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Records of the atmospheric inputs of loess and pollutants in Japanese lake sediments

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Abstract – The atmosphere is a significant pathway for the transport of loess and pollutants from Asian continental interior to Japan. Loess would play a critical role in many processes during transport either indirectly (e.g., climate) or directly (e.g., health). For kick-off of our research, loess as an Asian monsoon proxy and historical record of sedimentary PAH were reviewed, and research plans to investigate the impact of climate and human activity on loess delivery to Japanese lake systems were proposed.

I. Introduction

Loess falldown from the inland arid in central Asia is called “Kosa (=yellow sand)” in Japan. Frequent dust storms in the arid area of central Asia result in increased delivery of loess to the north Pacific via the prevailing westerlies [1], as well as to the Loess Plateau in China [2]. Dust outbreaks occur in the Asian deserts during spring resulting in seasonally elevated aerosol concentrations as for downwind as Hawaii and the north-western United States [3]. About 80% of the annual aerosol mass deposition on Mauna Loa is due to mineral dust from Asian sources [4].

On geologic time scale, cyclic variations in the Asian monsoon are linked to the orbital cycle of solar radiation and the changing configuration of land and sea resulting from glacial-eustatic changes of sea level [5]. During glacial ages, the buildup of Northern Hemisphere ice sheets results in a stronger atmospheric pressure gradient between land and ocean which intensifies the winter monsoon circulation [6]. The contemporaneous fall in sea level increases the distance between the continental interior and the ocean, thereby contributing to the enhanced pressure gradient and further strengthening the winter monsoon circulation. Under these conditions, dust is deflated, transported downwind, and deposited as loess.

The East Asian monsoon paleoclimate has been well documented by loess-paleosol sequences in the Loess Plateau of China [5]. Several proxy indicators have been proposed to reflect variations of monsoon climate through quasi-independent pathways in the continental and atmospheric systems. For example, grain-size variations of the coarse quartz fraction in loess indicate the relative wind strength of the dust-bearing winter monsoon [6]. Magnetic susceptibility of loess-paleosol sequences responds to the intensity of pedogenesis and records the circulation change of the summer monsoon. However, each of these monsoon proxies needs to be verified by other indices that are independent and vary synchronously. Thus, it is necessary to develop new proxy indices. Some geochemical parameters, such as the Ge/Si ratio of opaline silica [7] and the strontium isotopic ratio of marine carbonates [8, 9], have proved to be important in reconstructing the history of continental weathering. The Rb/Sr ratio may also be used as an indicator of chemical weathering in relict profiles [10]. Although such geochemical parameters are useful for the estimation of monsoon strength, in order to estimate loess flux from the sedimentary record, it is necessary to distinguish subcomponents within detrital component, specify origin, and estimate their content.

As mentioned above, the geochemical, geophysical and mineralogical investigations of loess can provide useful information about climatic history. On the contrary, from the viewpoint of the material cycle, the role of loess as a media of reaction and material transportation in troposphere is also important due to their high chemical affinity. It was well documented that mineral aerosol particles are mixed with aerosols from pollution sources in Eastern Asia [11], and the originally alkaline aerosol is neutralized by acidic sulfates [12]. If the loess records the atmospheric transport and input of anthropogenic pollutants into marine or lacustrine sediments, their vertical distributions of the pollutant would be used as an excellent proxy of human activities.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and have been identified in a variety of soils, natural waters and wastewaters. Although they also occur naturally, high levels of PAHs are mainly attributed to anthropogenic origin. They are also emitted into the atmosphere from numerous combustion process, e.g., traffic, domestic heating, biomass burning, etc. Potential toxic effect of PAHs, that has gained attention in recent years, is endocrine disruption. PAHs and their metabolites have been shown to influence endocrine functioning, although the evidence is limited because of only few PAHs have been studied so far.

Terrestrial sediments, especially, lacustrine sediments have some advantages that include high-resolution environmental records; biological-information-rich records

as well as physical and chemical ones, compared with deep-sea sediment records and ice core records [13]. Fortunately, one of the author (K.K.) has conducted on many studies of lacustrine sediments from central and eastern Asian lakes such as Biwa, Baikal, Hubsugul. From these efforts, we can approach to a lot of cores of the lacustrine sediments which have been already dated and characterized. Until now, the studies lacustrine sediments focused on grain size of the constituent materials such as sand, silt, biogenic silica, and so on. In this study, clay fractions and organic materials as component of loess, and contaminants such as PAHs and heavy metals will be focused on. Goal of our research is to understand the historical flux of loess from the record of the deposit and to show principal effects of loess on the environment in Pan Japan sea area. For kick-off of our research, loess as Asian monsoon proxy and historical record of sedimentary PAH are reviewed, and research plans to investigate the impact of climate and human activity on sediment delivery to lake systems in Japan are proposed.

