Mineralogical Characteristics of Aerosols Collected at Matsue and Kanazawa with a Special Emphasis to Transportation and Neutralization of S-related Acid Pollutants

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学位授与の題目	Mineralogical Characteristics of Aerosols Collected at Matsue and Kanazawa with a Special Emphasis to Transportation and Neutralization of S-related Acid Pollutants （松江および金沢において採集したエアロゾルの鉱物学的な特徴－イオウ酸性物質の輸送および中和作用について－）
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学位論文要旨

Abstract The mineralogical characteristics of aerosols collected in Matsue and Kanazawa were investigated by XRD and SEM-EDX analyses, in the light of the relationship between mineral aerosols and S-related pollutants. The seasonal variation of major minerals in the aerosols collected in Matsue during a one year period revealed two peaks of the abundances during spring and early winter. The ratios of S/Al and Fe/al all show two peaks in late winter and spring. A number of submicrometer S-rich particles were present as the coatings on the surface of large aerosol particles such as clay minerals, calcite and pollen. The sequence favorable to be attached by S substances was calcite (83%) > clay minerals (68%) > fly ash (55%) > quarts and feldspars (36%). The reaction experiment between aerosols and simulated acid rain solutions with pHs 3, 4 and 5, respectively indicated that the sample with high Kosa flux contained relatively high contents of calcite and gypsum, then showed larger neutralizing ability. The ratios of gypsum to clay minerals, quartz, calcite and halite, respectively suggest an increase of gypsum during the transport. The reaction experiment between pure calcite powders and simulated acid rain solutions with pHs 3, 4 and 5, respectively showed the formation of gypsum crystals after 12 hrs. reaction, suggesting that sulfur coatings on the surface of calcite could lead a reaction between sulfur substance an calcite to form gypsum during the long-range transport. The estimation of gypsum source contribution indicated that this conversion occurred mainly in winter and spring with the contribution ranging between 5-34%. The results of this study indicate that mineral aerosols from the Asian continent carried a large amount of solfur pollutants to the Japanese Islands during winter and spring. This may be one of the reasons causing lower pH of rain and snow in winter on the Japan Sea district of Japan. On the other hand, the conversion of calcite to gypsum suggests that mineral aerosols, as nuclei of acid rain and snow, partially neutralized S-related pollutants during long-range transport. On the Japan Sea coast, the

transport of mineral aerosols during winter and spring by northwestern monsoon and the reaction between mineral aerosols and the S-ralated pollutants attached on the surface of mineral aerosols could play an important role for buffering the speed of acidification on terrestrial and aquatic ecosystems in Japan.

Chapter-1 Background and purpose of this study

The emission of acidic gases predominated by sulfur dioxide gas into the atmosphere, in the recent decades, has dramatically increased with the development of industry in the eastern Asian countries. Especially, in China coal combustion has been a dominant energy source for a long time, contributing more than 70% of total energy production. It was expected that about 2500 Mt SO_2 had been emitted in China during 1995. Although emission of SO_2-related pollutants is relatively low in Japan, higher deposition rates of non-sea-salt (nss)-sulfate in winter and early spring in the Japan Sea coastal areas have been reported. Acid rain and snow with pH ranging between 4-5 prevail. On the other hand, the content of SO_4^{2-} in the rain water in northern cities of China is as nearly rich as that in Chongq and Guiyang of southwestern cities in which acid rain prevails, while no acid rain in the northern cities. Some studies concerning long-range transport of air pollutants from the Asian continent have indicated that the northwestern monsoon in winter could transport the air pollutants from the Asian continent to the Pacific. How these pollutants are transported or what relationship is present between the air pollutants and other aerosols. Little is known about these matters and more detailed works are needed.

Until recently, in the studies on the atmospheric pollution and acid rain, particularly on the long-range transport of acid pollutants in the Japan Sea coast areas, much of the focus has been on the chemical composition of atmospheric aerosols and precipitation chemistry. These studies are almost on the basis of chemically analytical data of rain water and filtered snow water or water soluble components of aerosol. On the atmospheric mineralogy such as mineral composition and abundance in aerosol, there have been relatively few studies. The data about content variation of calcite in aerosol has rerely been reported. Particularly gypsum has not been given large attention. Mineral dust is an important component in atmospheric aerosol. If we like to investigate the long-range transport of acid pollutants, it is necessary to examine the relations between mineral dust and acid pollutants which may contribute very important information of the conversion of SO_2-related acid pollutants during long-range transport.

