Morphological and Chemical Modification of Mineral Dust : Observational Insight into the Heterogeneous Uptake of Acidic Gases

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It is becoming more evident that the mineral dust acts as a sink for the acidic trace gases (e.g. SO_2, NOx, HNO_3). The role mineral dust should play in the global environment would be significantly altered following such reaction.

Strictly speaking, every dust particle has its unique morphology and mineralogy, and no particles are identical despite their abundance. Thus, this study focuses on the mixing state of individual dust particles and sulfate/nitrate in the actual atmosphere, with particular emphasis on the hosting mineralogy.

Total four aerosol samples were obtained (2004 Oct 28th 17:30LST; 29th 12:30LST) in the outskirts of Beijing (39°48'N, 116°28'E), China, using Low Volume Impactors (LVI) onboard a tethered balloon. The balloon allowed collection of particles at variable atmospheric conditions between the height ranges 0-600m. Carbon-coated nitrocellulose film supported by Ni-grid was selected as the sampling substrate. Additional nitron coating was applied for the detection of particulate nitrate (Isawa and Ono, 1979). Particles were analyzed on individual basis under two electron microscopes for their morphology (TEM, JEOL JEM-2010 & SEM, HITACHI, S-3000N) and composition (EDX, HORIBA, EMAX-500 coupled with the SEM). Details on the sampling and analysis can be found elsewhere (Matsuki et al., 2005a)

Based on the individual particle analysis, irregularly shaped mineral dusts were separated into two large groups. Those having elemental ratio Ca>50% (or (Mg+Ca)>50%) was termed here as [Carbonate], and the rest to be [Silicate]. They are often the dominant components of the mineral dust. Interestingly, particles resembling [Carbonate] in composition, but spherical in shape [Ca-rich spherical particles] were spotted frequently in Beijing (Figure 1).

The fraction of particles detected with sulfur (detected by EDX) / nitrate (detected by nitron film) in the respective mineral group is compared in Figure 2. The particles termed as [Sea salt], and [Ca-rich spherical particles] were also included for better comparison.

[Carbonate] seems to take up acidic gases faster than [Silicate] due probably to their basic nature. Sulfur was detected simultaneously from about 80% of the nitrate bearing mineral dust. These results indicated that the distribution of sulfate and nitrate has similar trend over mineral dust particles. It is worth noting that [Ca-rich spherical particles] even showed larger fractions to contain sulfur and nitrate than did the former two dust species.

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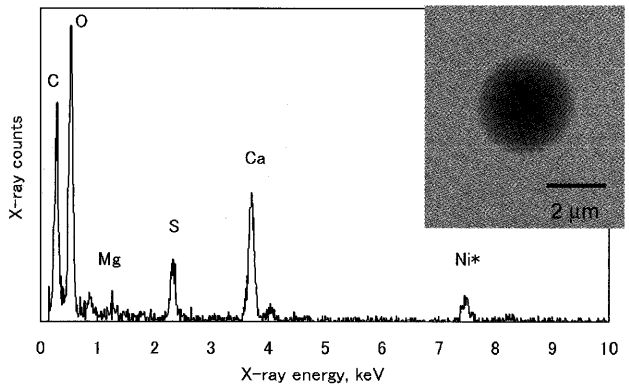

Figure 1 Typical electron micrograph and X-ray spectrum of a Ca-rich spherical particle, spotted frequently in Beijing near the surface. *Ni originates from the grids used to support the sampling substrate.

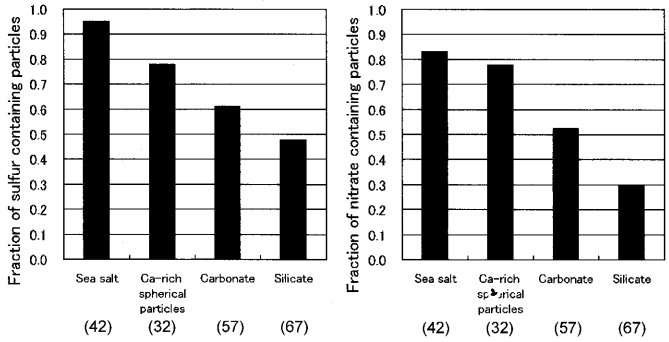

Figure 2 Fraction of particles containing sulfur (left) / nitrate (right) in the respective particle class. Total number of particles found in the current four samples is shown in brackets.

[Ca-rich spherical particles] are most likely the modified product of [Carbonate]. Calcite ($CaCO_3$) may react with gaseous HNO_3 to form $Ca(NO_3)_2$ which could then deliquesce even under conditions as dry as r.h.<20% (Krueger et al., 2004). This is supported by the following observations: (i) Nitrate was detected from majority (78%) of the [Ca-rich spherical particles] (Figure 2). (ii) [Carbonate] particles were found in very small numbers, especially among those collected under humid conditions (Figure 3a). In turn, [Ca-rich spherical particles] were often more abundant under humid conditions (Figure 3b). It is proposed therefore, that [Carbonate] fraction, which comprises 20-50% (Matsuki et al., 2005b) of mineral dust in East Asia, has the potential to form spheres in the actual atmosphere.

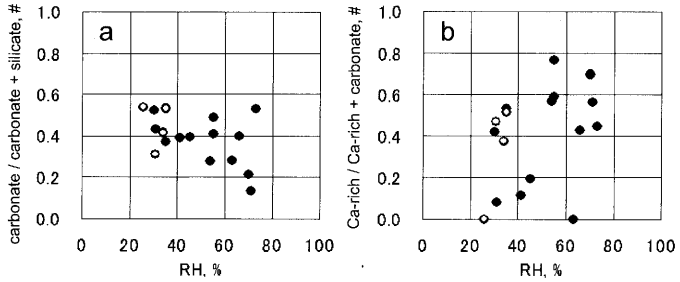

Figure 3 Change in abundance of (a) carbonate relative to silicate, and (b) Ca-rich spherical particles relative to carbonate, as functions of RH at point of sampling. Plotted in solid circles are the data from previous measurements [Matsuki et al., 2005b].

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