986 b and 1989; Okada et al., 1990; Fan et al., 1996).
2. The ratio of Ca to Al in the aerosol approaches that of Chinese desert surface soil (Tanaka et al., 1989).
3. The concentration of carbonate in the aerosol collected during *kosa* event is higher than those collected during non-*kosa* event. (Hayakawa and Sakamoto, 1989).

However, the chemical analysis methods used in past studies all require large amounts of sample and complicated preparations; they are not suitable for small amounts of sample such as are collected in the free troposphere using a sampler mounted on an aircraft. Chemical analysis of water soluble components in an aerosol sample is suitable for small amounts of sample, because low blank value is expected, since no chemicals are added to the sample in the experimental procedure.

The surface soils of the loess areas and desert regions of the Asian continent from where the *kosa* aerosol is thought to originate are known to be rich in calcium carbonate (Quan et al., 1994). Calcium carbonate is an easily soluble material though its solubility depends on the solution pH. Its solubility in water (25℃) is 1.4 mg l^{-1}. Past investigations frequently indicated a relationship between Ca and the *kosa* phenomenon. However, the fluctuation of Ca concentration in aerosol alone may not indicate a transport of *kosa* aerosol because higher calcium concentrations in the aerosol may be the result of contributions from sea, road dust, cement or Japanese soils derived aerosols (Tsuruta, 1991).

The calcium and strontium contained in *kosa* aerosol gradually effuse out of solution according to the amount of time they are in water (Nishikawa et al., 1991 b). Strontium is one of the trace elements in a calcite crystal structure. During calcite crystal formation, strontium closely follows the same changes that calcium undergoes, because strontium is an alkaline earth with a similar ionic radius to Ca. Strontium in a sea salt or *kosa* particle easily effuses out of solution, when it contacts with a solvent. However strontium in silicate does not easily effuses out when it contacts a solvent. The same is true for calcium. Water soluble strontium in aerosol could therefore possibly be used to discrimination *kosa* aerosol transport.

In this chapter, I will discuss a new discrimination method for transport of *kosa* aerosol based on chemical analysis of the water soluble component of the aerosol. The new method can be applied to small samples such as are collected in the free troposphere using a sampler mounted on an aircraft.

2.2. Sample and Chemical Analysis

2.2.1. Aerosol

A low volume sampler was used to collect aerosol particulate matter for a continuous period of 1 month at the National Institute for Environmental Studies in Tsukuba, Japan (May 1991 and April 1994), at the Yamaguchi Prefectural Research Institute of Health in Yamaguchi (April 1994) and the Fukuoka Institute of Health and Environmental Sciences in Dazaifu, Japan (April 1994) (Fig. 2.1). All sampling was conducted on the roofs of the facilities. Aerosol particulate matter was collected on a membrane filter (TM-3) attach in the low volume sampler. The total volume of sampled air for each sample collection was 36-160 m^3 depending on sampling duration.

After collection, one half of the filter was used for analysis of water soluble component. It was extracted ultrasonically within 10 minutes with 10 g ultra pure water. Analysis of Na, Mg, Ca, Sr was conducted using both inductively coupled plasma atomic emission spectrometry (ICAP-61E Trace, Thermo Jarrell-Ash) and ion chromatography (DX-100, DIONEX). Detection limits for the samples were Na (0.25 ng/m^3), Mg (0.1 ng/m^3), Ca (0.4 ng/m^3) and Sr (0.1 ng/m^3).

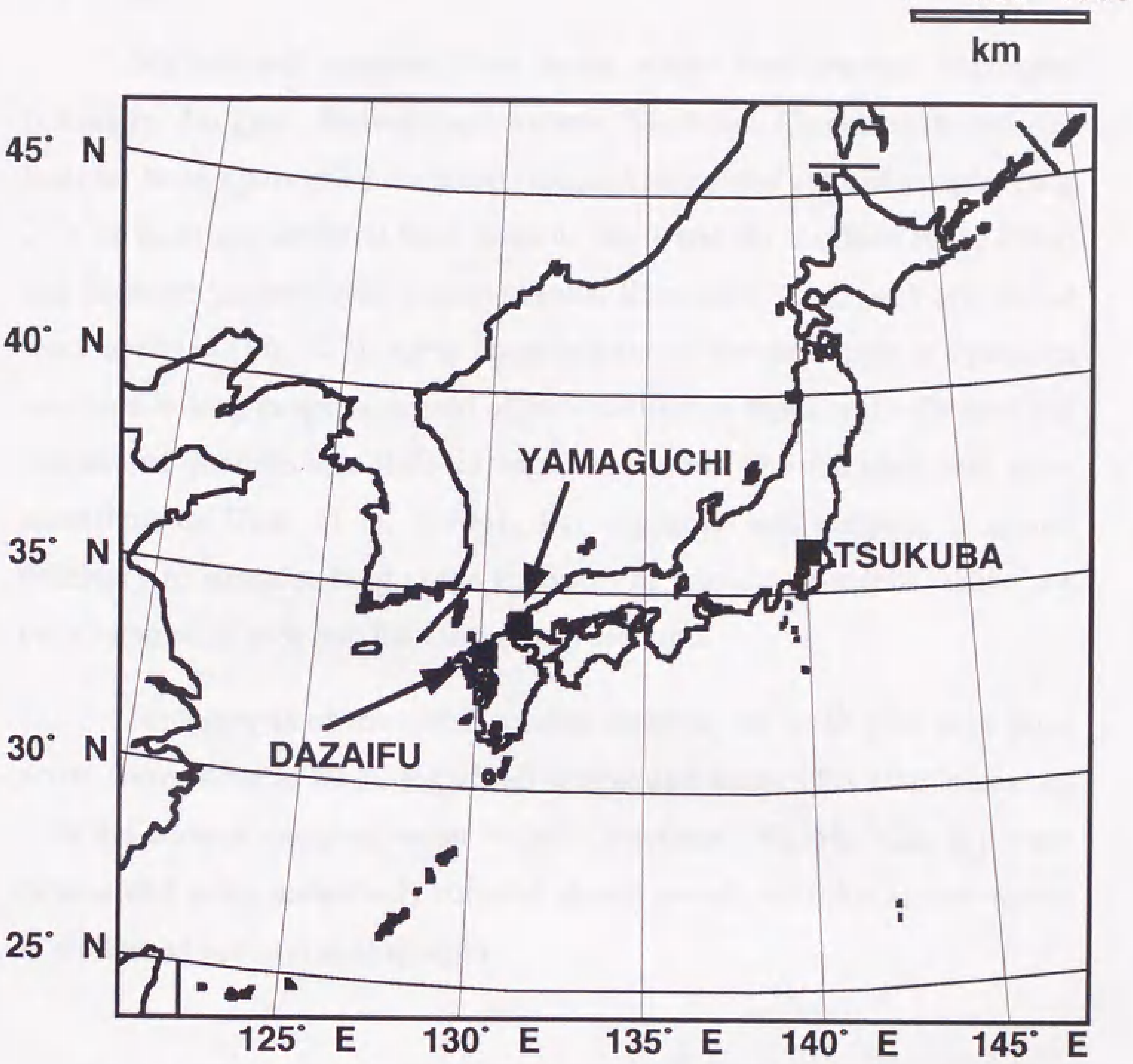

Figure 2.1 Aerosol sampling location.

2.2.2. Soil

Surface soil samples from areas where *kosa* aerosol originates (Zhangye, Tengger, Badanjilin, Lanzhou, Yinchuan; China) were obtained in order to compare their chemical compositions to the aerosol samples (Fig. 2.2). In addition, artificial *kosa* aerosols No. 1 and No. 2 (Quan et al., 1996) and Japanese surface soils from Tsukuba, Kanazawa, Nagoya, Yaku Island were obtained (Fig. 2.2). After consideration of the atmospheric dynamics involved in long range transport of *kosa* aerosol to Japan, only Chinese soil samples of particle size 0.43-11 mm were used. Classification was done according to Quan et al. (1994). For Japanese soil samples, it is not necessary to consider long range transport of particulate matter, therefore only samples of size less than 0.5 mm were used.

For analysis of the water soluble contents, 10 to 20 g of ultra pure water were added to 20-50 mg of soil sample and washed for 10 minutes. As with the aerosol samples, water soluble fractions (Na, Mg, Ca, Sr) were determined using inductively coupled plasma atomic emission spectrometry as well as an ion chromatography.

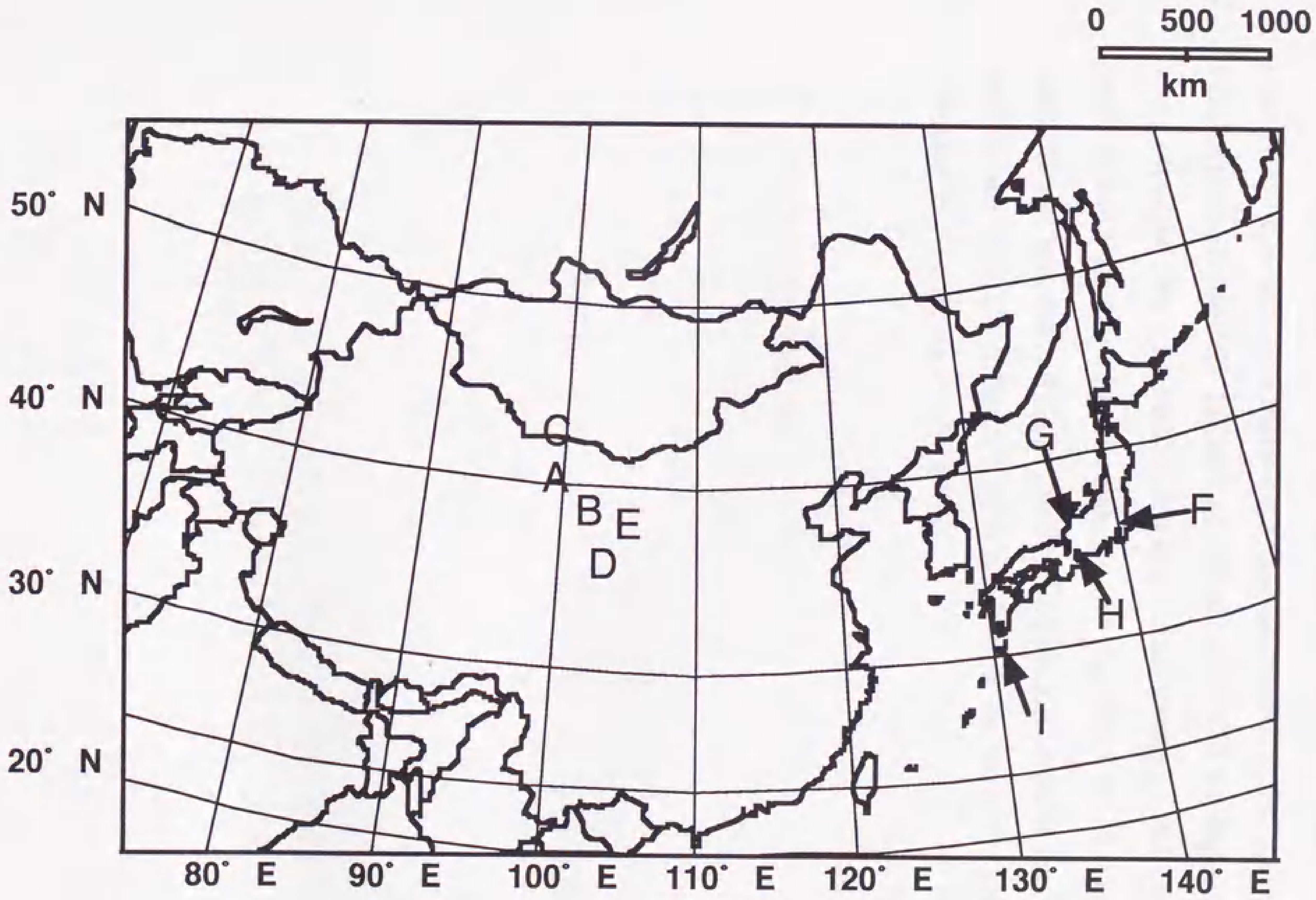

Figure 2.2 Soil sampling location: (A) Zhangye; (B) Tengger; (C) Badanjilin; (D) Lanzhou; (E) Yinchuan; (F) Tsukuba; (G) Kanazawa; (H) Nagoya; (I) Yaku Island.

2.3. Definition of *Kosa* Period and Non-*Kosa* Period Aerosols

"*Kosa* period aerosol" is defined as aerosol collected during *kosa* event was reported by a meteorological observatory. Furthermore, "non-*kosa* period aerosol" is defined as aerosol collected during no *kosa* event was reported by a meteorological observatory, and the average concentration of aerosol particulate matter measured by β-ray absorption methods was less than 50 μg/m^3, each precipitation amounts less than 10 mm because the possible influence of precipitation on aerosol's structure was indicated in Nishikawa et al. (1992).

2.4. Water Soluble Calcium and Strontium in Aerosol

Table 2.1 displays the concentration ranges of water soluble calcium (Ca^{2+}) and strontium (Sr^{2+}) in aerosol particulate matter. These data were compiled and taken from reports by Nishikawa et al. (1988) and Kanamori et al. (1991). When comparing the mean and median values of strontium during *kosa* and non-*kosa* periods, it is evident that concentrations of Ca^{2+} and Sr^{2+} during *kosa* periods are roughly 10 times that of normal periods. However, the difference is less than 10% when comparing the lowest concentrations during *kosa* periods with highest concentrations during normal periods. From this, it is possible to determine the transport of *kosa* aerosol by examining Ca^{2+} and Sr^{2+} concentrations, but only in cases where large scale *kosa* transport occurs. Small scale *kosa* aerosol transport remains difficult to predict, however.

In general, large amounts of materials of sea salt origin are contained in the water soluble constituents of atmospheric aerosol. The average concentrations of Ca^{2+} and Sr^{2+} in sea water are 412 mg/kg and 7.9 mg/kg respectively (Wilson, 1975). These are significant amounts and therefore cannot be ignored. Excluding sea salt origin Ca^{2+} and Sr^{2+}, non-sea salt calcium ($nssCa^{2+}$) and non-sea salt Sr ($nssSr^{2+}$) concentrations show clear differences between *kosa* and non-*kosa* periods (Table 2.1), though accurate prediction of small scale *kosa* aerosol transport based on changes in the concentrations of these constituents alone remains difficult as before.

Table 2.1 Concentration of water soluble component in aerosol particulate matter (ng m^{-3})

Species	Ca^{2+}	Sr^{2+}	$nssCa^{2+}$	$nssSr^{2+}$
Kosa				
Mean	3080	19.0	2960	16.7
s. d.	2220	16.3	2130	14.4
Median	2170	10.8	2090	9.2
Maximum	6330	47.0	6030	41.3
Minimum	874	3.8	847	3.4
N	11	11	11	11
Non-Kosa				
Mean	417	1.9	376	1.1
s. d.	187	0.93	183	0.83
Median	374	1.6	329	0.8
Maximum	819	3.6	776	2.8
Minimum	222	0.8	180	(0.2)
N	12	12	12	12

Non sea salt (nss) Ca^{2+} and Sr^{2+} are estimated from the following equations based on the average concentrations in sea water:

$nssCa^{2+} = Ca^{2+} - 0.0384Na^{+}$

$nssSr^{2+} = Sr^{2+} - 0.00079Na^{+}$

Fig. 2.3 shows the relationship between nssCa^{2+} concentration and nssSr^{2+} concentration contained in the aerosol samples. Lines A, B and C represent the Sr^{2+}/Ca^{2+} ratio in sea water (0.019), the average Sr^{2+}/Ca^{2+} ratio in surface soil of loess and desert regions of China (n=9, 0.0052 ± 0.0011), and the average ratio of Japanese soils in the aerosol collection area (n=4, 0.0029 ± 0.0011), respectively. A trend was recognised in that during *kosa* periods, the Sr^{2+}/Ca^{2+} ratios are more similar to the ratios of the Chinese soils whereas during non-*kosa* periods the ratios are more similar to those of Japanese soils. This means there is a strong influence of Japanese soil on the nss(Sr^{2+}/Ca^{2+}) ratio in aerosol during non-*kosa* periods but during *kosa* periods the influence of Chinese soils is more prevalent.