In this study particular attention was put on gypsum to investigate its content variation and the relations with other minerals, since gypsum, as a sulfate composed of Ca^{2+} and SO_4^{2-}, may give some useful information on the interaction between SO_2-related pullutants and calcite.

Chapter-2 Samples and Methods

For the above purposes, the mineral composition in aerosols collected, with a high-volume air sampler, in Matsue, Shimane Prefecture during a one year period from October, 1992 to September, 1993, and collected in Kanazawa during one week from March 28 to April 4, 1994, and snow as well as rain samples collected in Kanazawa during 1993-1995, has been investigated by X-ray powder diffraction (XR D) analysis. To investigate the conversion history of acid pollutants, individual particle analysis by scanning electron microscope (SEM) witn energy dispersive X-ray analyzer (EDX), and experments of reaction between calcite and simulated acid rain solutions were conducted.

To understand mineral composition of aerosols in the Asian regions, falling dust in four cities of northern China (Beijing, Shengyang, Dalian and Benshi) during Oct. 10-14, 1994, and in Seoul, Korea, in Dec. 18, 1993 were collected, respectively. One loess and arid soil samples from the loess area of Xian and Taklamanka desert, China, respectively were also

analyzed for the comparison. Four road dust samples collected in Matsue and Kanazawa during May, 1994 and 1995, respectively, and three samples of emission dust collected from the chimneys of two oil-fired boilers and one incinerator of the power plant in Japan were analyzed for the comparison.

Chapter-3 Mineral composition of aerosols

Major minerals identified by XRD analysis complimented by SEM-EDX analysis are shown as follows : smectite, chlorite, illite/smectite mixed layer, kaolin minerals, quartz, cristobalite, feldspars, lepidocrocite, Fe-containing sulfates including ferricopiapite and metavoltine, gypsum, calcite, dolomite, halite, rutile, homblende, zincocopiapite, magnetite, talc, wallostonite, mullite, pyrite, acmite, rhodoctocite, barite, ilmenite, aluminocopiapite, According to the SEM-EDX analysis, following minerals and materials were confirmed : apatite, glauberite, goethite, alunite, amorphous-silicon, Al, Si-spheres, Fe-spheres, Ti-spheres, S-spheres and carbonaceous soot. Of the above minerals clay minerals, quartz, feldspars, gypsum, calcite and iron oxide iminerals were detected in most of the samples. In the falling dust in northern China, wallostonite was one of the characteristic minerals, and it was only detected in snow samples in Kanazawa and some aerosol samples in Matsue in winter and spring times.

Chapter-4 Main particle types an size distribution

Six major particle types in the aerosols were observed in this study, including crustal minerals (47-68%), fly ashes (5-17%), sulfur constituents (4-26%), sea salt (0-3%), biological & botanical particles (1-5%) and miscellaneous particles (3-6%). The crustal minerals amount to about 50-70% of the aerosols, indicating that soil or crustal dust had an important effect on the atmospheric quality. Among these particle types, fly ashes, miscellaneous particles and most of S-rich particles in the sulfur constituents type have an anthropogenic source. The size distribution of Al, Si-rich particles in aerosols for the winter type (November-May) had size peaks at 2-5μm and $>$ 10μm, whereas only at 2-3μm for the summer type (June-October). This suggests that the size of aerosols are largely controlled by seasonal wind. Individual particle analysis revealed that about 80% of the smooth fly ash particles had Al and Si as major compositions, which suggests coal as the fuel, and the number concentrations of Al, Si-rich smooth fly ash were two times higher in winter and spring than in summer and autumn during a one year period.

Chapter-5 Seasonal variation of mineral aerosols

The seasonal variation of major minerals in the aerosols collected in Matsue dring a one year period revealed two peaks of the abundances during spring and early winter (Fig. 1). The seasonal variation of major elements was very similar to that of major minerals. These abundance peaks are consistent with the number peaks of the dust storm reports in China reported by WMO (the World Meteorological Organization) (Merrill et al., 1989), except for the influence from the rainfall and some meteorological factors such as the inversion layer formed easily near the ground during early winter which results in greater atmospheric stability and should favor widescale accumulation of the atmospheric aerosols. Relatively high concentration of Fe in late winter is correlated with relatively high concentration of S, which could suggest a non-soil dust source of these Fe-bearing substance. The ratios of S/Al and Fe/Al all show two peaks in late winter and spring. This means that some anthropogenic substances rich in S and Fe contributed to the atmospheric aerosols.