II. Global dust and the glacial cycles

Records of dust accumulation from ice cores, marine and lacustrine sediments, and loess deposits clearly demonstrate that glacial periods were dustier than interglacial periods throughout the Quaternary. The high concentrations of atmospheric dust during glacial periods make this time period an excellent test of our ability to model the processes that determine fluxes, concentrations, and feedbacks of dust in the atmosphere. Mineral dust is emitted to the atmosphere from areas with sparse vegetation, low soil moisture, and sufficiently intense surface winds. The natural sources today are mainly in the arid subtropics. However, human activity may be increasing the atmospheric burden of dust through wind erosion of agricultural land, industrial and construction activities. The increases in anthropogenic dust sources may be countered by source region decreases due to anthropogenically-induced climate changes.

Mineral dust plays multiple roles in mediating physical and biogeochemical exchanges among the atmosphere, land and ocean, although the net effect of atmospheric dust is still unknown. The magnitude and even the sign of dust radiative forcing depends on dust optical properties. The total effect of dust under different climates is not obvious without detailed model calculations. In terms of biogeochemistry, dust provides a key micronutrient (e.g., Fe [14]) source for both terrestrial and marine ecosystems. The input of loess to high-nutrient and low-chlorophyll regions of the ocean could be a factor contributing to the regulation of marine primary production, ecosystem composition, and thus to the export of carbon to the deep ocean. In terms of atmospheric chemistry, SO_2 adsorption by dust particles could significantly reduce the radiative cooling of sulphate aerosols, while heterogeneous reactions on the surface of dust particles may reduce the concentrations and radiative warming effect of O_3 in the troposphere.

The dust content of the atmosphere has varied in association with natural climate change and was massively increased during glacial periods, as shown by stratigraphic records from polar and tropical ice caps, marine and lacustrine sediments, and loess deposits. The last glacial maximum (LGM ca. 21,000 calendar yr B.P.) is a key period for modeling the fluxes, concentrations and interactive effects of dust in the atmosphere. This is partly because the LGM atmosphere was far dustier than it is today and so should have a large effect on the Earth system The LGM has been a primary target for palaeoclimate modelling, and observational data sets describing the state of the Earth's surface (vegetation, hydrology, surface deposits).

III. PAHs in environment and their records in sediments

According to Hites, Laflamme, Farrington [15], at present, there is consensus that these PAH mixtures are not produced biologically but rather that they result from the deposition of combustion-generated airbone particulate matter. There is, however, no consensus on whether these particulates are natural or anthropogenic. This is an important question. If the source were natural (ex., forest fire), human would have been exposed, for much of their history, to a burden of carcinogenic PAH to which human may well have developed a certain toletance. On the other hand, if the source were human activities, this tolerance probably would not exist since the level of environmental PAH would have been continuously increasing. In most cases, increased level of fossil fuel (primarily coal) combustion over the past 100-125 yr are probably responsible for the elevated PAH concentrations in the surface sediment layers compared to deeper layers in several lakes. PAH are widely dispersed by the atmosphere when adsorbed onto soot and airbone particulates. In fact, low levels of PAH were found in sediments remote from combustion sources, at least in part, to long-range atmospheric transport [16].

PAH are generally present as complex mixtures containing both alkylated and non-alkylated species, the relative distribution of which can provide information on the probable source of the PAH in the sediments. If the source is the direct deposition of petroleum (for example, a spill or seepage), the PAH mixture is deficient in unsubstituted species. If the source is the deposition of combustion generated PAH, the mixture is characterized by homologs which decrease in abundance as the degree of alkyl substitution increases. This type of mixture results from both natural (e.x., forest fire) and anthropogenic (e.x., fossil fuel) combustion. If the source is the *in situ* aromatization of naturally occurring precursors such as plant terpenes, the PAH mixture is less complex and contains compounds which are directly related to the skeletal structures of the precursors. Examples of naturally derived PAH are perylene, retene and certain alkyl chrysene and picene species [16].

These three sources have different relative distribution patterns and, therefore, can be identified by quantitative measurements of various alkylated and non-alkylated PAH.

Unfortunately, the ability to distinguish between natural and anthropogenic combustion by this method alone is limited. To make this distinction, the historical record of PAH deposition in sediment cores should be examined.

Soils and sediments are universal sinks for PAHs. Under certain sediment condition, it is possible to determine the historical record of deposition of PAH. Until now, the historical record of PAH pollution was largely derived from the analysis of marine and lacustrine sediments, which were deposited under anoxic conditions [15, 17-24]. For example, Fig. 1 shows the vertical distribution profiles of PAH in floodplain sediments [24]. In the profiles the PAH contents decrease rapidly from the surface horizon to a depth of 52 cm and then remains on an almost constant low level further downwards. Among the PAHs, phenanthrene is present in relatively high contents compared with the higher molecular weight in the section below a depth of 40 cm. Because phenanthrene is the most water soluble and biodegradable compound of the investigated PAH, it is necessary to note the subsurface transport by seepage water, biodegradation, adsorptive properties of the PAH for determination whether the profiles is original or altered after deposition.