When the *kosa* period aerosols are divided into stronger and weaker events and the comparing Sr^{2+}/Ca^{2+} ratios, the former range from 0.0041-0.0069 and the latter range from 0.0035-0.0043. This indicates that when *kosa* period aerosol and normal period aerosol mix, the Sr^{2+}/Ca^{2+} ratio becomes significantly lower, compared to ratios of aerosol gathered only during *kosa* periods. Therefore the nss(Sr^{2+}/Ca^{2+}) ratio in aerosol is considered to be a possibly effective means of determining *kosa* transport.

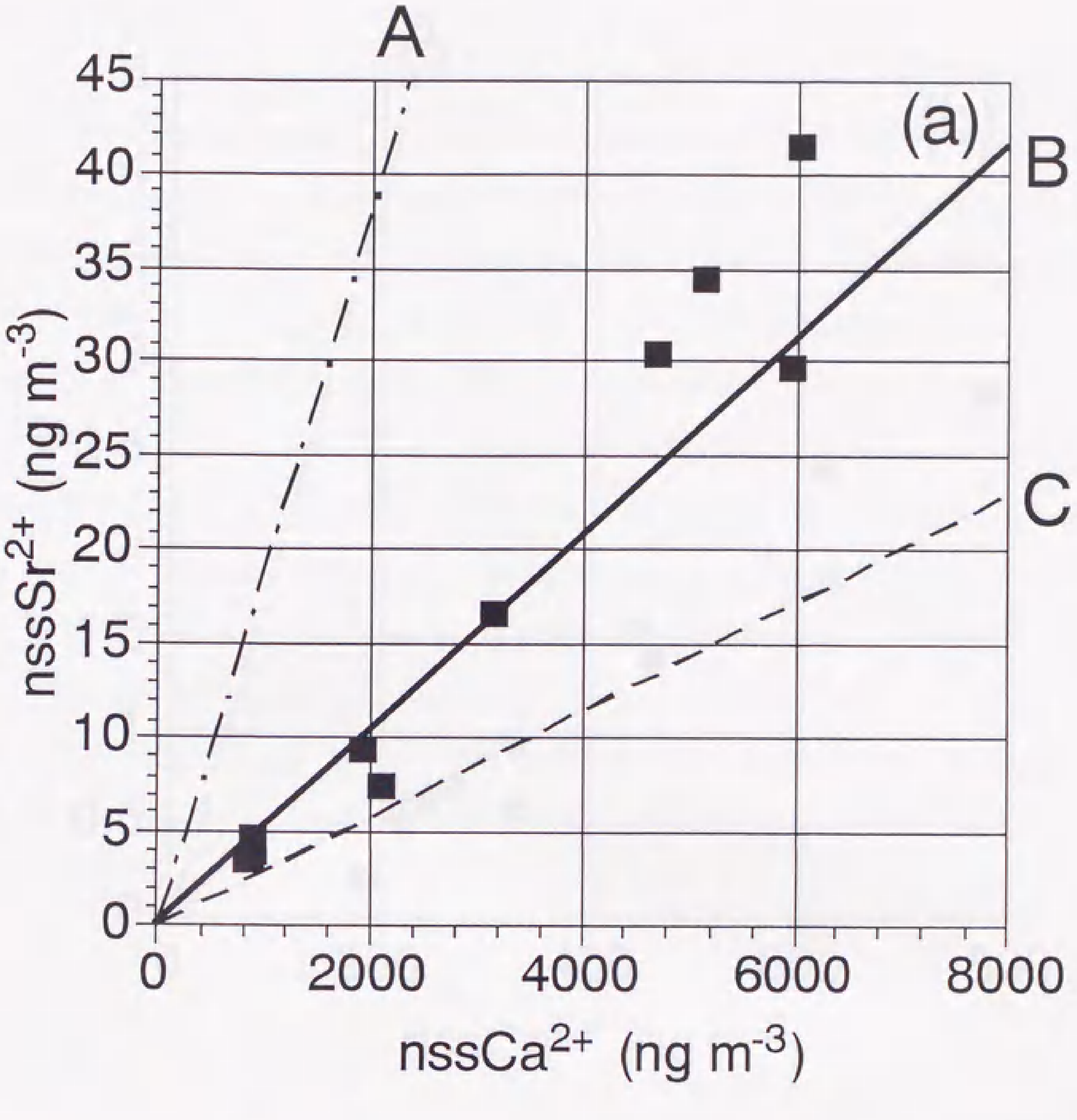

Figure 2.3 (a) The relationship between $nssSr^{2+}$ and $nssCa^{2+}$ concentrations in aerosol samples collected during *kosa* events. Lines A, B, and C represent the Sr^{2+}/Ca^{2+} ratio in sea water, average Sr^{2+}/Ca^{2+} ratio in surface soil of loess and desert regions in China, and that of Japanese soil, respectively.

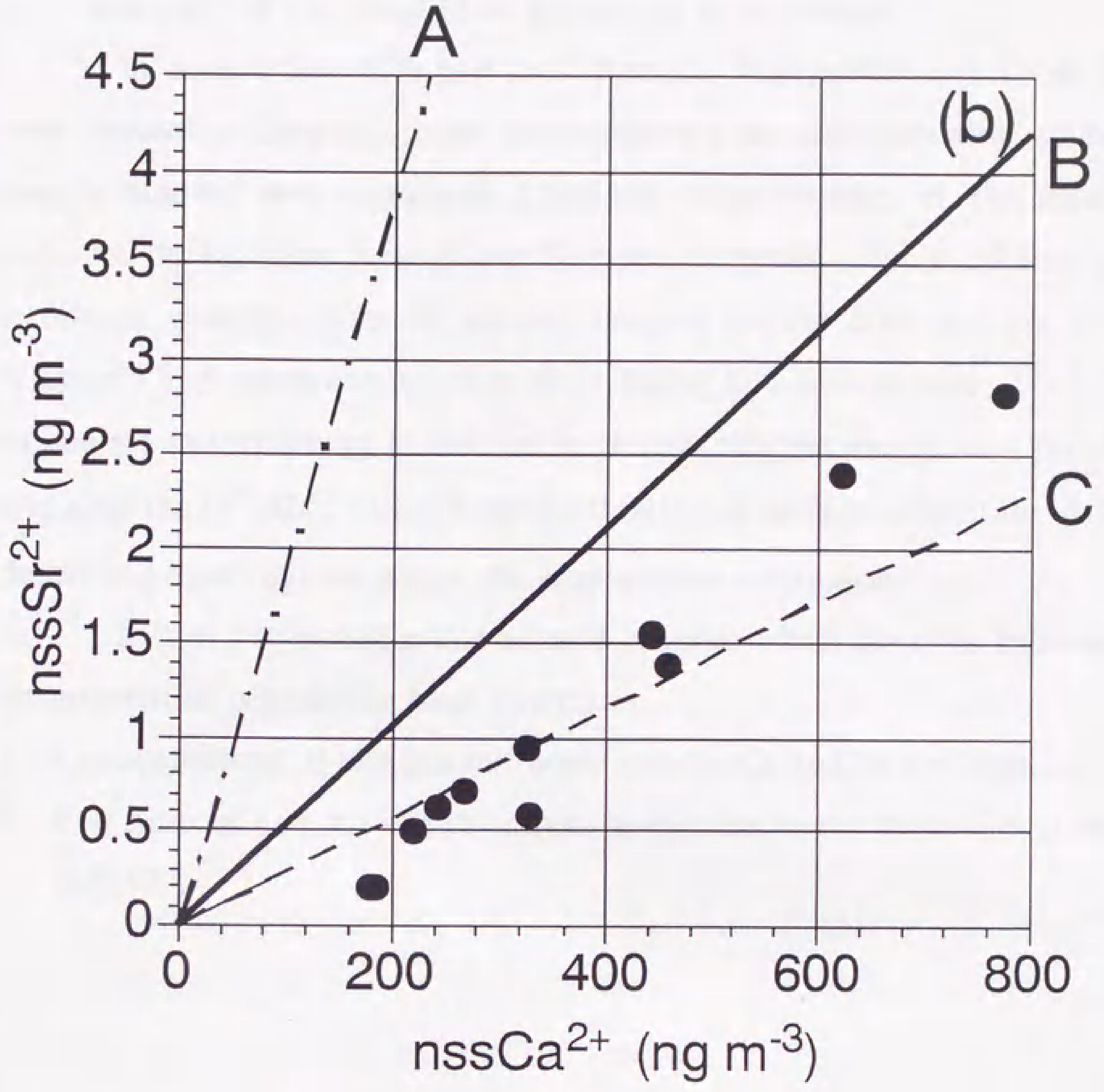

Figure 2.3 (b) The relationship between $nssSr^{2+}$ and $nssCa^{2+}$ concentrations in aerosol samples collected during no *kosa* events. Lines A, B, and C represent the Sr^{2+}/Ca^{2+} ratio in sea water, average Sr^{2+}/Ca^{2+} ratio in surface soil of loess and desert regions in China, and that of Japanese soil, respectively.

2.5. Summary of Chemical Identification of *Kosa* Aerosol

In comparison with previous chemical determination methods for *kosa* aerosol, a simpler, faster discrimination method requiring smaller sample amount was examined. Chemical characteristics of the aerosol collected during *kosa* periods are: Non sea salt water soluble calcium and strontium concentrations in aerosol samples during *kosa* periods were relatively high when compared to those during non-*kosa* periods; The ratio of non sea salt strontium to calcium in aerosol samples during *kosa* periods was near the Sr^{2+}/Ca^{2+} ratio (0.0052 ± 0.0011) of surface soils in the Asian desert and loess regions where the *kosa* aerosol originates.

It is highly possible that aerosol samples which have the following characteristics contain the *kosa* aerosol.

1. Concentrations of non sea salt water soluble Ca and Sr are high.
2. The ratio of non sea salt strontium to calcium in the aerosol is around 0.0052.

3. *Kosa* aerosol in the Free Troposphere

3.1. Necessity of Investigation of the *Kosa* Aerosol in the Free Troposphere

A large amount of *kosa* aerosol is transported and deposited over East Asia and the North Pacific. The *kosa* aerosol deposited on lands and /or oceans in this region impacts the geochemical cycle of terrestrial material, and the ecosystem. The *kosa* aerosol in the free troposphere (during transport) also impacts tropospheric chemistry and climate forcing. Reaction of *kosa* aerosol with other atmospheric substances may change the magnitude of those impacts, because physical and chemical characteristics of the free tropospheric aerosol will change. However, observation of aerosols during transport is not enough to evaluate these reactions, because of the lack of information on chemical characteristics.

In this chapter, I will discuss the physical and chemical characteristics of the free tropospheric aerosol over the Japan Sea coast, and discuss the possibility of chemical modification of *kosa* aerosol.

3.2. Sampling and Analysis

3.2.1. Aircraft Measurements

Aircraft measurements were conducted between 1991 and 1994 over the Japan Sea coast, Wakasa Bay (35.5°N, 135°-136°E) and Goto Islands (33°-34°N, 128°-130°E) (Fig. 3.1), at altitudes of 2 and 4 km using a sampler mounted on aircraft (Cessna 402 and 404) (Table 3.1). The altitude 4 km is in the free troposphere, while 2 km is sometimes within and above the boundary layer. Westerly winds prevail over east Asia, except in summer. Results of back trajectory analysis revealed that the sampled air masses had possibly passed over the Asian content, except the air mass on 29 July 1994 (Fig. 3.2). There is no strong anthropogenic aerosol source near the observational areas.

3.2.2. Analysis

The air was introduced into the aircraft cabin through an isokinetic decelerator, then passed to an optical particle counter (OPC), aerosol sampler and so on (Fig. 3.3).

3.2.2.1. Measurements of Number Concentration with Optical Particle Counter

An optical particle counter (DAN Sangyo Co., Model PM-730) with a halogen lamp and a phototube detector of light scatter by particles was mounted on the aircraft to measure a number size distribution covering fine to coarse particle size. A sizing of the particles was made at 0.3, 0.4, 0.5, 0.6, 0.8, 1.0, 1.2, 1.5, 2.0, 3.0, 4.0, 5.0 6.0. 8.0 and 10 μm diameter. The calibration of the counter was done according to Japanese Industrial Standard (JIS-Z-8813) instructions as decided by the Japan Ministry of International Trade and Industry.

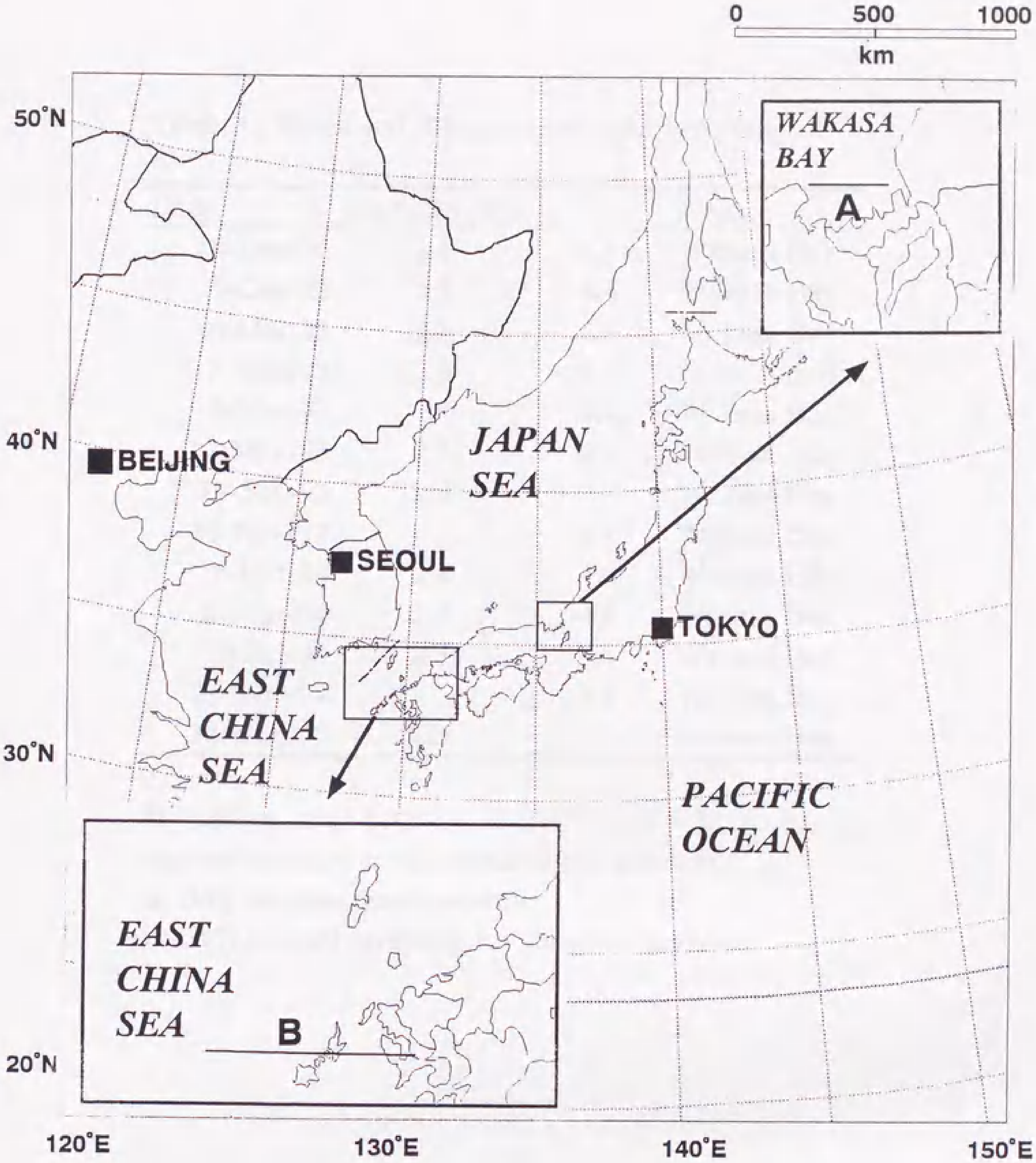

Figure 3.1 Aerosol sampling locations and typical flight tracks: (A) Wakasa Bay; (B) Goto Islands.

