Spectrochimica Acta Part B 61 (2006) 393 – 399

SPECTROCHIMICA
ACTA
PART B

www.elsevier.com/locate/sab

Single-particle characterization of soil samples collected at various arid areas of China, using low-*Z* particle electron probe X-ray microanalysis ☆

HyeKyeong Kim, HeeJin Hwang, Chul-Un Ro *

Department of Chemistry, Inha University, Incheon, 402-751, Republic of Korea

Received 8 September 2005; accepted 30 January 2006
Available online 6 March 2006

Abstract

Individual soil particles collected at arid areas of China are analyzed using a single particle analytical technique, named low-*Z* particle electron probe X-ray microanalysis (EPMA). The major chemical species encountered in soil samples are SiO_2, aluminosilicates, $CaCO_3$, Fe-containing particles, and carbonaceous particles. Aluminosilicate particles are the most abundant in soil samples, followed by SiO_2 particles. For soil samples collected at Loess plateau nearby the Yellow river, aluminosilicate and $CaCO_3$ species are more abundantly observed than for soil samples collected at the Tengger and the Hungshandake deserts. Whereas, sand desert soils have higher content of SiO_2 than loess soils.

In this work, using the low-*Z* particle EPMA, it is clearly demonstrated that the relative abundances of each chemical species significantly vary among soil samples. The frequencies to encounter aluminosilicates and the contents of minor elements in aluminosilicate-containing particles are different between soil samples. Also, the contents of calcite, dolomite, and Fe-containing particles vary from sample to sample. This kind of detailed information on chemical composition of source soils could be useful for the identification of the source region of mineral particles in aerosol samples and in the research of chemical modification of Asian Dust particles during long-range transport.

Keywords: Soils; Loess soils; Desert soils; Asian dust; Single particle analysis; Low-*Z* particle EPMA

1. Introduction

Although mineral dust aerosols are the most abundant particulate matters in coarse atmospheric aerosols, researches on mineral dust have much less been carried out than that on anthropogenic aerosols. It might be due to the fact that the mineral dusts are naturally born from soils and observed mostly in coarse fraction. However, the recent recognition for multiple roles of mineral dust aerosols to atmospheric processes has brought researches on mineral dust to a central topic in environmental studies [1,2]. For example, mineral dust can influence global climate, directly by scattering and absorbing solar radiations and indirectly by serving as cloud condensation nuclei [3]. In order to better understand its role of mineral dust in global climate change, it is important to elucidate physicochemical properties of mineral dust, such as its particle size distribution and chemical composition. Since airborne mineral dust is uplifted from soil, the characterization of soil particles is required for understanding characteristics of mineral dust aerosols.

On a global scale, arid and semi-arid areas, such as Saharan desert and the central China, are major sources of airborne mineral dust. Nearly every spring, usually from March to May, "Asian Dust" originating mostly in Central China's arid areas is transported into Eastern China, the industrialized regions of China and over the Yellow Sea to Korea, Japan, and even the Pacific Ocean. Major source regions of Asian Dust are known to be the Yellow River (40°N, 100–110°E), the northwest of the Tibetan Plateau with the Taklimakan desert (40°N, 80–90°E), the Loess plateau (37°N, 100–115°E), and the Gobi desert (43°N, 100–110°E), which are all high-plateau regions with the altitude of 1–2 km [4]. A vast amount of soil particles lifted from the source regions can be transported to eastward and have adverse influence on human health. Moreover, airborne mineral dust can alter chemical balance of the atmosphere by modifying their composition due to heterogeneous chemical reactions. The reactivity of mineral dust is closely related to the mineralogy of source soil particles. For example, calcite ($CaCO_3$) and

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☆ This paper was presented at the Colloquium Spectroscopicum Internationale XXXIV, held in Antwerp, Belgium, 4–9 September 2005 and is published in the special issue of Spectrochimica Acta Part B, dedicated to that conference.

* Corresponding author. Tel.: +82 32 860 7676; fax: +82 32 867 5604.
E-mail address: curo@inha.ac.kr (C.-U. Ro).

0584-8547/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2006.01.012

dolomite ($CaMg(CO_3)_2$) particles can react with NO_x to form nitrate species, and yet gypsum ($CaSO_4.2H_2O$) does not [5]. Therefore, the characterization of source soil particles in fine fraction, which can be transported in long distance, is important to disclose the role of mineral dust in atmospheric environment.

Soil particles are mainly composed of rock-forming minerals. According to their chemical composition, minerals are classified into several types such as silicate, carbonate, oxide, sulfate, phosphate, etc. [6]. Silicate mineral is the most abundant form of minerals constituting earth's crust. The silicate minerals include quartz, feldspar, pyroxene, olivine, mica, and clay minerals. Thus, major elements of silicate minerals, such as O, Si, Al, Na, K, Mg, Ca, and Fe, are major constituents of soil particles. It is known that chemical compositions of mineral dust around the world do not vary so much with the contents of ~ 60% SiO_2 and ~ 10–15% Al_2O_3, and yet the detailed mineralogy of soils can be different at different areas [2].