IV. Major challenges for this project

For estimation of loess and PAH fluxes into Pan-Japan Sea area, the following three challenges are primarily in this project;

(1) to determine the loess layers in Japanese lacustrine sediments and indices for the reliable historical information,
(2) to quantify the dust forcing effects from the records in Japanese lacustrine sediments and the resulting impacts on to climate
(3) to assess the impact of increased dust input on lacustrine productivity and possible effects of high dust concentrations and human activity windward on heterogeneous chemistry in atmosphere, the atmospheric PAH cycle, and ecosystem in the lake leeward.

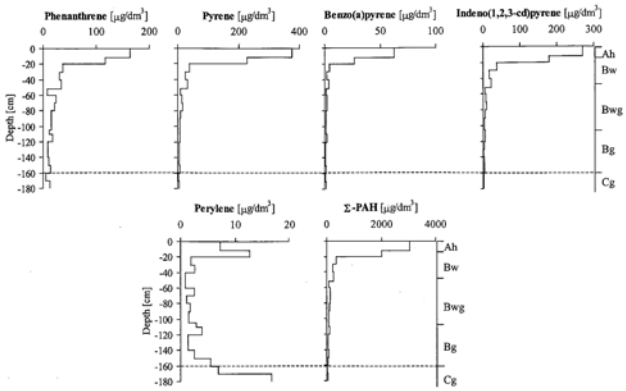

Fig. 1 Depth profiles of PAH. The interrupt line at the depth of 160 cm symbolizes the facies change from overlaying loamy to sandy sediments [24].

V. Main approaches of this project

As mentioned above, until now, the studies of lacustrine sediments has been extensively performed and mainly focused on grain size of the constituent materials such as sand, silt, biogenic silica. In this project, mineralogical and geochemical analysis will be applied to the same lacustine sediments previously studied and compared with already obtained geophysical and geochronological data. In order to obtaine the short-term and *in situ* data, sediment traps will be set up at several lakes in Korea and Japan where are leeward of strong dust storm in spring. And to specify the source, compositions of stable isotopes, minerals and contaminants in the individual sample will be measured by direct observations using laser abrasion inductively coupled plasma mass spectroscopy (LA-ICP-MS) and transmittion electron microscopy (TEM) with either energy-dispersive X-ray spectrometry (EDS) or electron energy-loss spectroscopy (EELS). Sequential extraction method will also be applied to the samples to determine which phase is the most effective for the sorption of PAHs and heavy metals. In addition, atomic force microscopy (AFM) and ESEM are useful for measuring particle sizes and morphologies under ambient conditions, although the particles are not in the air but on a collection surface. Both microscopies can be put to use in the study of the hygroscopic behavior of individual particles, by measuring size changes in an environmental cell under precisely controlled relative humidity conditions. If it is necessary, we can measure the XRD patterns under precisely controlled relative humidity conditions.

LA-ICP-MS is a powerful analytical tool for small, solid samples. The advantages of LA-ICP-MS over conventional solution nebulization ICP-MS are as follows: (A) Analysis of solid samples is direct and requires no lengthy dissolution processing which may be incomplete and can also potentially introduce contamination to the sample; (B) Analysis of solid samples by LA-ICP-MS requires little preparation (a flat surface may be required if the entire sample is to be probed, but it need not be parallel to better than 200 μm provided that the focus of the laser does not change from one part of the sample to another, resulting in different ablation characteristics); (C) a dry sample is introduced to the plasma with a resulting lack of polyatomic interference species produced by the interaction of water and acid species with the argon plasma.

Compared to other micro analytical techniques, LA-ICP-MS has several distinct advantages: 1) Laser probing utilizes light rather than charged particles and can, therefore, analyze both conducting and non-conducting material without the need for a conductive coat and/or other charge balancing techniques, as in SIMS and electron microprobe techniques; 2) no vacuum is required in the sample chamber, although an airtight seal is; 3) LA-ICP-MS, unlike Atomic Emission Spectroscopy, separates the ionization step from the sampling step---the laser is used to ablate the sample only and the material is transported to the secondary plasma source in the torch of the ICP. Therefore,

both steps can be independently controlled and optimized; 4) the high sensitivity of the ICP-MS allows small samples to be quantified, which is ideal for LA-ICP-MS in that spatial resolution can be used to investigate compositional gradients across a sample, even though the laser sampling area is 5-10 times greater than that obtained for the electron or ion microprobes. However, the spatial resolution and detection limit of LA-ICP-MS is being constantly reduced for in situ analysis of solid samples. Finally, trace-element analysis using LA-ICP-MS does not require involved interference corrections inherent in SIMS analysis. Given this proviso, it has been found that a larger number of elements can be accurately quantified by LA-ICP-MS over SIMS, provided well characterized standards are available, with a detection limit similar to that of SIMS.

Consequently, LA-ICP-MS is a technique used for the *in situ* analysis of trace elements in solid samples. It can determine many elements in the periodic table to high degrees of accuracy and precision. The technique complements electron microprobe analysis, typically measuring trace elements at a lower concentration range (1 ppb - 100 ppm). By using LA-ICP-MS, mineralogical and geochemical information in sub-mm scale of the sediments may be obtained

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