Table 3.1 Dates and altitudes of aerosol sampling

Date	Altitudes (km)		Place
4-Dec-92	2.1	4.4	Wakasa Bay
5-Dec-92	2.3 [a]	4.4	Wakasa Bay
6-Mar-93	2.3	4.4	Wakasa Bay
8-Mar-93	2.3	4.4	Goto Islands
9-Mar-93		4.4	Wakasa Bay
12-May-93	2.3	4.4	Wakasa Bay
19-Sep-93	2.3		Wakasa Bay
10-Nov-93		4.4 [b]	Wakasa Bay
6-Feb-94	2.4	4.4	Wakasa Bay
26-Apr-94	2.3	4.4	Wakasa Bay
29-Jul-94	2.3	4.4	Wakasa Bay
21-Nov-94		4.6	Wakasa Bay
24-Nov-94	2.3		Wakasa Bay

It was fine in all days.
Aerosol collection was conducted in daytime.
a: Only number concentration
b: Only aerosol sampling for chemical analysis.

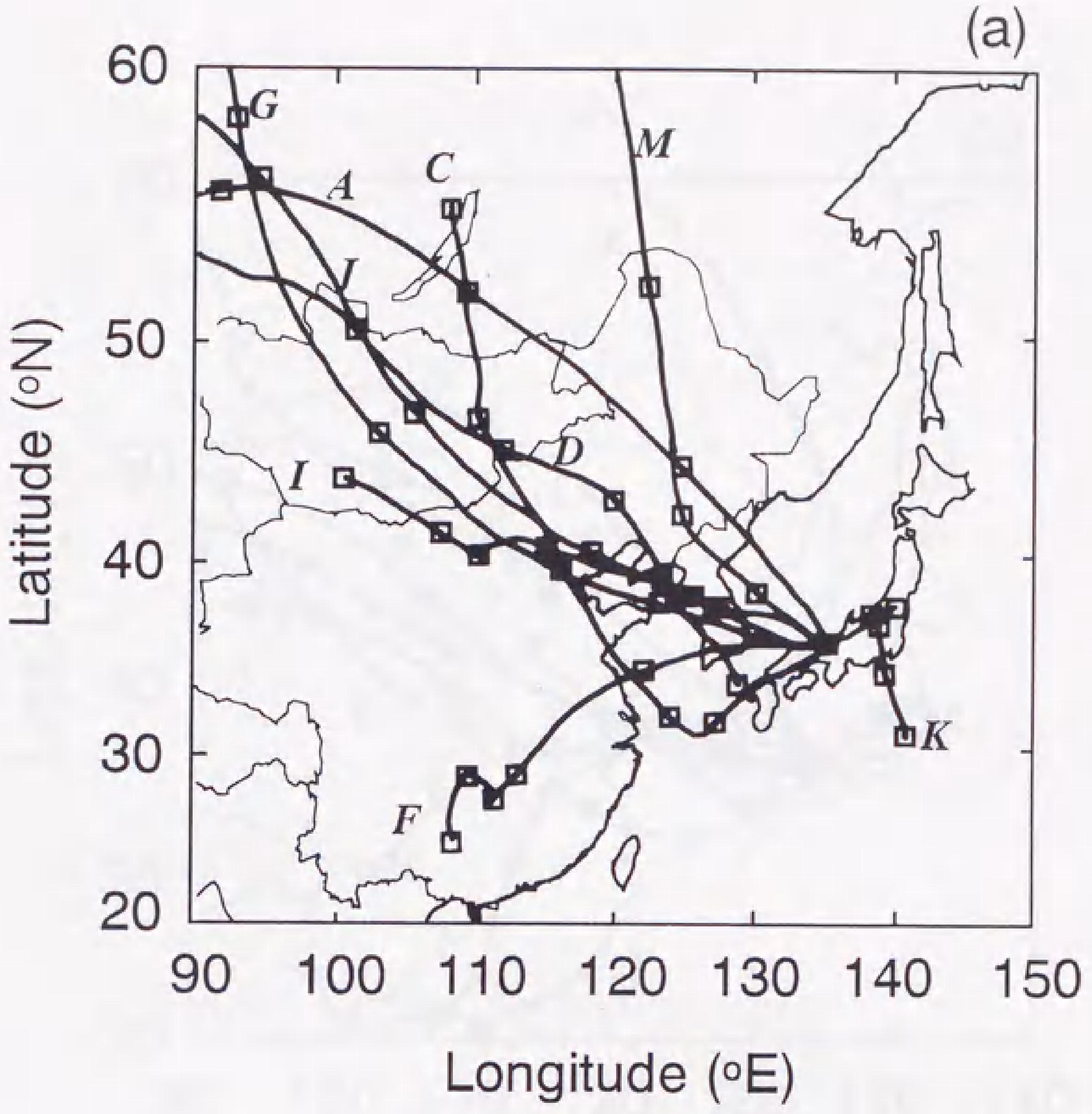

Figure 3.2 (a) Isentropic back trajectory analysis starting from Wakasa Bay (35.5°N, 135.5°E) and Goto Islands (33.5°N, 129.0°E) at noon LT on 4 Dec. 1992 (A), 6 Mar. 1993 (C), 8 Mar. 1993 (D), 12 May 1993 (F), 19 Sep. 1993 (G), 6 Feb. 1994 (I), 26 Apr. 1994 (J), 29 Jul. 1994 (K), and 24 Nov. 1994 (M) at 2 km. Time intervals of 1 day are indicated by solid squares.

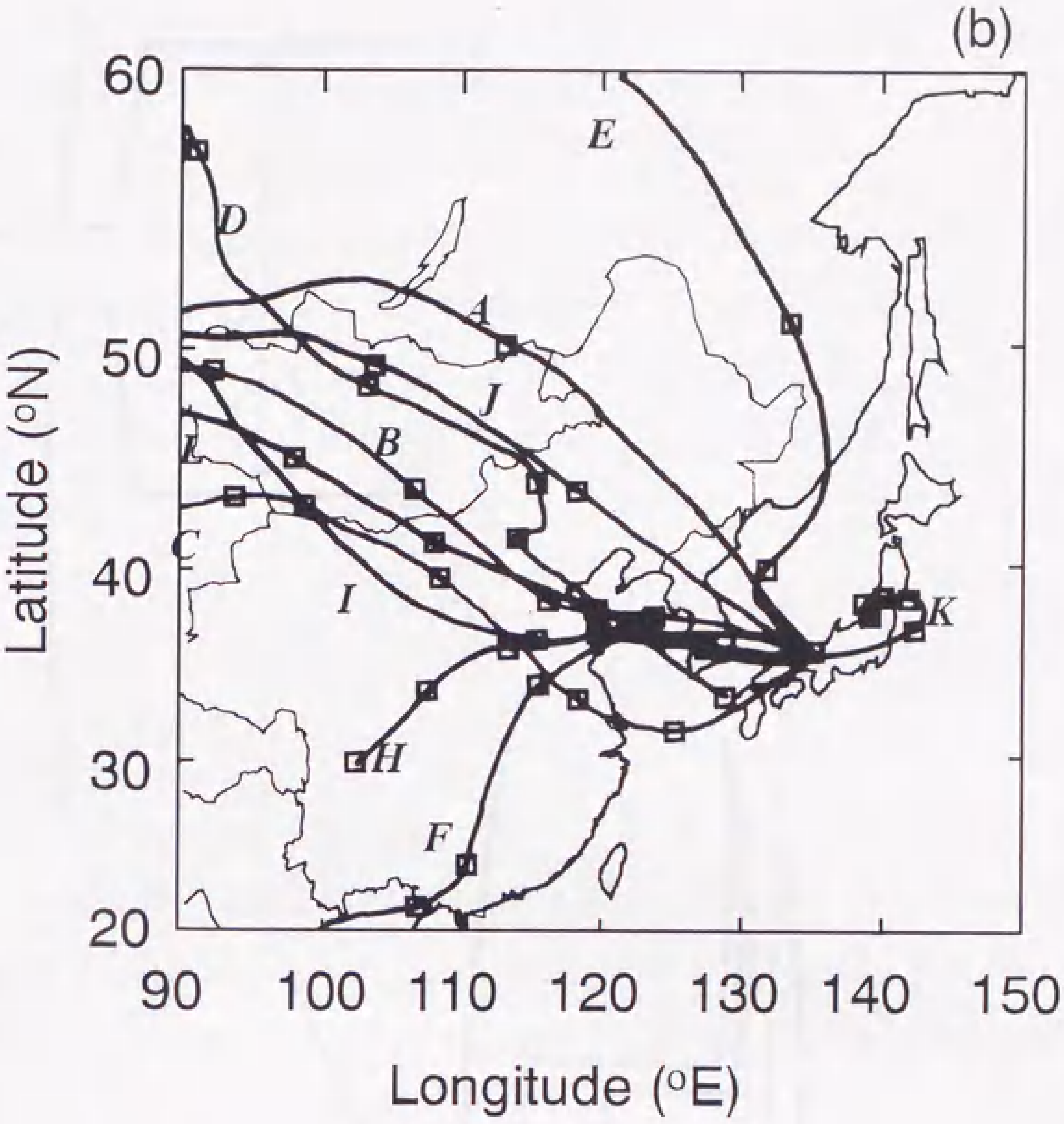

Figure 3.2 (b) Isentropic back trajectory analysis starting from Wakasa Bay (35.5°N, 135.5°E) and Goto Islands (33.5°N, 129.0°E) at noon LT on 4 Dec. 1992 (A), 5 Dec. 1992 (B), 6 Mar. 1993 (C), 8 Mar. 1993 (D), 9 Mar. 1993 (E), 12 May 1993 (F), 10 Nov. 1993 (H), 6 Feb. 1994 (I), 26 Apr. 1994 (J), 29 Jul. 1994 (K), and 21 Nov. 1994 (L) at 4 km. Time intervals of 1 day are indicated by solid squares.

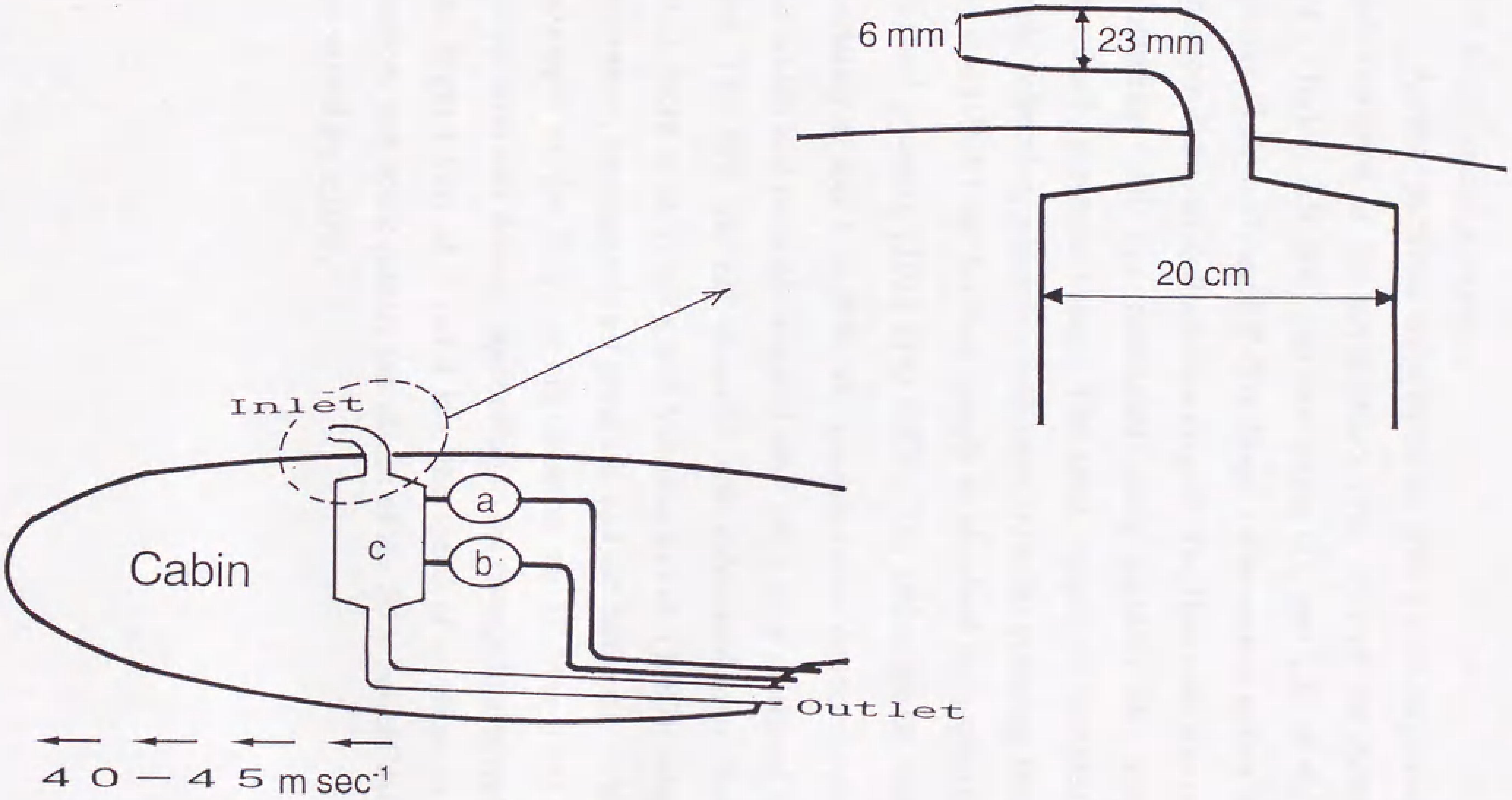

Figure 3.3 Schematic picture of the atmospheric aerosol sampling system used on the aircraft. The air was introduced from the inlet into instruments (a, b; cascade impactor and other instruments) through the isokinetic decelerator (c).