Chapter-6 Surface enrichment or heterogeneities in large particles by sulfur

A number of submicrometer S-rich particles were present as the coatings on the surface of large aerosol particles such as clay minerals, calcite, fly ash and pollen (Fig. 2). Sulfur

was detected at various levels in different pollens. A washing experiment of the aerosol samples contained with pollens with distilled water was conducted. Before the immersion 20 pollen particles measured all contain S, then of 16 pollen particles measured, only 6 pollen particles contain sulfur after the immersion with 200 ml distilled water for 1 hour. Furthermore, after the immersion with longer time (400 ml, 2 hours), of 15 pollen particles measured only 3 contain sulfur. This result indicates that most sulfur on the pollen particles are coatings accumulated on the surface and water soluble. For the mineral particles, the sequence favorable to be attached by S substances was calcite (83%) > clay minerals (68%) > fly ash (55%) > quartz and feldspars (36%). The accumulation of S substances on the large particle surface suggests that the large particles could serve as surface for the heterogeneous nucleation of SO_2 and conversion to sulfates and as carrier of the acid pollutants.

Chpter-7 Neutralization of acid pollutants by mineral aerosols

The reaction experiment between aerosols and simulated acid rain solutions with pHs 3, 4 and 5, respectively, showed that the solutions of pHs 4 and 5 were significantly neutralized by the aerosols (Fig.3A and B). Whereas the solution of pH 3 was only slightly neutralized by the sample with high Kosa flux (Fig. 3C), indicating that pH of the immersion solutions depended on both acidic or alkaline properties of the aerosols, that is the balance between cation and anion ions dissolved. The sample with high Kosa flux contained relatively high contents of calcite and gypsum, then showed larger neutralizing ability.

The ratios of gypsum to clay minerals, quartz, calcite and halite suggest an increase of gypsum during the transport (Fig. 4). This increase could be caused by (1) transport from arid area of the Asian continent, (2) an addition of sulfates from the Japan Sea, (3) an addition of local air dust containing gypsum due to desulfurization products from power plants in Japan. The nonagreement of abundance between gypsum and calcite implies the possibility that gypsum could result from the reaction between calcite and sulfuric acid attached on the surface of the calcite. The reaction experiment between pure calcite powders and simulated acid rain solutions with pHs 3, 4 and 5, respectively, showed the formation of gypsum crystals after 12 hrs reaction (Fig. 5). This suggests that sulfur coatings on the surface of calcite could lead the reaction between sulfur substances and calcite to form gypsum during the long-range transport. The estimation of gypsum source contribution indicated that this conversion occurred mainly in winter and spring with the contribution ranging between 5-34% (Fig. 6). The conversion is important for the partial neutralization of S-related pollutants during long-range transport.

Chapter-8 Conclusions

The results of this study indicate that mineral aerosols from the Aasian continent arried a large amount of sulfur pollutants to the Japanese Islands during winter and spring. The mineral aerosols could serve as surface for the heterogeneous nucleation of SO_2 and conversion to sulfates. This may be one of the reasons causing lower pH of rain and snow in winter on the Japan Sea district of Japan.

On the other hand, this study indicated that acidity of wet precipitation is depended not only on the SO_4^{2-} concentration, but also on the concentrations of some mineral aerosols such as calcite and clay minerals favorable for neutralizing acids in the atmosphere. The mineral aerosols, as nuclei of acid rain and snow, partially neutralized the acidity of wet precipitation during the long-range transport. This study suggested a possibility that calcite in aerosol could partially neutralize sulfur pollutants as gypsum. On the Japan Sea coast, the transport of mineral aerosols during winter and spring by northwestern monsoon and the reaction between mineral aerosols and the S-related pollutants attached on the surface of mineral aerosols could play an important role for buffering the speed of acidification

on terrestrial and aquatic ecosystems in Japan.

