

***Single-particle characterization of Asian  
Dust samples collected in the spring of  
2000 and 2001, in Korea***

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***Chemical Modification of Asian Dust  
During Long-Range Transport***

\* Reports on chemical modification with sea-salts and CaCO<sub>3</sub>

1. Chemical modifications occurred:

- \* J.C. Choi, et. al., *J. Geophys. Res.* 2001, 106, D16, 18067. (Korea)
- \* B.G. Kim and S.U. Park, *Atmos. Environ.* 2001, 35, 3191. (Korea)
- \* M. Nishikawa, et al., *Sci. Total Environ.* 1991, 107, 13. (Japan)
- \* K. Okada, et al., *Atmos. Environ.* 1990, 24, 1369. (Japan)
- \* X. Fan, et al., *Atmos. Environ.* 1996, 30, 347. (Japan)
- \* C.J. Ma, et al., *Atmos. Environ.* 2001, 35, 2707. (Japan)
- \* M. Fang, et al., *Atmos. Environ.* 1999, 33, 1803. (Hong Kong)
- \* H. Zhuang, et al., *Atmos. Environ.* 1999, 33, 4223. (Hong Kong)

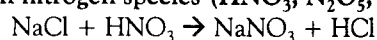
2. No chemical modifications occurred:

- \* J. Zhang, et. al., *Atmos. Environ.* 2001, 35, 5007. (China)
- \* M. Zhou, et. al., *Atmos. Res.* 1996, 40, 19. (China)
- \* D. Zhang and Y. Iwasaka, *Atmos. Environ.* 1999, 33, 3213. (China)
- \* D. Zhang, et. al., *Atmos. Environ.* 2003, 37, 3895. (China)

## Atmospheric Chemical Reactions (I)

### 1. Reaction of sea salt particles

- \* with nitrogen species ( $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{ClONO}_2$ ,  $\text{NO}_2$ )



- \* Lab Experiments

Finlayson-Pitts, *Nature* 1983, 306, 676.

Finlayson-Pitts, et. al., *Nature* 1989, 337, 241.

Knipping, et. al., *Science* 2000, 288, 301.

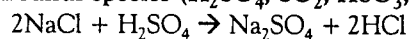
Laskin, et. al., *Science* 2003, 301, 340.

- \* Real Atmospheric Observations

Gard, et. al., *Science* 1998, 279, 1184.

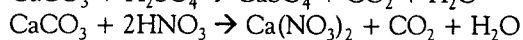
C.-U. Ro, et. al., *Env. Sci. Technol.* 2001, 35, 4487.

- \* with sulfur species ( $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$ ,  $\text{HSO}_3$ , ...)



## Atmospheric Chemical Reactions (II)

### 2. Reaction of mineral dust particles



- \* Just pure guess on its effect of the reactions  
on global warming:  
(regarding the reaction of Asian Dust)

Dentener, et. al., *J. Geophys. Res.* 1996, 101, 22869.

- \* Implications of its real occurrence:

C.-U. Ro, et. al., *Env. Sci. Technol.* 2000, 34, 3023.

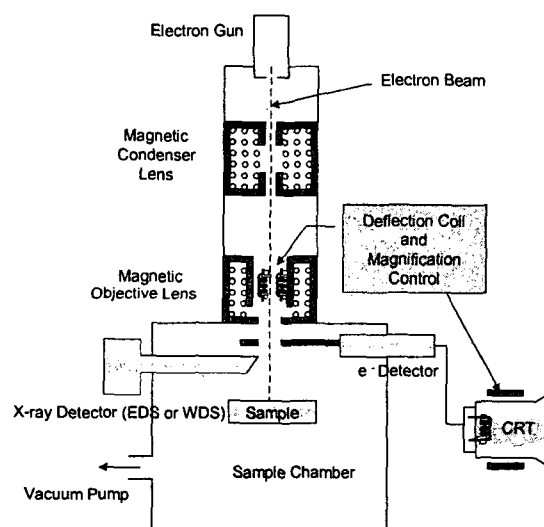
C.-U. Ro, et. al., *Env. Sci. Technol.* 2002, 36, 4770.