3.2.2.2. Chemical Analysis

Aerosol particles were collected with a nine stage cascade impactor which consisted of the seven stages (No. 1-7) of the Andersen sampler (Tokyo Dylec; AN-200) and two stages (L1 and L2) of the low pressure impactor (Tokyo Dylec; LP-20). Stage 1 was used to define the upper limit of particle diameter collected on stage 2. The flow rate was monitored with a rotameter and was calibrated using ambient air temperature and atmospheric pressure values. The total volume of sampled air for each sample collection, which was estimated from the sampling time and the flow rate, was 0.9-2.1 m^3 for one sample at standard atmospheric temperature (0℃) and pressure (1013 hPa) (STP). The estimated air volumes have an uncertainty of about ±10%. The particles were collected on a polyethylene sheet which had been pre-cleaned with ultra pure methanol and ultra pure water. The 50% cut off diameter was calculated after Ranz and Wong (1952), Stern et al. (1962), and Yoshihara et al. (1985), using ambient air temperature, atmospheric air pressure, and the flow rate. Table 3.2 presents an example of the 50% cut off diameter on 12 May 1993 for spherical particles with unit density. According to the change in atmospheric pressure at the flight levels of 2 and 4 km, the speed of air flow at the inlet was disturbed, and consequently the values of the 50% cut-off diameter in each stage varied by ±10%.

Table 3.2 Sampling parameters and 50% cut off diameters, 12 May 1993.

Altitude (km)	2.3	4.4
Flow rate (l min^{-1} STP)	17.6	14.8
Sampling time (min)	96	124
Air volume (m^3 STP)	1.7	1.8
Stage #	50% cut off diameter (μm)	
1	7.7	7.5
2	5.1	4.9
3	3.5	3.3
4	2.1	2.0
5	1.2	1.1
6	0.65	0.61
7	0.44	0.40
L1	0.26	0.23
L2	0.14	0.14

The water soluble components in the particulate matter were extracted ultrasonically within 10 minutes with 15 g of ultra pure water in a PTFE case. To the extent possible, sample manipulation in the laboratory was conducted in a clean booth (class 1000). The concentrations of selected chemical species in the extracts were measured immediately after extraction using ion chromatography (IC; Dionex/DX-300). The separation columns were AS-11 for the anion analysis (F^-, CH_3COO^-, $HCOO^-$, $CH_3SO_3^-$, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, PO_4^{3-}) and CS-12 for the cation analysis (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). A NaOH solution (0.5-28 mM) at a flow rate of 2.0 ml min^{-1} was used for the anion analysis and a CH_3SO_3H solution (20 mM) at a flow rate of 1.0 ml min^{-1} was used for the cation analysis. Stock standard solutions (1000 mg l^{-1}) of organic acid were prepared from high purity sodium salts (analytical grade; Wako, Japan). Commercial standard ion solutions (1000 mg l^{-1}; Wako, Japan) were used for inorganic anion and cation. A series of working standard solutions in which the concentration of each ionic species was 0.5-100 ppb were prepared from commercial standard solutions and stock standard solutions. Quantitative analysis was carried out by the calibration curve method with 95% precision which was determined by replicate measurements on working standard solutions .

The extracts of samples collected on 26 April 1994 were also analysed for water soluble strontium with an inductively-coupled argon plasma source mass spectrometer (ICP-MS; Hewlett Packard/HP-4500). Two working standard solutions (1 and 10 ppb) for ICP-MS were prepared from commercial mixed-standard solutions (SPEX, USA). The ICP-MS analysis was performed under the following conditions: ^{86}Sr and ^{88}Sr (measured m/z), 3 channels/(m/z) (number of channel), 0.5 sec/channel (dwell time), 5 times (replicate), 16 sec/sample (total run time). Water soluble Sr concentration in the aerosol particulate matter was calculated from the ^{88}Sr value, which was then compared with the ^{86}Sr value in each sample for analytical quality control.

The chemical blanks were treated in the same manner as the collected samples. Using three times the standard deviation of the blank values, the detection limits for particulate phase species were (in neq m^{-3} at STP): 0.2 (F^-), 0.4 (CH_3COO^-), 0.3 ($HCOO^-$), 0.1 ($CH_3SO_3^-$), 0.9 (Cl^-), 0.2 (NO_2^-), 0.1 (Br^-), 0.3 (NO_3^-), 0.5 (SO_4^{2-}), 0.1 ($C_2O_4^{2-}$), 1.0 (PO_4^{3-}), 1.6 (Na^+), 0.2 (NH_4^+), 0.5 (K^+), 0.1 (Mg^{2+}), 0.4 (Ca^{2+}), 0.0012 (Sr^{2+}) in an average air volume of 1.8 m^3 STP. Sample values were obtained by subtracting the mean ion concentrations of the blanks from those of the samples. Their overall uncertainties for concentration of particulate phase species were about 15-20%, mainly due to the calibration of air volume. Number concentration

3.3. Number Concentration

Table 3.3 summarises number concentrations of the aerosol collected over the Japan Sea coast (Wakasa Bay and Goto Islands) at 2 km and 4 km on the basis of the results of an optical particle counter mounted in an aircraft. The concentration range of each altitude extended over 1 order of magnitude. The concentration range at 4 km was similar to that measured over the northwestern Pacific (0°-34°N) at the altitude 4.5 km in March (Ikegami et al., 1993).

Table 3.3 Number concentration of aerosol over the Japan Sea coast.

Altitude (km)	2	4
Median (m^{-3})	1.0×10^7	4.0×10^6
n	10	10
Minimum (m^{-3})	1.2×10^6	5.3×10^5
Maximum (m^{-3})	1.3×10^8	1.3×10^7

3.4. Number Size Distribution

The number-size distributions of aerosols measured over the Japan Sea coast (Wakasa Bay and Goto Islands) at 2 km and 4 km are presented in Fig. 3.4. Most of the curves in Fig. 3.4 show small peaks around 1.0 μm diameter at both altitudes. Kristament et al., (1993) and Lechner et al. (1989) observed the number size distribution patterns of the free atmospheric aerosols around New Zealand and over the south west Pacific. A comparison of the present results with those shows the number concentration, dN/dlogD (D: diameter), in the diameter range of 0.7-2.0 μm over Japan in spring is 10-100 times of the marine atmospheric particles. Ikegami et al. (1993) described that Asian dust-storm particles contributed to high concentrations of particles with radii $\geq 1\ \mu$m at the altitude 4.5 km over mid-latitude northwester Pacific. The density peak of coarse size particles in the surface atmosphere is considered to be due to soil and /or sea salt particles which are directly injected into the atmosphere from the local ground sources (e.g., Gillette and Hanson, 1989; Patterson et al., 1976; Twomey, 1976). It is difficult, however, to clear what caused the high concentration of coarse size particles only from a results of number size distribution of aerosols.

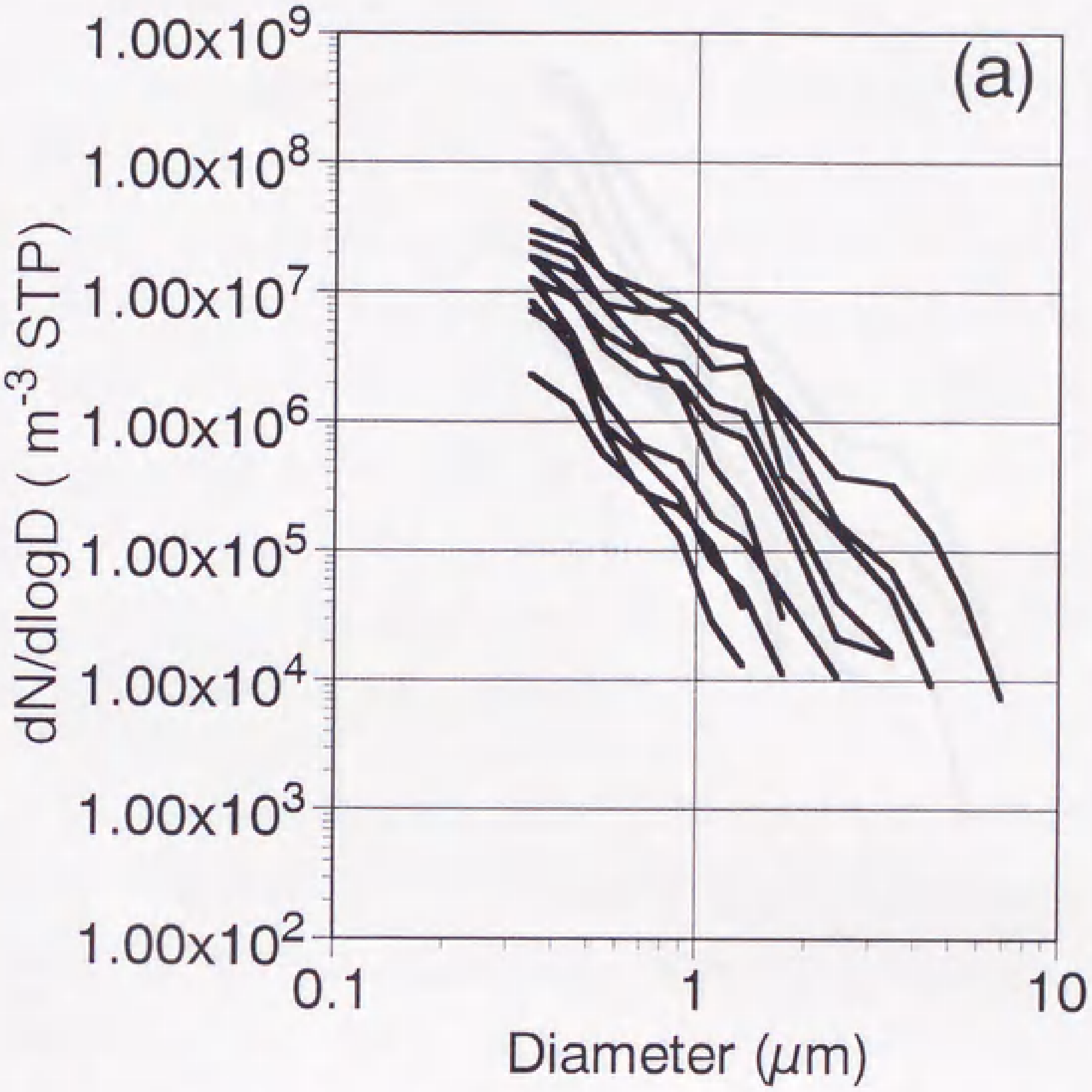

Figure 3.4 (a) Number size distribution of aerosols over the Japan Sea coast at altitude 4 km.

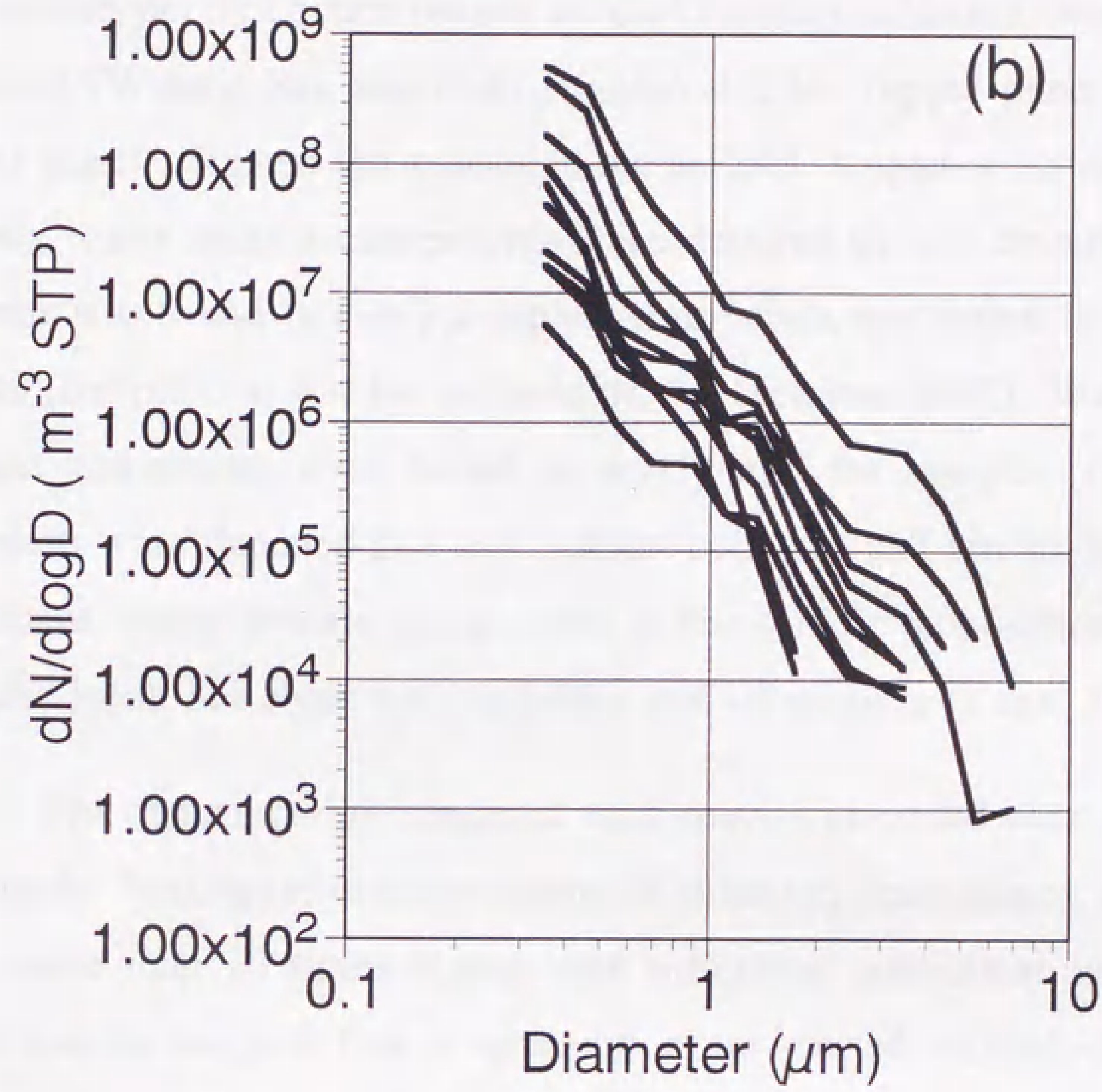

Figure 3.4 (b) Number size distribution of aerosols over the Japan Sea coast at altitude 2 km.

3.5. Concentration of Water Soluble Components

Table 3.4 summarises total concentrations of water soluble components derived from twenty aerosol samples collected over the Japan Sea coast (Wakasa Bay and Goto Islands) at 2 km (upper panel) and 4 km (lower panel). Sixteen ion species in the aerosol samples were analysed and only six water soluble components were detected by ion chromatography. Sulphate was found in every sample. Ammonium was found in all but one sample (collected at 4.4 km altitude on 5 December 1992). Water soluble calcium and nitrate were found in nearly half the samples. Oxalate and potassium were detected in a few samples collected at 2 km but not at 4 km. The major water soluble components in the middle tropospheric aerosols over the Japan Sea coast were sulphate and ammonium (Table 3.4).