Many studies on elemental chemical composition of mineral dust originated from Chinese arid areas have been reported [7–10]. Also, two certified reference materials (CRMs) with thirteen certified elemental concentrations for Asian Dust particles are available, which were collected from a loess area and a desert of China [11]. Those works are based on bulk analysis, by which the average elemental composition of mineral dust can be obtained. However, it is somewhat difficult to get detailed information on chemical composition of dust particles based on the bulk analysis. For example, it is not easy to know from the bulk analysis whether calcium element of a mineral dust exists as calcium carbonate or as calcium oxide. Since mineral dust particles are chemically and morphologically heterogeneous, and the average composition and the average aerodynamic diameter do not describe well the population of the particles, micro-analytical methods can be useful for studying mineral dust particles. Electron probe X-ray microanalysis (EPMA) is capable of simultaneously detecting the chemical composition and morphology of a microscopic volume as a single particle. Up to now, many studies on individual mineral aerosols using EPMA have been carried out and it has been proven that more detailed information on chemical composition and morphology of mineral dust can be obtained by the use of the conventional single particle analysis [12–15].

In this work, a recently developed single particle analysis, named low-*Z* particle EPMA, is applied for the characterization of soil particles collected from various arid areas of China. The low-*Z* particle EPMA uses an energy-dispersive X-ray (EDX) detector equipped with an ultra-thin window. The conventional EPMA has a limitation with no ability to detect the elements with atomic number below 11 due to a thick Be window protecting the detector. The use of an EDX detector with ultra-thin window allows the determination of concentrations of low-*Z* elements such as C, N, and O as well [16]. In addition, it was shown that quantitative specification of the chemical compositions can be done by the application of a quantification method, which employs a Monte Carlo simulation combined with reverse successive approximations [17]. Furthermore, the chemical species, in addition to elemental compositions, in individual particles can be determined by the application of the low-*Z* particle EPMA [18]. Since the low-*Z* particle EPMA can clearly identify carbonate, sulfate, and nitrate particles, it has been proven to be useful for the characterization of diverse environmental aerosols [19–21]. Therefore, this low-*Z* particle EPMA is expected to provide detailed information on chemical compositions of source soils and in this work it is clearly demonstrated that soils collected from different arid areas have different characteristics according to their chemical compositions of mineral particles.

2. Experimental

2.1. Soil samples

In this work, chemical compositions of individual soil particles collected at six source regions of Asian Dust particles are analyzed by using the low-*Z* particle EPMA. Geographical data and sampling locations for six soil samples are shown in Table 1 and Fig. 1, respectively (from now on, the six samples will be denoted by city names of sampling locations). Soil samples collected at six locations are divided into two types; loess soil type is for samples Luochuan and Ganquan which were collected at Loess plateau nearby the Yellow river, and sand soil type is for samples collected at sand dunes of two different sand deserts. Samples Shaptou and Minqin were collected at the Tengger desert, and samples Zangbei and Hungshan were collected at the Hungshandake desert located at about 300 km north of Beijing. The soil samples were dried in a convection oven at 105 °C for 24 h and the soil particles were spread out on Ag foil before low-*Z* particle EPMA measurements. Since large soil particles rapidly fall down nearby via gravitational settling after being uplifted into the air, and thus mineral dust in the size range of 1–10 μm is known to be major in Asian Dust aerosols [4], soil particles that are smaller than 10 μm in diameter were analyzed. 500 individual particles for each soil sample, totaling 3000 particles, were analyzed.

2.2. EPMA measurements

The measurements were carried out on a Hitachi S3500N environmental scanning electron microscope equipped with an Oxford Link SATW ultra-thin window EDX detector. The resolution of the detector is 133 eV for Mn-K_α X-rays. X-ray spectra were recorded under the control of EMAX (Hitachi) software. To achieve optimal experimental conditions, such as a low background level in the spectra and high sensitivity for low-*Z* element analysis, a 10 kV accelerating voltage was chosen.

Table 1
Geographical data for sampling locations

Soil type	Sampling site	Location	Altitude (m)
Loess	Luochuan	35.5°N, 109.2°E	1094
Loess	Ganquan	36.4°N, 109.2°E	1029
Desert	Shaptou	37.3°N, 105.0°E	1330
Desert	Minqin	38.3°N, 102.5°E	1378
Desert	Hungshan	42.1°N, 116.3°E	1266
Desert	Zhangbei	41.2°N, 114.5°E	1416