C.-U. Ro, et. al., *Env. Sci. Technol.* 2004, submitted.  
(Today's talk)

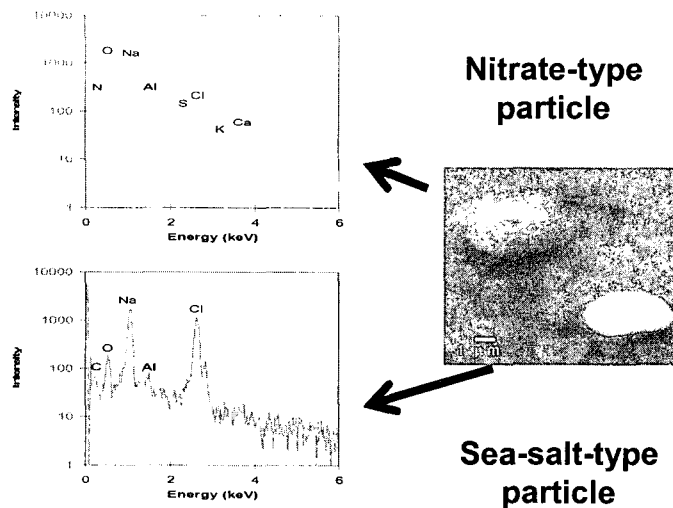
## *Low-Z EPMA (Electron Probe X-ray Microanalysis) for Single Particle Analysis*

1. SEM-EDX (Scanning Electron Microscopy – Energy Dispersive X-ray Spectrometer)
  - Individual Particle Analysis
    - \* shape and size : secondary / backscattered electron images
    - \* chemical compositions : X-ray spectrum
2. Ultra-thin window EDX for low-Z elements detection (e.g., C, N, O, F)
3. Data Measurements at liquid N<sub>2</sub> temperature for beam sensitive particles (e.g., (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, etc.)
4. Metallic collecting substrates for minimizing charging effect (e.g., Ag, Al)
5. Monte Carlo calculation for Quantification
6. Chemical speciation of aerosol particles – Expert System