The concentration range of each species extended over 1 order of magnitude. Maximum concentrations of sulphate, ammonium, and nitrate were more than 10 times higher than minimum concentrations at 2 km. Those results suggest that a sporadic event caused mixing of the free tropospheric atmosphere (low aerosol concentration) with air mass from the boundary layer (high aerosol concentration).

Table 3.4 Concentration range of water-soluble components in aerosol particulate matter collected over the Japan Sea coast.

	NO_3^-	SO_4^{2-}	$C_2O_4^{2-}$	NH_4^+	K^+	Ca^{2+}
2 km (n=9)						
Median (neq m^{-3} STP)	0.60	25.7	B.D.	22.8	B.D.	1.4
Range (neq m^{-3} STP)	B.D.-23.5	4.1-96.2	B.D.-1.7	3.3-92.8	B.D.-7.2	B.D.-22.0
Detection Rate (%)	89	100	22	100	33	67
4 km (n=11)						
Median (neq m^{-3} STP)	B.D.	5.4	B.D.	4.2	B.D.	B.D.
Range (neq m^{-3} STP)	B.D.-2.0	2.0-9.6	B.D.	B.D.-8.2	B.D.	B.D.-16.7
Detection Rate (%)	45	100	0	91	0	45

"B.D." represents value below detection limit.

Concentrations of F^-, CH_3COO^-, $HCOO^-$, $CH_3SO_3^-$, Cl^-, NO_2^-, Br^-, PO_4^{3-}, Na^+, and Mg^{2+} were below the ion chromatography detection limit in all samples.

3.6. Size Distribution of Water Soluble Components

Fig. 3.5 shows examples of size distributions of water soluble components in aerosol particulate matter collected over the Japan Sea coast. Most size distributions peaked in stage 7 (Fig. 3.5 a and c) or stage 5 (Fig. 3.5 d); some of their distributions had two peaks, one at stage 7 and the other at stage 5, with a local minimum at stage 6 (Fig. 3.5 b). On the basis of these characteristics of the size distributions, we defined particles collected on stages 6-L2 (aerodynamic diameter; $D \leq$ ca. 1 μm) as "fine" particles, and particles collected on stages 2-5 ($D \geq$ ca. 1 μm) as "coarse" particles.

Most of the sulphate was present in fine particles (Fig. 3.5 a). However, sulphate in the particulate matter collected at about 4 km on 6 March 1993 and 6 February 1994, and at 2.3 km on 26 April 1994, had distributions with two peaks, one corresponding to fine particles and the other to coarse particles. All the ammonium data corresponded to peaks in the fine particles (Fig. 3.5 c). Nitrate concentrations peaked in the coarse particles, except for samples collected at 2.3 km on 12 May 1993 and 26 April 1994 when concentration peaks were found in both the fine and coarse particles (Fig. 3.5 b). The distribution of water soluble calcium in the particulate matter peaked in the coarse size range (Fig. 3.5 d). Oxalate and potassium were found in the fine particle range (Fig. 3.5 e and f).

The size distribution pattern of nitrate in the fine size range and sulphate showed good correspondence with that of ammonium (Fig. 3.5 a, b, and c). It is reasonable to consider that nitrate in the fine size range and sulphate were present as ammonium salts as suggested in Appel et al. (1978).

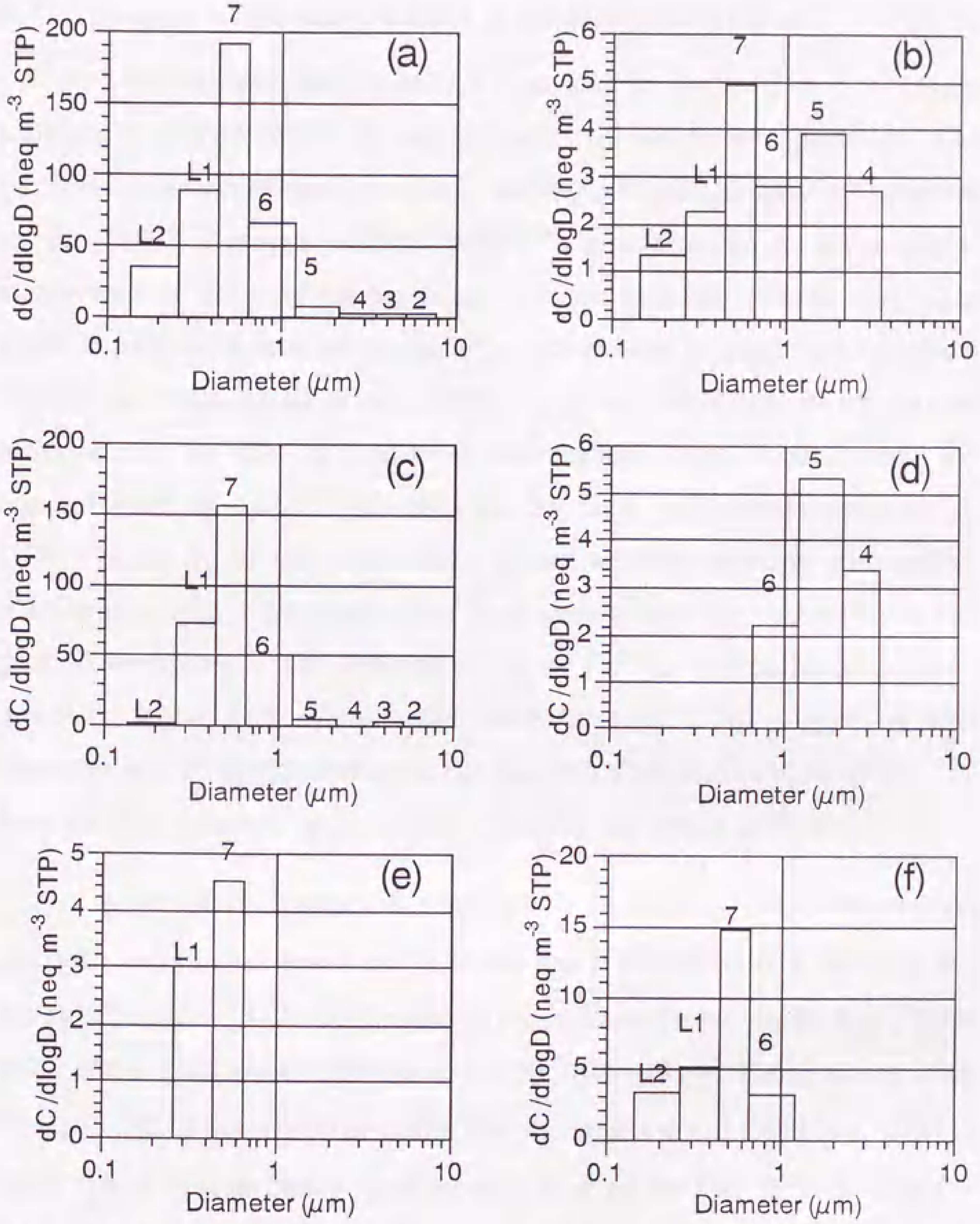

Figure 3.5 Size distributions of water soluble components of aerosol particulate matter collected at 2.3 km on 12 May 1993: (a) sulphate; (b) nitrate; (c) ammonium; (d) water-soluble calcium; (e) oxalate; (f) water-soluble potassium. Values below the detection limits are not included. The numbers in the figure represent the stage number of the cascade impactor. The figures are made after Roesler et al. (1965), Kadowaki (1974) and Wall et al. (1988).

3.7. Transport of the *Kosa* Aerosol in the Free Troposphere

The size distribution of Ca^{2+} peaked in the coarse size range. Calcium is considered to be a component of sea-derived particles. The particulate Ca^{2+}, however, was likely non-sea salt calcium ($nssCa^{2+}$) (Savoie et al., 1987), because sodium, which is also thought to be a major component of sea-derived particles, was not detected (Table 3.4). One possible process of increase in $nssCa^{2+}$ concentration is long range transport of *kosa* aerosols. Mori et al. (1996) suggested, on the basis of aerosol observations in the ground-level atmosphere over Japan, that the concentration of $nssCa^{2+}$ increases during *kosa* episodes. Iwasaka et al. (1988) pointed out that weak *kosa* layers were detected in the middle troposphere with lidar even when *kosa* events were not observed in the ground atmosphere. The concentrations of Ca^{2+} in tropospheric aerosols increased when dust events were observed (Fig. 3.6), suggesting that increases in Ca^{2+} concentration in the aerosols were due to the transport of *kosa* aerosols originating from dust events on the Asian continent.

A (Sr^{2+}/Ca^{2+}) ratio was reported to be a useful indicator of *kosa* aerosol and that of desert soil in China was 0.0052±0.0011 (Mori et al., 1996). The mean (Sr^{2+}/ Ca^{2+}) ratios for samples collected on 26 April 1994 at 2.3 and 4.4 km were 0.0046 and 0.0050, respectively. Those values were closer to that of desert soil in China than the Japanese soil (0.0029±0.0011) value. These results clearly indicate that most of the Ca^{2+} in these samples originated from *kosa* aerosols.

High number concentrations of the coarse size particles were observed over the Japan Sea coast. It was likely not due to sea salt but *kosa* aerosol.

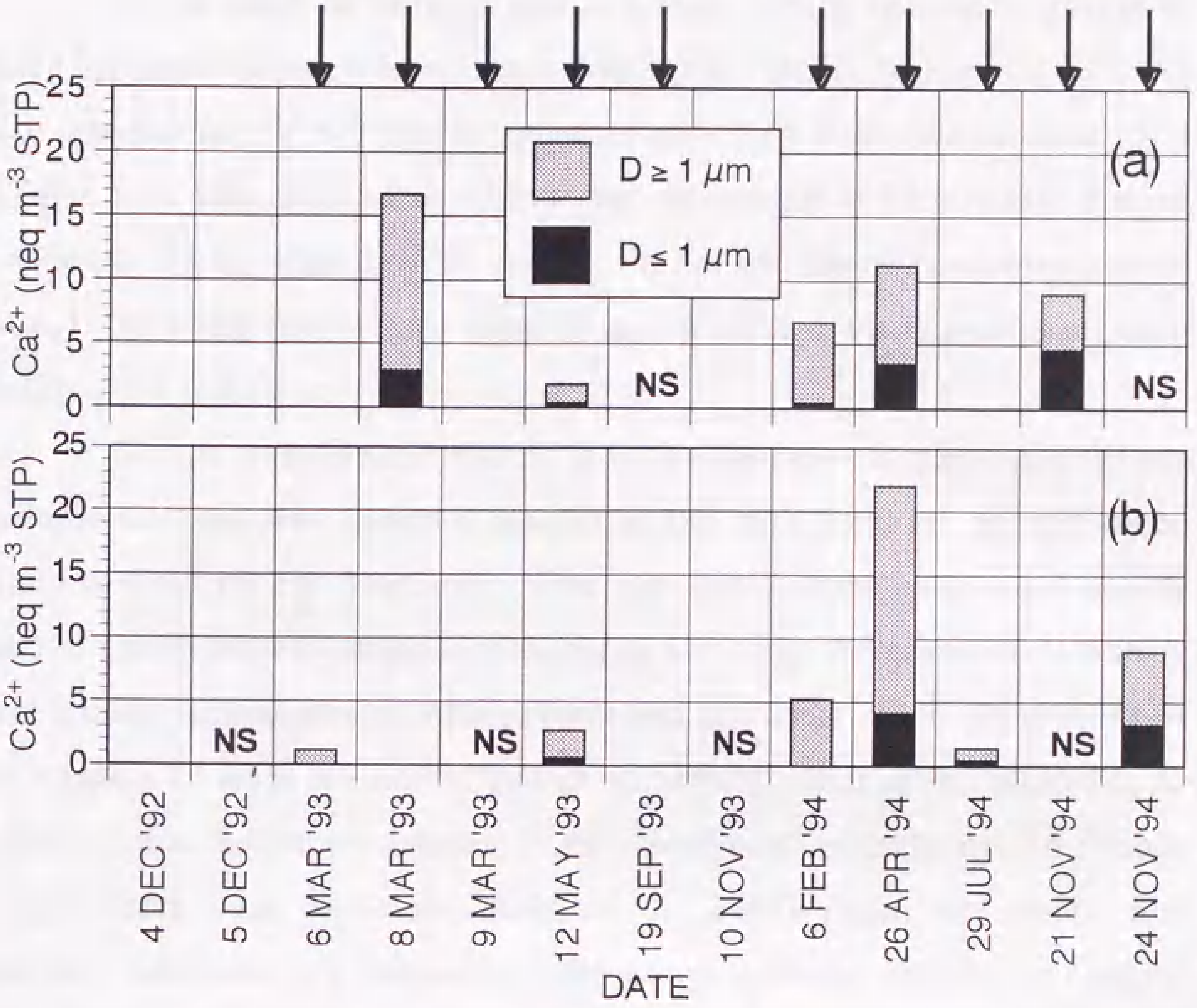

Figure 3.6 Concentration of water soluble calcium in aerosol particulate matter at 4 (a) and 2 (b) km altitude. The solid bars represent concentrations of ions in the fine size range aerosol; hatched bars represent concentration of ions in the coarse size range aerosol. Values below the detection limits are not included. "NS" represents no sample. Arrows represent dust events reported over the Asian continent during the 5 days before each sampling date or *kosa* events reported in Japan within 24 hours of sampling time.

3.8. Characteristics of Aerosol in the Free Troposphere When *Kosa* Aerosol Is Transported

We divided the samples into two cases because the concentration of Ca^{2+} increases during *kosa* episodes (Mori et al., 1996). In one case Ca^{2+} was not detected (case "A") and in the other case Ca^{2+} was detected (case "B") (Table 3.5). Fine particulate sulphate and ammonium at 2 km in case B were obviously higher than those in case A. Particulate nitrate concentrations in case B were also higher than those in case A, though median concentration ratios were not clear.

Nitrate was detected mainly in the coarse particle size range. Water soluble Ca was also detected mainly in the coarse range, though other cations were barely detectable. The size distribution pattern of nitrate showed good correspondence with that of Ca^{2+} (Fig. 3.5 b and d). Nitrate is not a major component of Asian desert soil and loess which are thought to be origins of *kosa* aerosol (Quan et al., 1994). Thus it is reasonable to consider that the nitrate detected in the coarse particle range has a different origin from *kosa* particles. Zhang et al. (1994) found that Asian dust particle surfaces are important site of particulate nitrate formation. Dentener et al. (1996) pointed out from results of a global three-dimensional model of the troposphere that an even larger fraction of gas phase nitric acid might be associated with and neutralised by mineral aerosol. Wu and Okada (1994) found that dust storm particles had nitrate on their surface on the basis of electric microscopic observation of the particles collected in the ground-level atmosphere during a *kosa* episode. Our results suggest the nitrate was formed on *kosa* particles in the free troposphere.