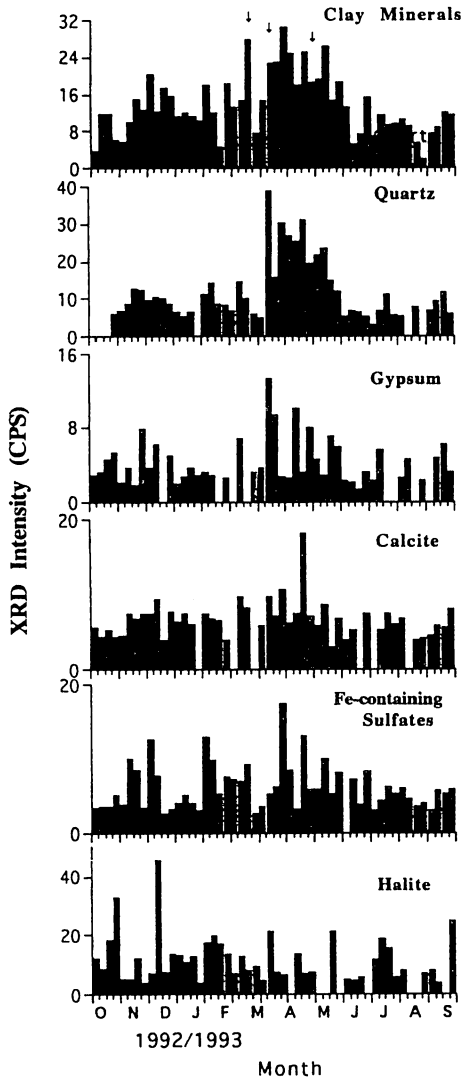

Fig. 1 Seasonal variation of clay minerals, quartz, gypsum, calcite, Fe-containing sulfates and halite in the aerosols collected in Matsue during a one year period. Arrows show the Kosa phenomena recorded by the Meteorological Station of Shimane Prefecture, Japan. Two peaks of abundances could be observed for clay minerals, quartz, gypsum and Fe-containing sulfates in spring and early winter.

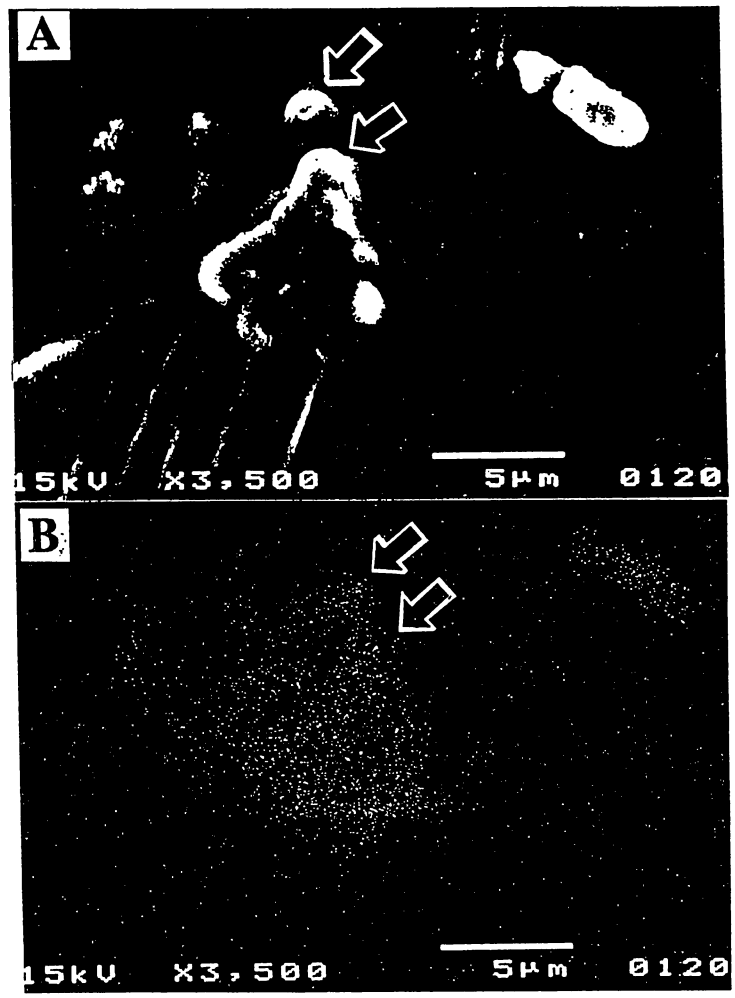

Fig. 2 Scanning electron micrograph (A) and S elemental content map (B) of S-containing fly ash (arrows) and soil particles in snow sample collected in Jan. 15, 1995. Almost all of the soil particles and two smooth fly ash particles (arrows) are all coated by sulfur.