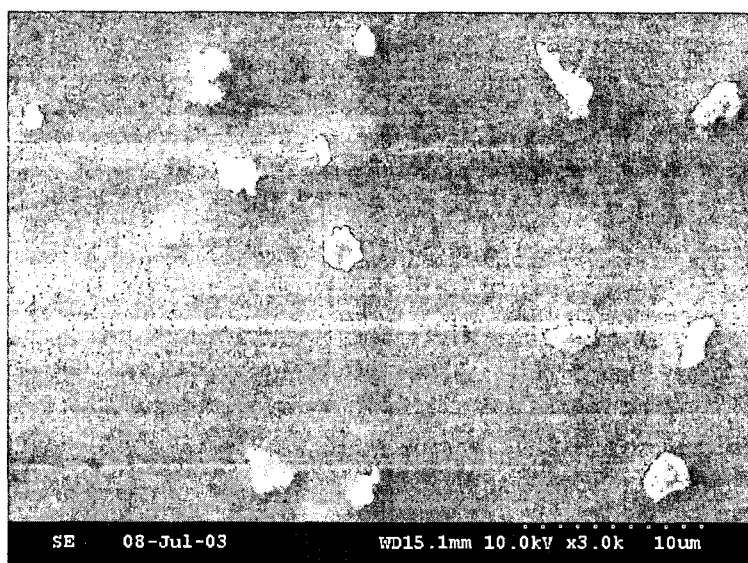
### *SEM-EDX schematic diagram*



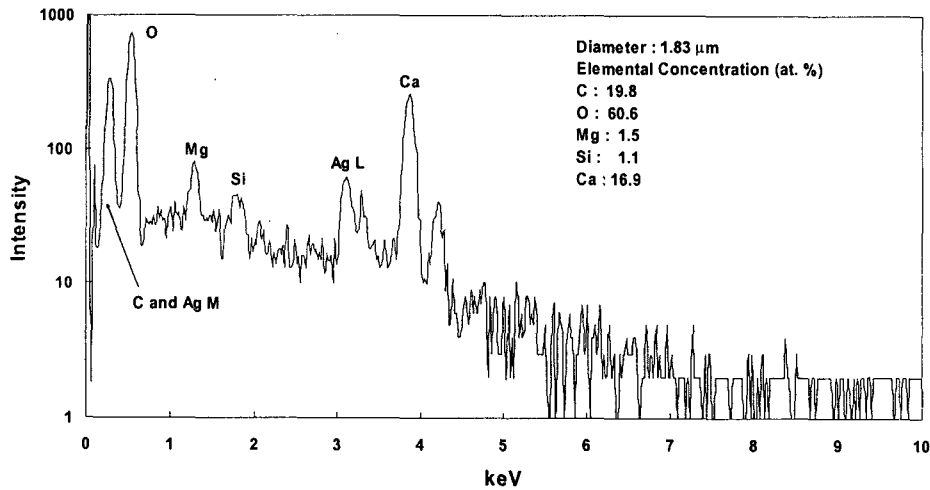
### Illustrative Example of Single Particle Analysis Using Low-Z EPMA



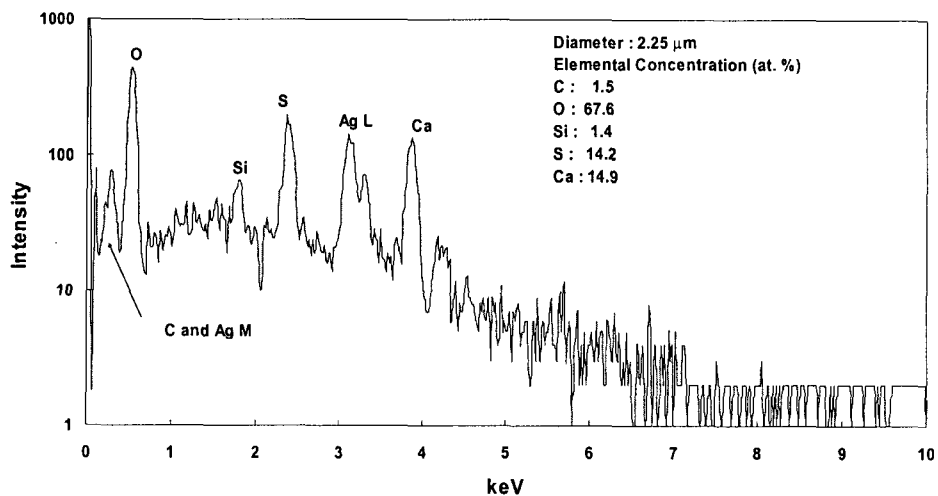
A typical secondary electron image showing well-separated individual particles for Asian Dust samples