Table 3.5 Median concentrations of water-soluble aerosol chemical species (neq m^{-3} STP)

Ca^{2+}	Kosa	Sulphate		Ammonium		Nitrate	
	Event	Fine	Coarse	Fine	Coarse	Fine	Coarse
2 km							
Not Detected (n=3) [A]	No	7.0 (3)	2.7 (3)	8.1 (3)	2.0 (2)	B.D. (1)	0.3 (3)
Detected (n=6) [B]	Yes	52.9 (6)	3.5 (6)	36.4 (6)	2.3 (6)	0.3 (4)	0.8 (5)
B/A*		7.6	1.3	4.5	1.2	-	2.6
4 km							
Not Detected (n=6) [A]	No	3.2 (6)	B. D. (2)	1.9 (5)	0.6 (3)	B.D. (0)	B.D. (1)
Detected (n=5) [B]	Yes	4.6 (5)	1.5 (4)	4.1 (5)	0.8 (3)	0.3 (3)	0.8 (4)
B/A*		1.4	-	2.2	1.3	-	-

Number in brackets represents the number of samples in which each species was detected.
"B.D." represents values below detection limit.
"-" represents no data.
"B/A" represents median concentration ratio of each species in case B (Ca^{2+} was detected) to case A (Ca^{2+} was not detected).

Fine particulate sulphate and ammonium at 2 km in case B were obviously higher than those in case A (Table 3.5). The size distribution pattern of sulphate showed good correspondence with that of ammonium (Fig. 3.5 a and c). Sulphate were likely present as ammonium salt, such as ammonium sulphate, as suggested in Appel et al. (1978). It is suggested external mixing of *kosa* aerosol and other types of aerosols (e.g., ammonium sulphate) during long-range transport of air masses containing *kosa* particles. Coagulation of *kosa* aerosols and other types of aerosols, in addition to gases up take on *kosa* particle surface, might be a process causing chemical transformation of *kosa* aerosols during long-range transport.

3.9. Summary of *Kosa* Aerosol Measurements in the Free Troposphere

Aircraft-borne measurements of atmospheric aerosols were made in the free troposphere (2 and 4 km heights) over the Japan Sea coast between 1992 and 1994, and the following results were obtained.

1. High number concentrations of coarse size particles were observed in the free troposphere.
2. Sulphate and ammonium were detected in nearly all samples and were the major water soluble components in aerosol particulate matter over the Japan Sea coast. Nitrate and water soluble Ca were detected in nearly half of the samples. Other water soluble components were barely detectable.
3. The concentrations of Ca^{2+} in tropospheric aerosols increased when dust events were observed.
4. The mean (Sr^{2+}/ Ca^{2+}) ratios for samples collected at 2 and 4 km were closer to that of desert soil in China than the Japanese soil value.
5. The concentrations of nitrate in coarse particles at 2 and 4 km were higher in samples in which Ca^{2+} was detected than in those in which it was not. The size distribution pattern of nitrate showed good correspondence with that of Ca^{2+}.
6. Concentrations of sulphate and ammonium in fine particles at 2 km when Ca^{2+} was detected were higher than those when it was not.

These results strongly suggest transport of *kosa* aerosol to the free troposphere over the Japan Sea coast. Formation of nitrate on *kosa* particles, physical and chemical interactions of *kosa* aerosol with other types of aerosols (e.g., ammonium sulphate) during transport in the free troposphere, are also suggested.

4. A Possible Chemical Reaction between *Kosa* and Ammonium Sulphate Aerosol

4.1. Necessity of Elucidation of the Chemical Reaction Process of *Kosa* Aerosol

The possibility of modification of *kosa* aerosol during transport has been pointed out by many researchers on the basis of observational results. Iwasaka et al. (1988) found soil particles coated by water or solution containing sulphate at altitude 4400 m over Japan, suggesting that such particles absorb various atmospheric gases. Okada et al. (1990) found that *kosa* particles are present as mixed particles (internal mixture of water soluble and -insoluble material) by use of an electron microscope equipped with an energy-dispersive X-ray analyser. *Kosa* particles mixed internally with sea salt were present in percentages of 16-100% among analysed dust particles in Nagasaki, Japan (Niimura et al., 1998). Wu and Okada (1994) found nitrate on the surfaces of dust particles during the *kosa* phenomenon. Nishikawa et al. (1991 a) collected *kosa* aerosols at Yaku Island, Japan and found high correlation coefficients among nitrate, non-sea-salt sulphate, and total surface area of aerosol particles for all size fractions of the coarse fraction, indicating that these ions are deposited on and transported with the *kosa* aerosol. The results of concentration of water soluble components in the aerosol particulate matter in the free troposphere over the Japan Sea, suggest association of nitrate with *kosa* aerosols and interactions of *kosa* aerosol with other types of aerosols (e.g., ammonium sulphate) during transport (Mori et al., 1999). Physical and chemical interaction between *kosa* and those aerosols might occur under such a condition. It is difficult, however, to determine the chemical reaction process in detail only on the basis of the observational results.

In this chapter, I will describe the possibility of chemical reaction during the coagulation between *kosa* and ammonium sulphate aerosols by a series of reaction experiments and analysis of an ambient aerosol sample.

4.2. Method

4.2.1. Model Experiment

4.2.1.1. Materials

Ammonium sulphate, calcium carbonate, and artificial *kosa* material ground to a particle size of 10 μm diameter or less (similar to an aerosol) were used in the experiments. The former two were special grade reagents, and the artificial *kosa* particles, made from representative loess soil, contained 10% calcium carbonate and gypsum was absent.

4.2.1.2. Chamber Experiment

A mixture (2 g) of calcium carbonate and ammonium sulphate, adjusted to a molar ratio of 1:1; a mixture (2 g) of artificial *kosa* particles and ammonium sulphate particles in which the molar ratio of calcium carbonate in the artificial *kosa* particles to ammonium sulphate was also adjusted to 1:1; and 2 g of each substance individually were evenly distributed on 90 mm diameter Petri dishes, and allowed to stand in a constant temperature chamber with a humidity control unit. To exclude pollutants such as ammonia gas, SO_2, etc. from the interior atmosphere, 99.999% argon at a controlled humidity was allowed to flow continuously through the chamber at a linear velocity of 4 cm/min (Fig. 4.1). These continuous exposure experiments were performed for a maximum of 8 days at relative humidities (RHs) of 40%, 60%, 70% and 80% (±5%).

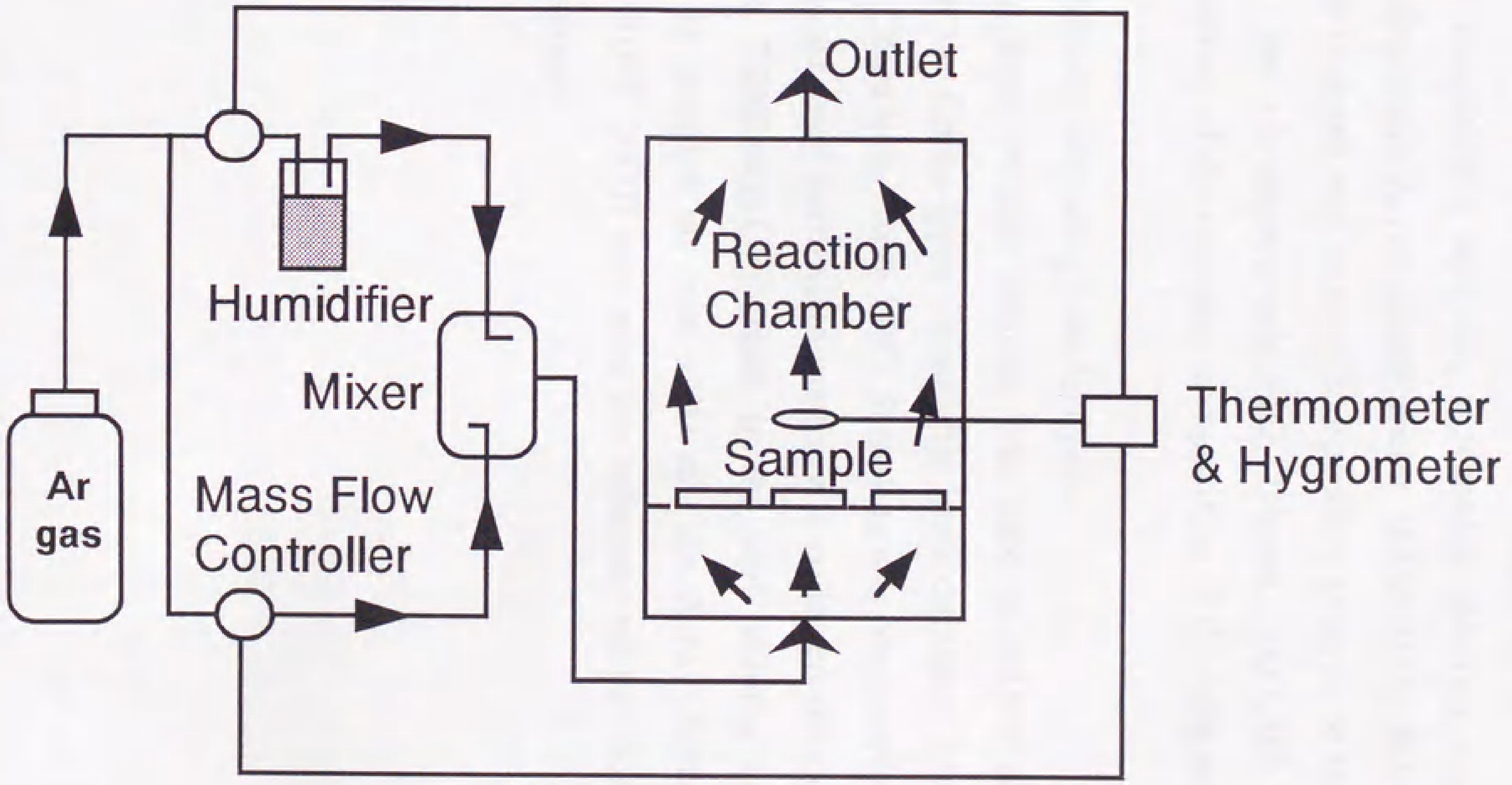

Figure 4.1 Experimental apparatus.

4.2.1.3. Analysis

An X-ray diffractometer (XRD; Rigaku, RINT 2000) was used for mineral composition analysis, a scanning electron microscope with an energy dispersive X-ray spectrometer (SEM-EDX; JEOL, JSM-5800LV) for particle shape and element composition analysis of the particle surface, and an ion chromatograph (IC; Dionex, DX-100) for quantitative determination of the chemical composition of the bulk samples.

4.2.2. Aerosol Sampling and Analysis

A high volume sampler was used to collect aerosol particulate matter at the China-Japan Friendship Environmental Protection Centre in Beijing, China in 6-7 May 1997. Sampling was conducted on the roofs of the facilities. Aerosol particulate matter was collected on a quartz fibre filter (Pallflex, 2500QAT-UP) attach in the high volume sampler. The total volume of sampled air was 1400 m^3. An X-ray diffractometer (XRD; Rigaku, RINT 2000) was used for mineral composition analysis for the aerosol sample.

4.3. Results of Model Experiment

At 23°C and 70% RH XRD analysis of the mixture of calcium carbonate and ammonium sulphate showed that koktaite formed after 1 day and that gypsum formed after 7 days (Fig. 4.2). A similar result was obtained for the mixture of artificial *kosa* particles and ammonium sulphate (Fig. 4.3). Substantial needle-shaped crystals were observed on the surface of the original particles in the mixtures in which koktaite and gypsum were found (Fig. 4.4). Both sulphur and calcium were detected in these crystals showing that they had been newly formed (Fig. 4.4). There was no difference in the composition of the unmixed substances before and after the experiments. These results revealed that new crystals were formed when calcium carbonate and ammonium sulphate particles reacted. The reaction formulae were estimated to be as follows:

$$CaCO_3+2(NH_4)_2SO_4 \rightarrow (NH_4)_2Ca(SO_4)_2 \cdot H_2O+2NH_3+CO_2 \qquad (1)$$

$$(NH_4)_2Ca(SO_4)_2 \cdot H_2O+ H_2O \rightarrow CaSO_4 \cdot 2H_2O+(NH_4)_2SO_4 \qquad (2)$$

The ratio NH_4^+/SO_4^{2-} at 70% RH decreased over time as the mixture was allowed to stand, typically in the order of days (Fig. 4.5). This result indicated that the release of ammonia as shown in Eq. (1) was actually taking place.

The decrease in the ratio NH_4^+/SO_4^{2-} at 70% RH for the mixture of artificial *kosa* particles with ammonium sulphate was faster than for that of calcium carbonate and ammonium sulphate (Fig. 4.5 and 4.6). This suggested that a constituent of the artificial *kosa* particles acted as a catalyst.

Furthermore, results of bulk analyses of NH_4^+/SO_4^{2-}, did not show the change as clearly as the results of surface analyses carried out by XRD and SEM-EDX. Thus the reactions were occurring at the particle surfaces.

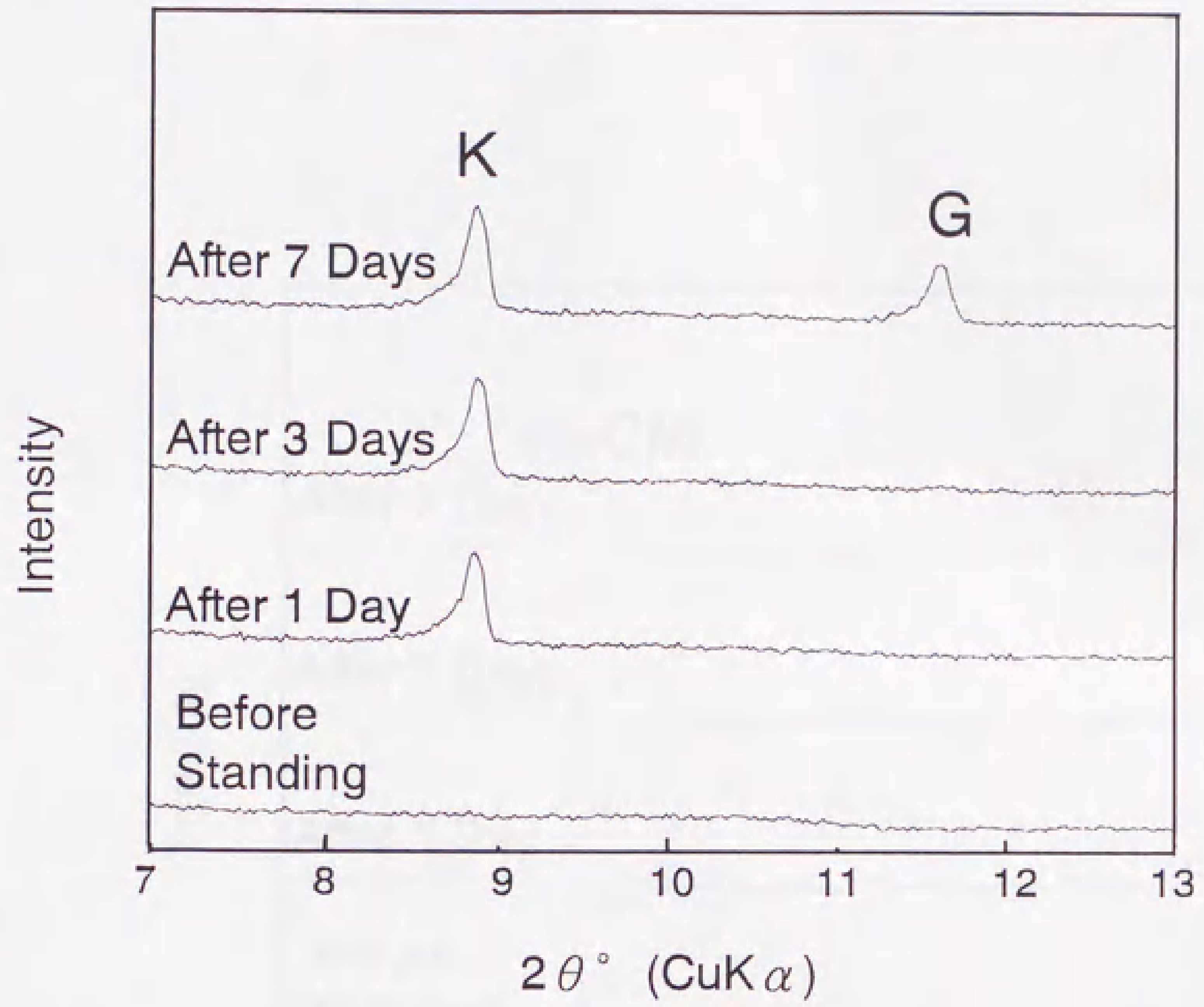

Figure 4.2 XRD spectra of the mixture of calcium carbonate and ammonium sulphate particles allowed to stand in an argon atmosphere at 23°C and 70% relative humidity for 1, 3 and 7 days. K, koktaite; G, gypsum.