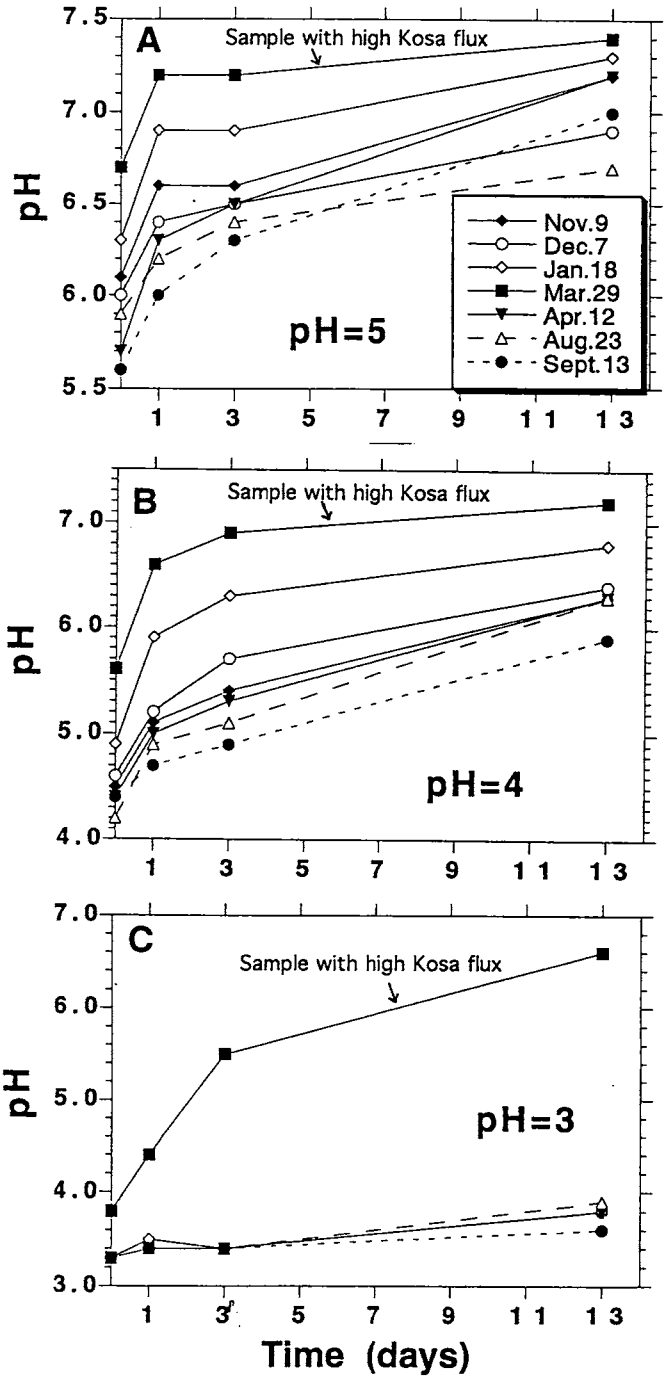

Fig. 3 Change in pH of the system when aerosols reacted with simulated acid rain solutions of pHs 3, 4 and 5, respectively. Samples were collected in Matsue.