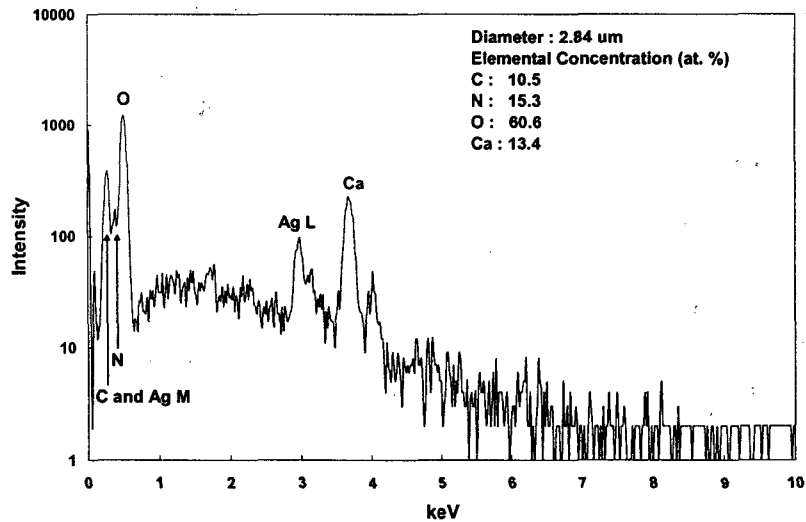
*X-ray spectra and atomic concentrations of a  $\text{CaCO}_3$  particle selected from Asian Dust samples*



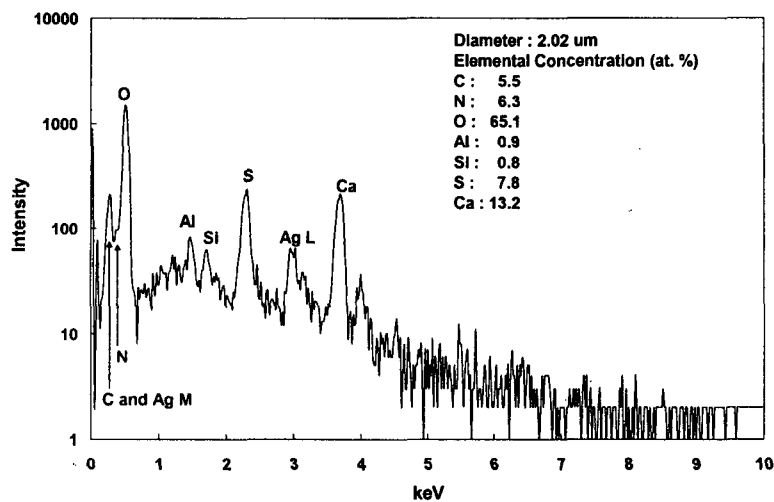
*X-ray spectra and atomic concentrations of a  $\text{CaSO}_4$  particle selected from Asian Dust samples*



*X-ray spectra and atomic concentrations of a particle internally mixed with  $\text{CaCO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  selected from Asian Dust samples.*



*X-ray spectra and atomic concentrations of a particle internally mixed with  $\text{CaSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$  selected from Asian Dust samples.*



## Asian Dust Sampling

**\* Samplings (During Asian Dust Storms)**

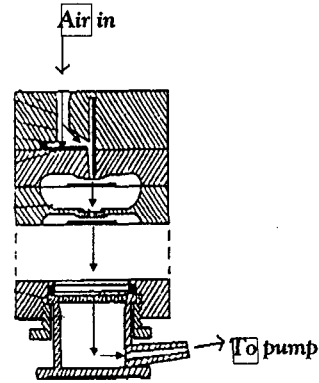
- 2000: March 7, April 7
- 2001: March 22, May 17

**\* Place : Hallym University, ChunCheon**

**\* Sampling substrate : Ag foil**

**\* May cascade impactor  
cut-off diameter (flow rate: 20 L/min)**

- stage 1 : 16 mm
- stage 2 : 8 mm
- stage 3 : 4 mm
- stage 4 : 2 mm
- stage 5 : 1 mm
- stage 6 : 0.5 mm