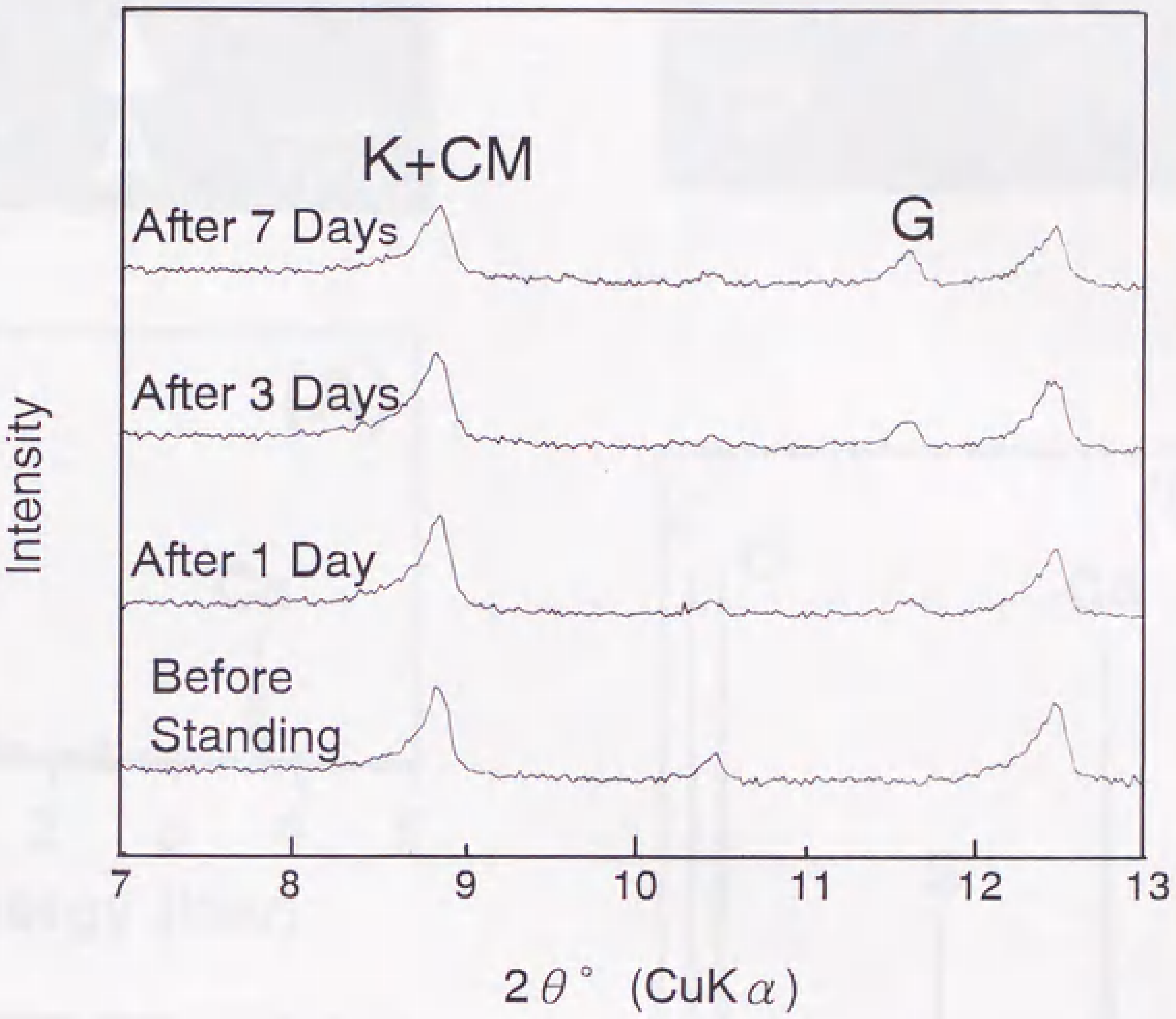

Figure 4.3 XRD spectra of the mixture of artificial *kosa* and ammonium sulphate particles. G, gypsum; K+CM, koktaite and clay minerals.

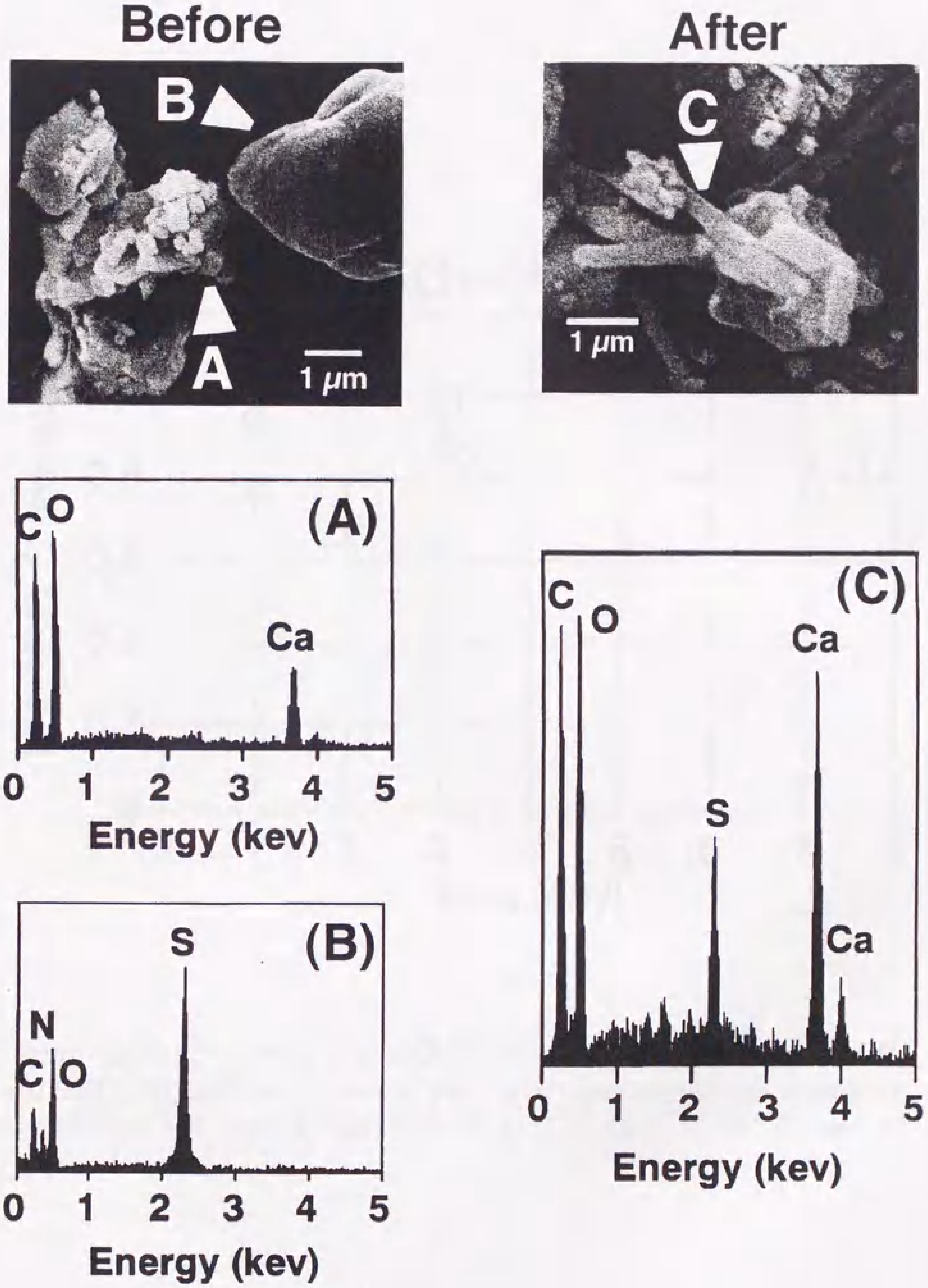

Figure 4.4 Scanning electron micrograph of the mixture of calcium carbonate and ammonium sulphate particles before and after standing in an argon atmosphere at 70% relative humidity for 1 day. X-ray spectra correspond to the particles A, B, and C in micrographs.

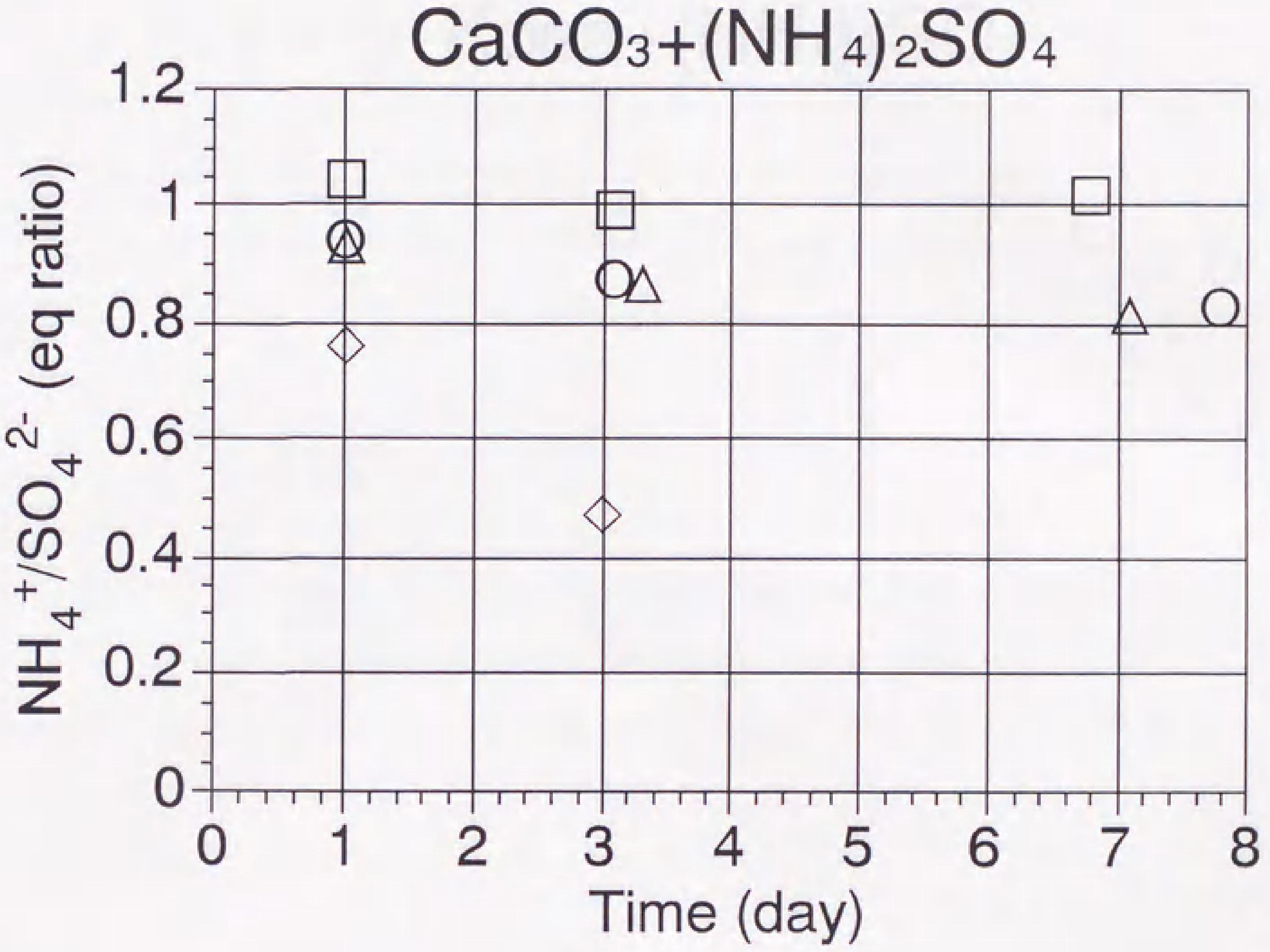

Figure 4.5 Time variation of the NH_4^+/SO_4^{2-} ratio for the mixture of $CaCO_3$ and $(NH_4)_2SO_4$ particles allowed to stand in an argon atmosphere at constant temperature and relative humidities of 40 (□), 60 (○), 70 (△) and 80 (◇) %.

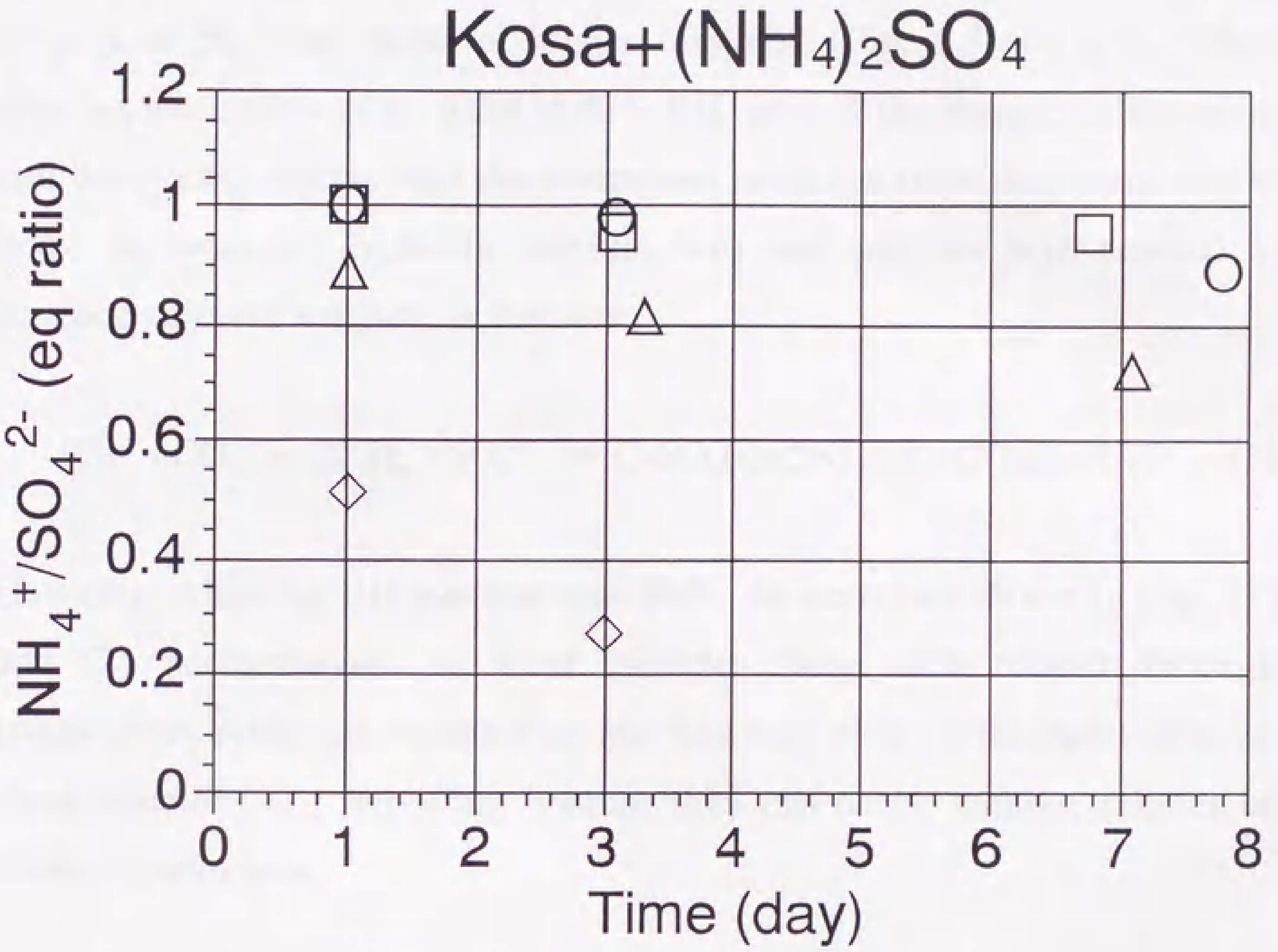

Figure 4.6 Time variation of the NH_4^+/SO_4^{2-} ratio for the mixture of artificial *kosa* and $(NH_4)_2SO_4$ particles allowed to stand in an argon atmosphere at constant temperature and relative humidities of 40 (□), 60 (○), 70 (△) and 80 (◇) %.