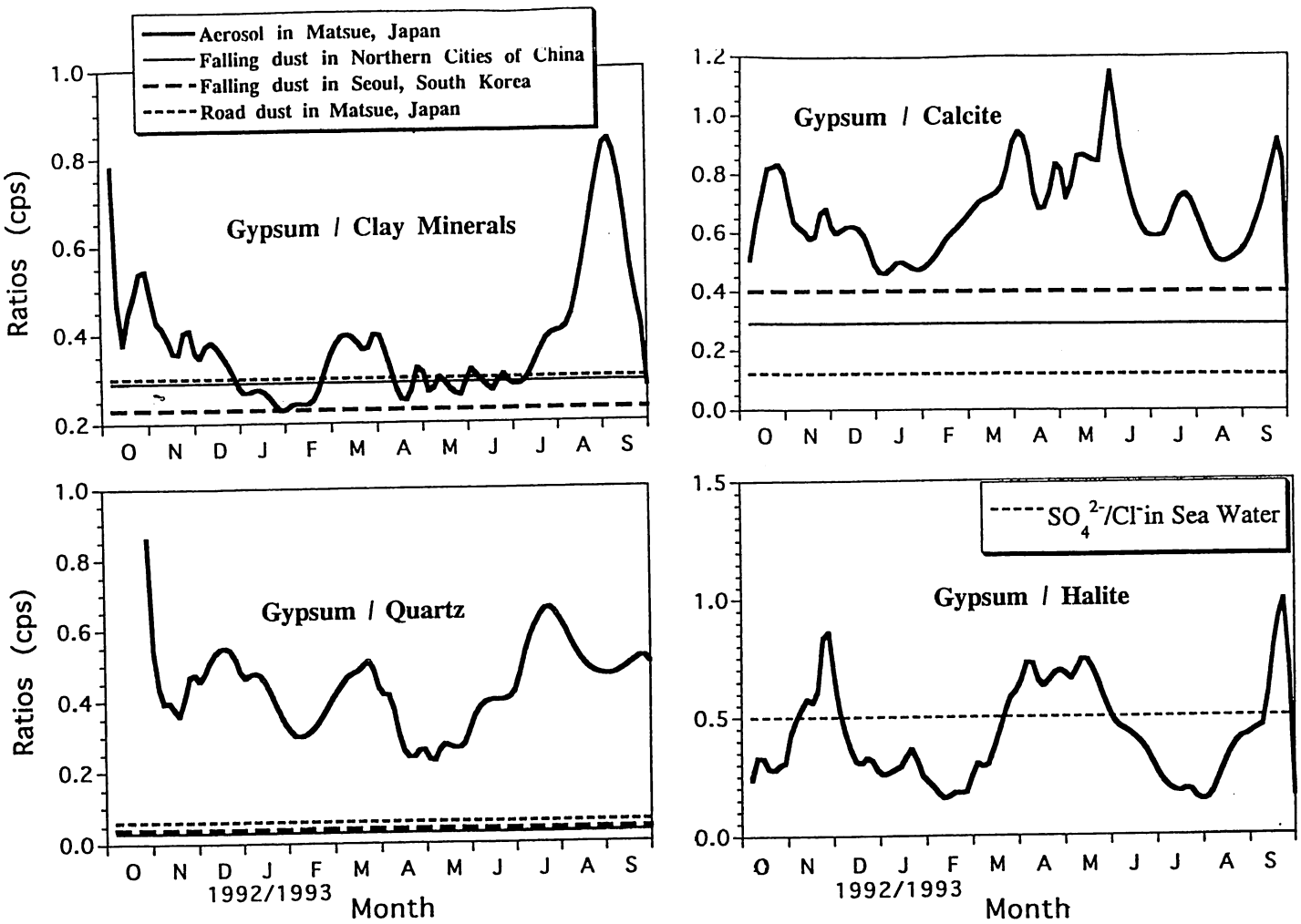

Fig. 4 Changes in the ratios of gypsum to clay minerals, quartz, calcite and halite, respectively, in the aerosols collected in Matsue, Japan. The same ratios in the falling dust collected in northern cities of China (Beijing, Shengyang and Dalian), Seoul, Korea and the road dust collected in Matsue, Japan are plotted as different lines in the graph. The ratio of SO_4^{2-}/Cl^- in sea water is also set in the graph.