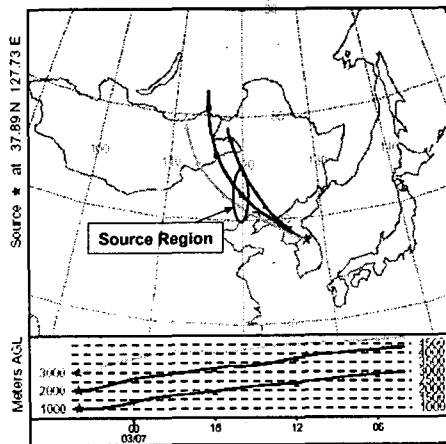


7 stage May cascade impactor

## Air-mass backward trajectories for Asian Dust samples

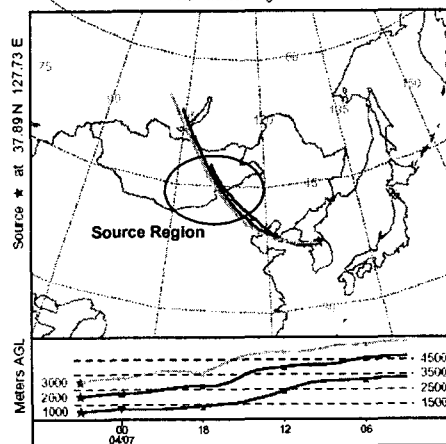
**(A) March 7, 2000**

NOAA HYSPLIT MODEL  
Backward trajectories ending at 04 UTC 07 Mar 00  
FNL Meteorological Data



**(B) April 7, 2000**

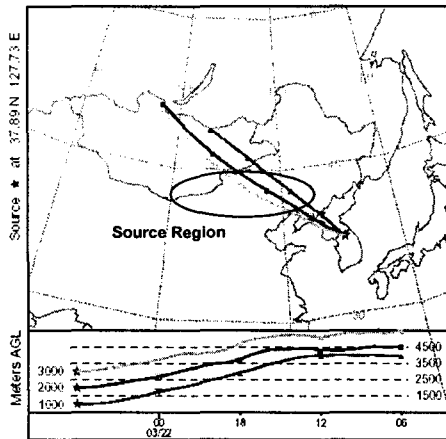
NOAA HYSPLIT MODEL  
Backward trajectories ending at 03 UTC 07 Apr 00  
FNL Meteorological Data



## Air-mass backward trajectories for Asian Dust samples

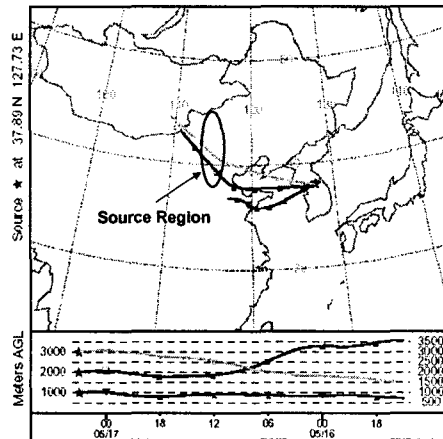
(C) March 22, 2001

NOAA HYSPLIT MODEL  
Backward trajectories ending at 06 UTC 22 Mar 01  
FNL Meteorological Data