The results at other RHs, (except at 40% RH) were similar to that at 70% RH, with koktaite and gypsum formation and the release of ammonia. At 23°C and 40% RH, neither koktaite nor gypsum was found by XRD analysis in either mixture after more than 7 days. The decrease of NH_4^+ relative to SO_4^{2-} was faster at higher humidity (Fig. 4.5 and 4.6). When samples were allowed to stand at 80% RH, part of the sample deliquesced, and this greatly accelerated the subsequent reactions since they were able to occur in solution. Probably calcium ions and sulphate ions reacted to produce calcium sulphate as follows:

$$(Ca^{2+}+CO_3^{2-})+(2NH_4^{+}+SO_4^{2-}) \rightarrow CaSO_4(s)+2NH_3(g)+CO_2(g)+H_2O \qquad (3)$$

However, when the RH was less than 80%, the reactions shown in Eqs. (1) and (2) predominated as solid particles came into contact through coagulation. Although the reaction rate was very slow, in the order of days, these reactions are important because they can occur without rainout or washout processes.

4.4. Results of Ambient Aerosol Sample

In an atmospheric aerosol sample collected in Beijing, China on 6-7 May 1997 during a *kosa* event, koktaite was present (Fig. 4.7), but it has never been found in the soils from which the *kosa* aerosol originates. Koktaite has also been identified, together with ammonium sulphate, and calcite and /or gypsum in aerosol samples collected in the U.S.A. (Tani et al., 1983), the U.K. (Harrison and Sturges, 1984), Germany (Voigt et al., 1984) and Canada (Sturges et al., 1989). It is likely that koktaite was formed in each case through the coagulation of ammonium sulphate and calcium carbonate-rich aerosols, and that a chemical reaction in the coagulation of the solid particles actually occurred.

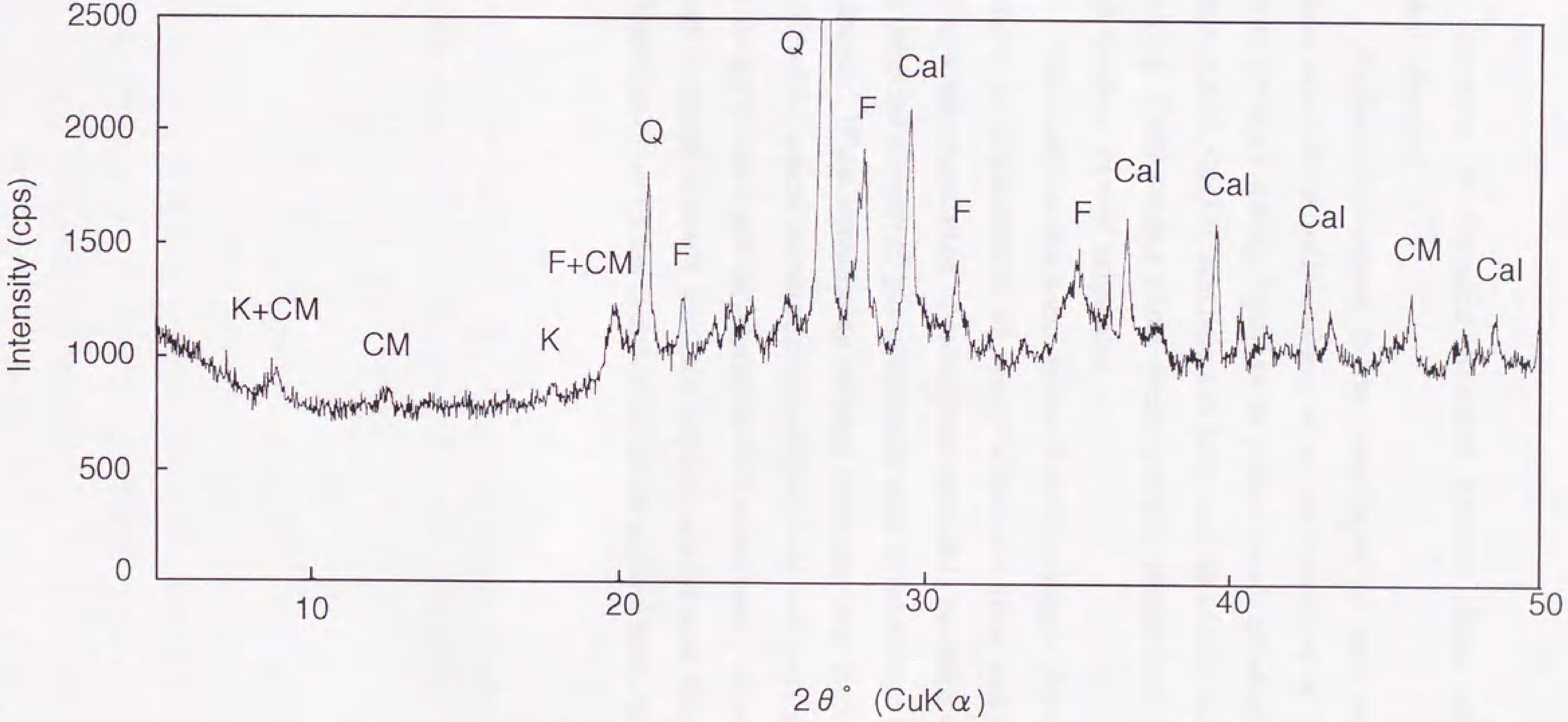

Figure 4.7 XRD spectrum of the aerosol collected in Beijing on 6-7 May 1997. Cal, calcite; CM, clay minerals; F, feldspar; Q, quartz; F+CM, feldspar and clay minerals; K+CM, koktaite and clay minerals.

4.5. Summary of Chemical Reaction between *Kosa* and Ammonium Sulphate Aerosol

A chemical reaction in the coagulation of *kosa* and ammonium sulphate aerosols actually occurs, at a rate measured in days, to yield koktaite [$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$] as an intermediate product and, finally, gypsum ($CaSO_4 \cdot 2H_2O$). Koktaite was present in an aerosol sample collected in Beijing, China during a *kosa* event, but it is absent from the soils from which the *kosa* aerosol originates.

This reaction can occur in the free troposphere during long-range transport, in consideration of experimental condition and reaction rate. Until now the coagulation of atmospheric aerosols has been studied mainly from the point of view of physical factors such as the change in particle size distribution. When considering aerosol reactions over East Asia and the North Pacific, where substantial amounts of *kosa* and ammonium sulphate aerosols are present and /or transported, it is necessary to consider a new process in which koktaite and then gypsum are formed through chemical reactions that occur in the coagulation of the aerosol particles.

5. Conclusions

Aerosol particulate matter was directly collected in the free troposphere over the Japan Sea coast between 1992 and 1994 using an aircraft-borne nine-stage cascade impactor (particle size range: 0.1-8 μm). Number size distributions of aerosols were also measured by use of an optical particle counter mounted on the aircraft. On the basis of these results, I have discussed the transport and chemical modification of the *kosa* aerosol in the free troposphere. The possibility of chemical reaction during the coagulation between *kosa* and ammonium sulphate aerosols was also investigated by a series of reaction experiments.

Additionally, a new discrimination method for *kosa* aerosol transport was developed. It can be applied to a small amounts of aerosol samples such as are collected by use of an aerosol sampler mounted on an aircraft. Chemical characteristics of aerosol samples which possibly contain *kosa* aerosols are: concentrations of water soluble Ca and Sr in the aerosol are high; the ratio of non sea salt strontium to calcium in the aerosol is around 0.0052.

Applying these characteristics to the results of chemical analysis of aerosol samples collected in the free troposphere, I have discussed the transport of the *kosa* aerosol to the free troposphere and the chemical modification of the *kosa* aerosol in the free troposphere. The results are:

1. High number concentrations of the coarse size particles and high concentrations of water soluble Ca in the coarse size aerosols were observed in the free troposphere. The concentrations of Ca^{2+} in aerosols in the free troposphere increased when dust events were observed. The mean (Sr^{2+}/ Ca^{2+}) ratios for samples in the free troposphere were closer

to that of desert soil in China than the Japanese soil value. These results strongly suggest the transport of the *kosa* aerosol to the free troposphere over the Japan Sea coast.

2. The concentrations of nitrate in coarse particles at 2 and 4 km were higher when Ca^{2+} was detected than when Ca^{2+} was not detected. The size distribution pattern of nitrate showed good correspondence with that of Ca^{2+}. These results suggest that nitrate is formed on the surfaces of *kosa* particles.
3. Concentrations of sulphate and ammonium in fine particles at 2 km when Ca^{2+} was detected were higher than those when it was not. Most of the sulphate and ammonium were present in fine particles. In the other hand, most of the Ca^{2+} was present in coarse particles. It is suggested that *kosa* aerosols were transported with other types of aerosols, such as ammonium sulphate, ammonium nitrate, etc. aerosols.

A chemical reaction may occur when a *kosa* aerosol collides with other aerosols. The possibility of chemical reaction in the coagulation of *kosa* and ammonium sulphate aerosols was investigated by a series of reaction experiments. The result is:

4. A chemical reaction in the coagulation of *kosa* and ammonium sulphate aerosols occurs, at a rate measured in days, to yield koktaite $[(NH_4)_2Ca(SO_4)_2 \cdot H_2O]$ as an intermediate product and, finally, gypsum $(CaSO_4 \cdot 2H_2O)$.

The *kosa* aerosol is a reactive substance. Chemical modification of the *kosa* aerosol in the free troposphere is suggested from the observational results. The results of the model experiments suggest that a chemical reaction occurs in the coagulation of *kosa* and ammonium sulphate aerosols. It is necessary to investigate the effects on scattering of solar radiation and the geochemical cycle of nitrogen and sulphur by the *kosa* aerosol itself and *kosa* aerosol associated with other substances in the free troposphere.

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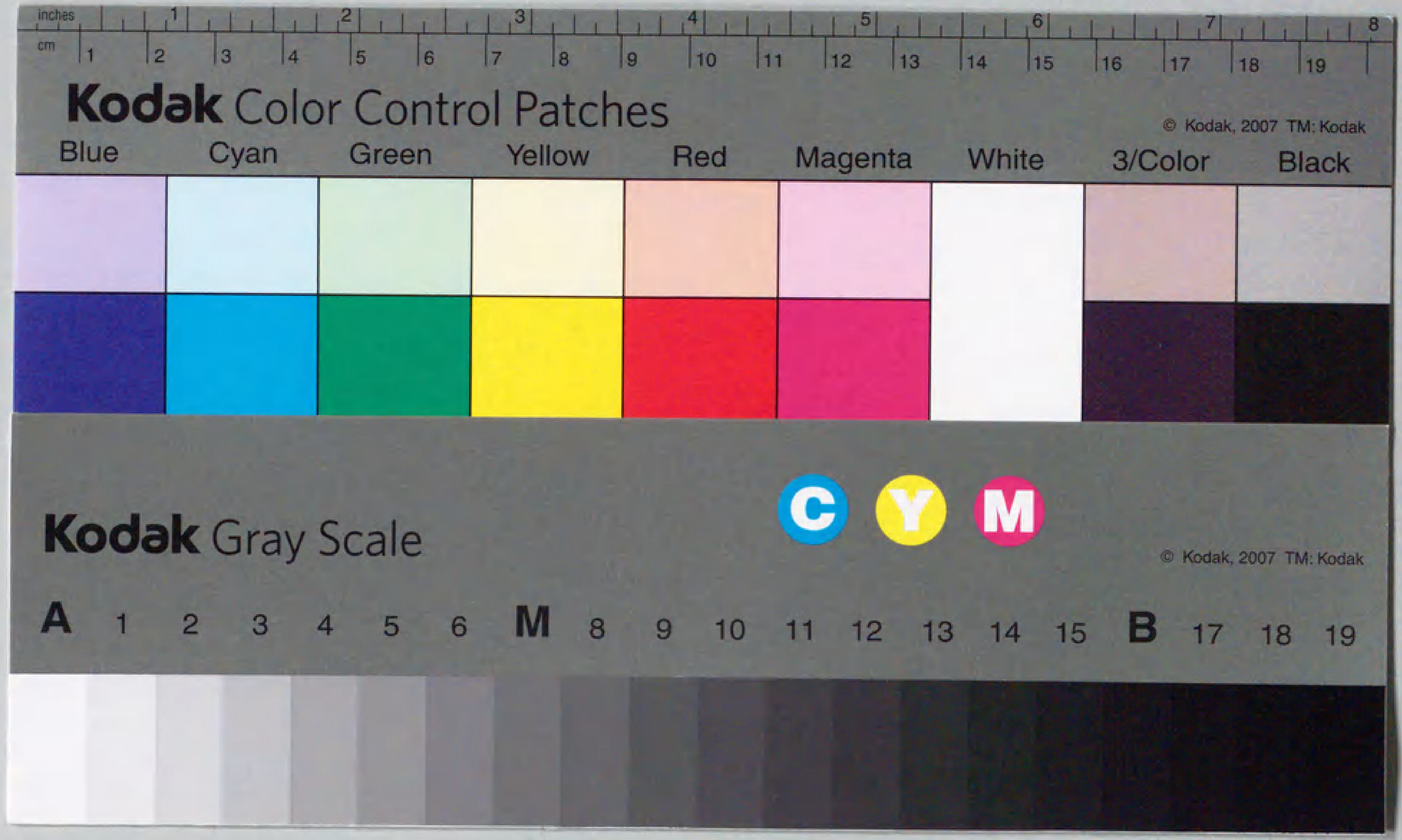
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