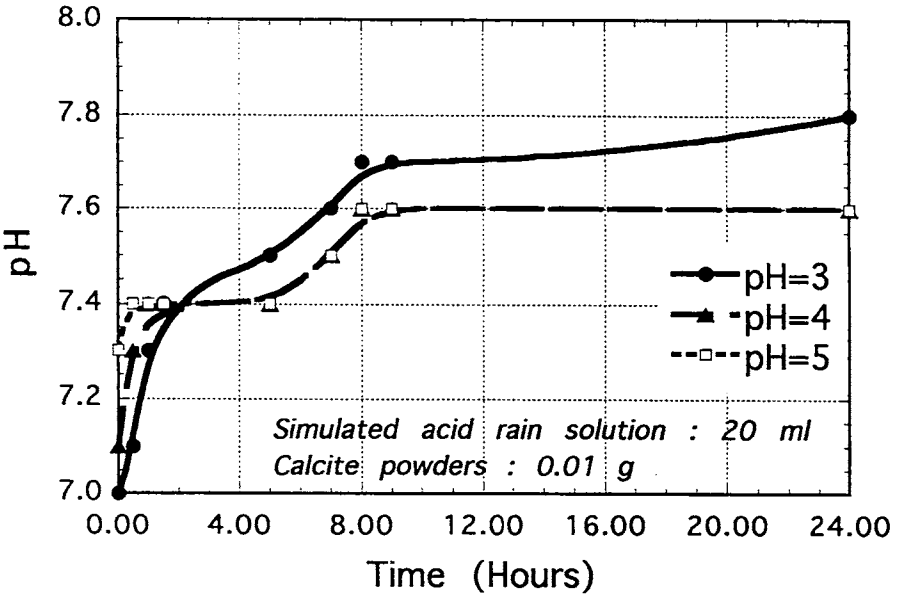

Fig. 5 Changes in pH of the system when calcite powders (0.01 g) reacted with simulated acid rain solutions (20 ml) with pHs 3, 4 and 5, respectively, at room temperature.

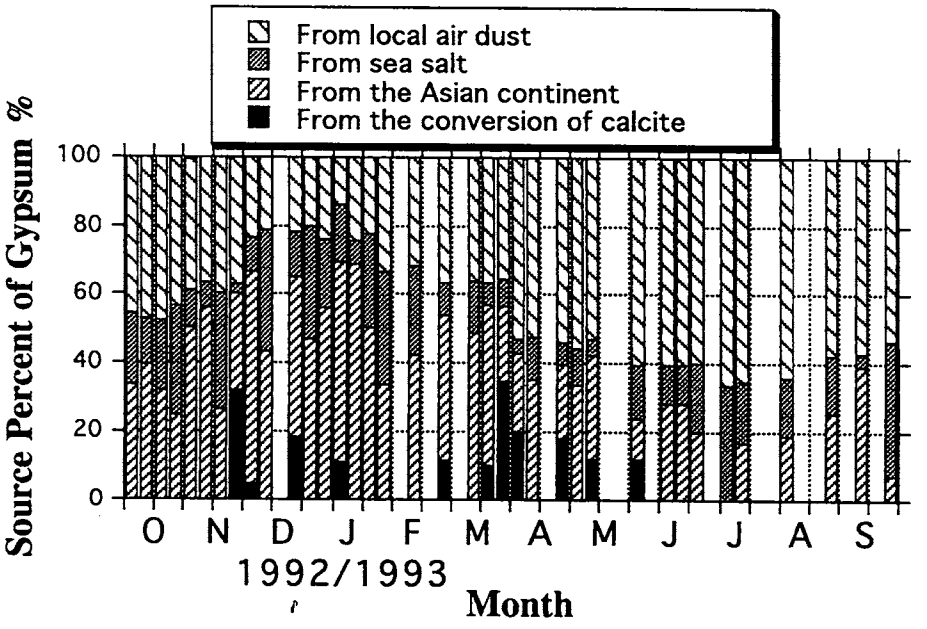

Fig. 6 Major four sources of gypsum during a one year period in Matsue. Gypsum formed in the atmosphere through the conversion of calcite occur mainly during winter and spring times (November -May).

学位論文の審査結果の要旨

周国平の学位論文は，日本の松江・金沢，そして中国各地における大気中の微細粒子を電子顕微鏡により，ミクロンオーダで，鉱物学的，化学的に検討し，さらにグローバルな視点で，その空輸システムとその特徴を明らかにした。エアロゾルの化学組成，鉱物組成の四季による変化は，黄砂とそれに含まれるジプサム，石英，粘土鉱物の含有量に相関しており，黄砂は，酸性降下物を中和する作用があることを示した。さらにXRD, SEM-EDX, TEMのデータからCa/S比の季節変化と発生源の可能性を論じた。以上のような膨大なデータを集め，定性的，半定量的に状況証拠をかためた上で，浸析実験なども行い，“雨にとけない無機物”の分解において，貴重なデータを提供した。地味な分野の新しいアプローチを開拓した点が評価される。参考論文は国際誌かつ一流誌に掲載されており，英語の語学力も高い。なお，学位論文は英語，発表も英語で行われたが，質疑応答は日本語で行い，約30分にわたる充実した内容であった。以上５名の審査員はいずれも，周国平の論文が学位に相当する質の高い論文であると評価した。