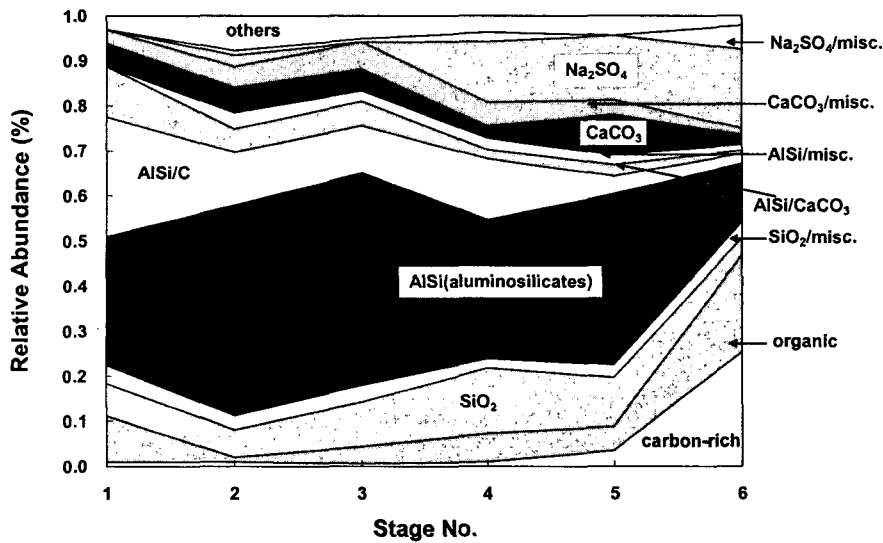
(D) May 17, 2001

NOAA HYSPLIT MODEL  
Backward trajectories ending at 03 UTC 17 May 01  
FNL Meteorological Data



## Relative abundance of chemical species (Asian Dust)

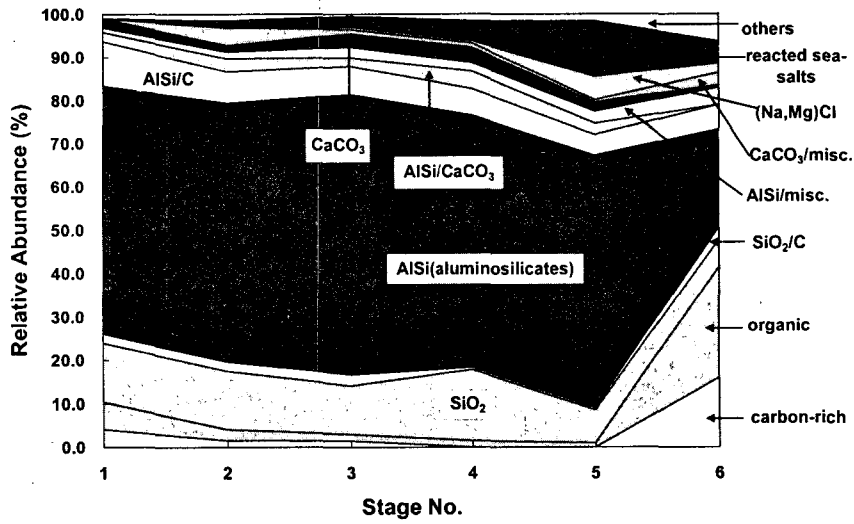
March 7, 2000





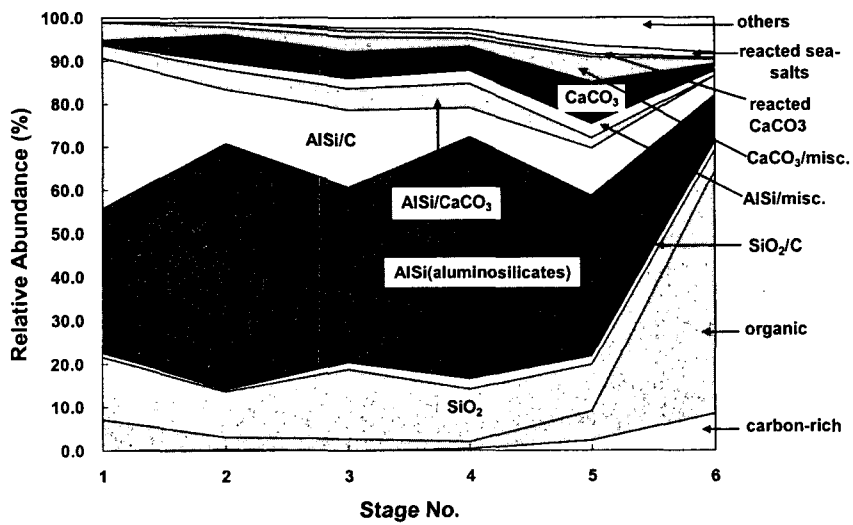
### Relative abundance of chemical species (Asian Dust)

April 7, 2000



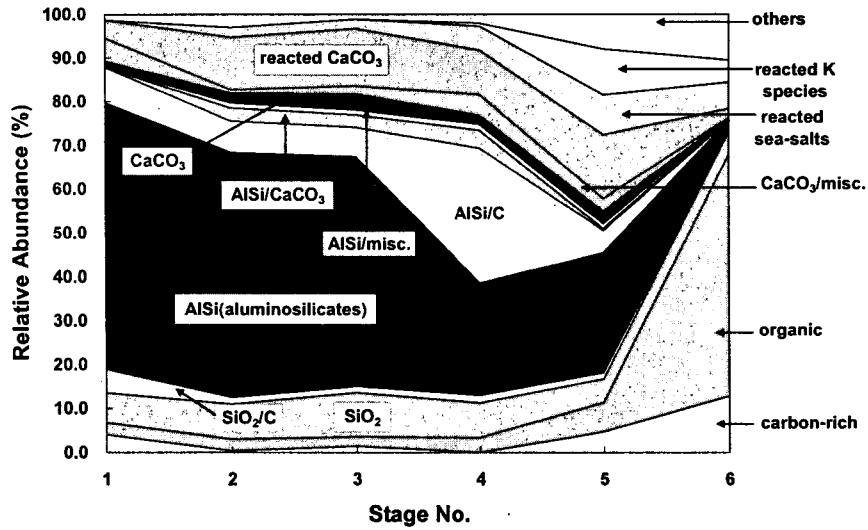
### Relative abundance of chemical species (Asian Dust)

March 22, 2001

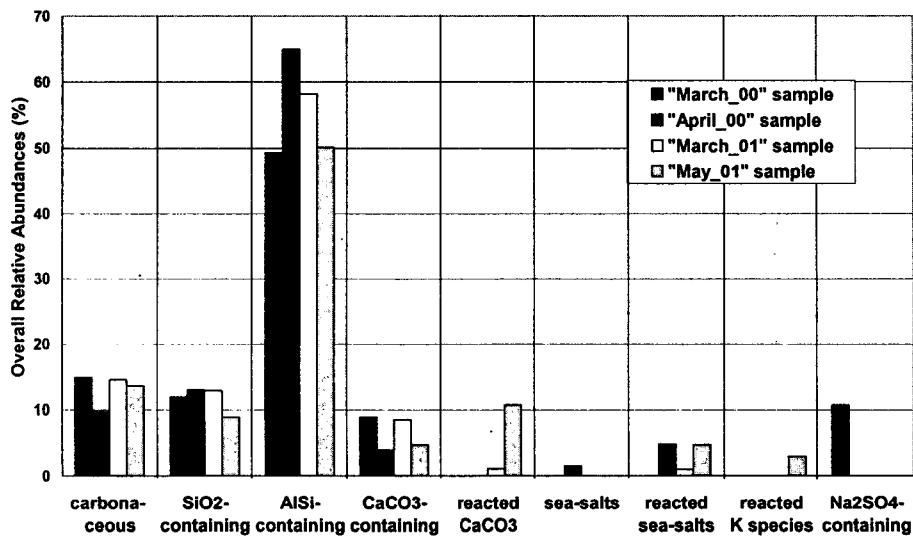


## Relative abundance of chemical species (Asian Dust)

May 17, 2001



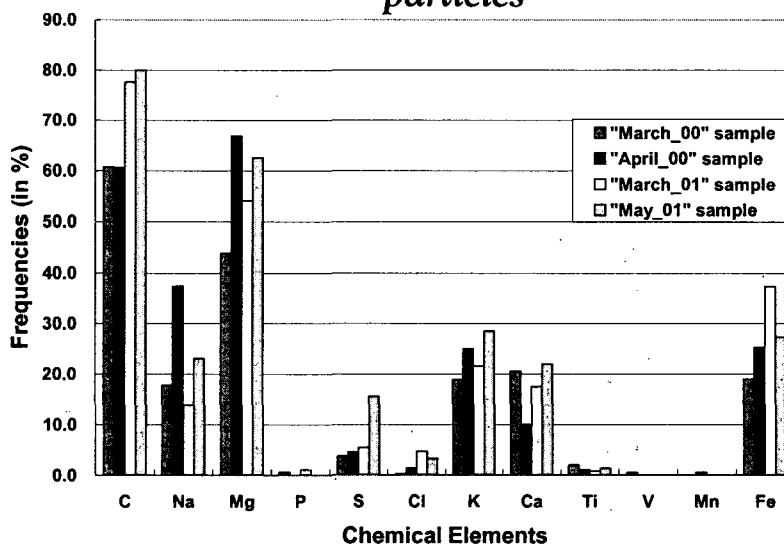
## Overall relative abundances of significantly encountered particle types



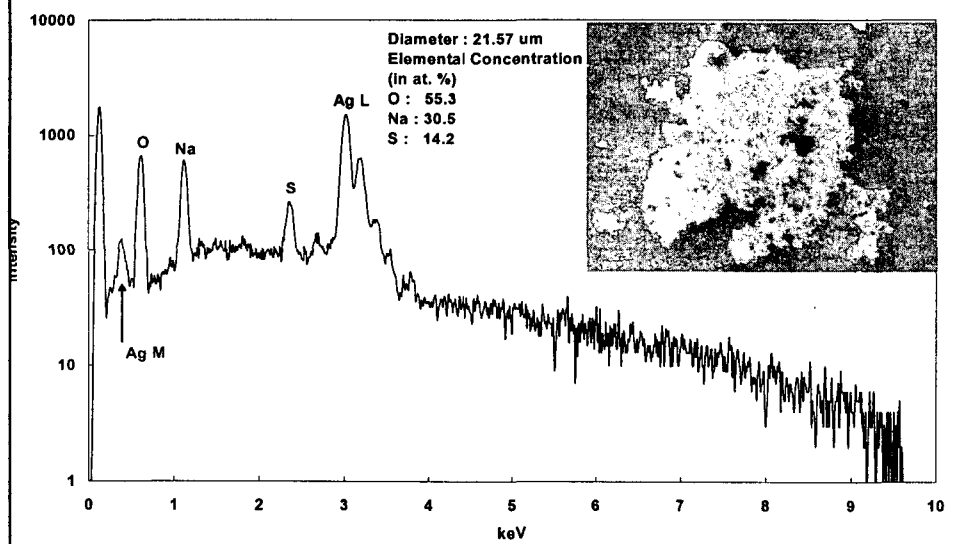
*Number of particles containing sulfate or nitrate  
due to atmospheric reactions of CaCO<sub>3</sub>, sea-salts,  
and K<sub>2</sub>CO<sub>3</sub>*

	Reacted CaCO <sub>3</sub>		Reacted Sea-salts		Reacted K species	
	CaSO <sub>4</sub> - containing	Ca(NO <sub>3</sub> ) <sub>2</sub> - containing	Na <sub>2</sub> SO <sub>4</sub> - containing	NaNO <sub>3</sub> - containing	K <sub>2</sub> SO <sub>4</sub> - containing	KNO <sub>3</sub> - containing
April 7, 2000			38	13		
March 22, 2001	7	6	11	5		
May 17, 2001	36	128	18	55	34	13

*Relative frequencies of minor chemical elements  
encountered in the aluminosilicate-containing  
particles*



## Typical secondary image of $\text{Na}_2\text{SO}_4$ particles and X-ray spectrum



## Conclusions

1. Quantitative single particle analysis:  
chemical speciation of Asian Dust particles
2. Detailed and direct analysis on chemical modification during long-range transport of Asian Dust particles
3. Different chemical modifications for different samples
4. Possibility for quantitative assessment on chemical modifications