The spatial and temporal distributions of spheroidal carbonaceous particles (SCPs) from sediment core samples from industrial cities in Japan and China

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Abstract Spheroidal carbonaceous particles (SCPs) are produced by the high-temperature combustion of fossil fuels and are emitted to the atmosphere. The distribution and concentration of SCPs in sediments have been used as a proxy of the distribution of pollutants emitted to the atmosphere. However, the effect on the distribution of SCPs of industrial activity at nearby industrial cities has yet to be quantified. To clarify the origin of SCPs of ~20 μm in size that are preserved in sediment, we evaluated the abundance, surface morphology, and chemical composition of SCPs in sediment core samples recovered from industrial cities in Japan (Tokyo, Osaka, and Nagasaki) and China (Beijing), with the cities being located at least ~500 km from each other. Vertical profiles of SCP concentration in sediment cores from the Japanese cities and Beijing are different, reflecting the contrasting industrial histories of the two countries. The SCPs from the different cities show contrasting morphological and chemical characteristics, suggesting that ~20 μm SCPs in sediments from industrial cities could represent the local combustion history in detail, as the influx of local SCPs is dominant at such sites.

Keywords Chemical composition · Combustion history · Industrial activity · Spheroidal carbonaceous particles (SCPs) · Sediments · Surface morphology · Transportation

Introduction

Spheroidal carbonaceous particles (SCPs) and inorganic ash spheres (IASs) are produced by the high-temperature combustion of fossil fuels and are emitted to the atmosphere. Elemental carbon particles, such as SCPs, are potentially characteristic of the source fuel material, based either on their composition or the parameters of combustion (e.g., Griffin and Goldberg 1979; Rose et al. 1994). Under favorable conditions, these combustion products are deposited in sediments, preserving a historical record of the burning of fossil fuels. Particles from different sources can then be mapped, revealing the pattern of particle distribution in regions and entire countries (e.g., Griffin and Goldberg 1979, 1981; Rose et al. 1994, 1996, 1999; Rose 1995; Alliksaar et al. 1998).

Although both SCPs and IASs are largely deposited within 70–100 km of their sources (e.g., Boyle et al. 1999; Rose et al. 2002, 2004; Larsen 2003), they are able to travel thousands of kilometers in air streams and their presence has been recorded in lake sediments at remote locations such as Greenland, Antarctica, and the Tibetan Plateau (Nagafuchi et al. 2009 and references therein). Furthermore, the generally smaller size range of IASs (0.05–10 μm) has resulted in their identification in mid-ocean air samples (Parkin et al. 1970), deep-sea marine sediments (Fredriksson and Martin 1963), high-latitude ice deposits in Greenland (Hodge et al. 1963; Bindler et al. 2001) and Antarctica (Hodge et al. 1967), and in rime ice and lake sediment in alpine areas (Nagafuchi et al. 1995, 2009). SCPs are generally larger than IASs, with particle sizes of >10 μm being dominant (Rose et al. 2002; Larsen 2003); consequently, their transportation distance is less than that of IASs. Although Larsen (2003) suggested that SCPs >5 μm in lake sediments could potentially provide a better signal of locally deposited atmospheric pollution, the effect of industrial activity from nearby industrial cities on the spatial distribution and concentration of SCPs has yet to be investigated.

In this study, to clarify the origin of ~20 μm SCPs preserved in sediments, we analyzed the abundance, surface morphology, and chemical composition of SCPs in sediment core samples recovered from industrial cities in Japan (Tokyo and Nagasaki) and China (Beijing). The distances between Tokyo and Nagasaki, Tokyo and Beijing, and Nagasaki and Beijing are 950, 2000, and 1450 km, respectively. Combined with data obtained previously at Osaka (Murakami-Kitase et al. 2010), located 410 km from Tokyo, we discuss the origin and transportation of ~20 μm SCPs in sediment core samples recovered from industrial cities located at least ~500 km from each other.

Materials and Methods

The sediment core samples were collected from Tokyo, Nagasaki, and Beijing (Fig. 1) and were analyzed with the aim of investigating the characteristics of SCPs in different industrial cities located in Northeast Asia. These cities are the largest industrial cities in Northeast Asia, thereby providing an important opportunity to explore the historical trend of urban atmospheric pollution in the region. The local dominant wind direction for each city investigated in this study changes significantly between in summer and winter: the sampling site in each city would be located on down–wind direction of the nearest (less than a few tens of kilometer) industrial area at least in a season over a year. Often, in palaeolimnological studies, a single deep-water sediment core is used as representative of the whole basin (lake, bay, swamp and so on), although potential problems from employing the single core approach undertaken at the other study sites could be identified. To use a single sediment core as a representative, it is necessary to choose the site area where is flat and undisturbed. In this study, we chose the sites to collect sediment core samples where are of (1) stable water flow, (2) deposition of muddy sediments, (3) distantness from water inflow and (4) there is no artificial disturbance.

Table 1 provides brief descriptions of the analyzed samples. Koike Pond (35°35'57"N, 139°41'51"E; elevation 30m above sea level) located in Tokyo, is the closest industrial area, Kawasaki City that has power stations is 20 km south of the pond. Nagasaki Bay (32°44'35"N, 129°51'44"E) is a 4 km long bay that has harbors; the area around the bay is an industrial area. Fire power stations locate 30 km northwest of the bay. Huairou Reservoir (40°18'18"N, 116°16'39"E; elevation 60m above sea level) is located in a residential area, 50 km northeast of the center of Beijing. Power plants locate 50–100 km southwest from the reservoir. The sediments from Tokyo, Nagasaki, and Beijing cover the period at least from the 1940s to the 2000s, the 1940s to the 2000s, and the 1960s to the 2000s, respectively. The sediments were dated by the vertical profiles of ^{137}Cs and ^{210}Pb activities in the sediment cores (Fig. 2). The method of the age determination has been described in some papers (e.g., Yasuhara and Yamazaki, 2005; Katahira et al., 2007) in detail. The ^{210}Pb profiles in the upper part of each sediment core are almost fit to the decay curve calculated from a half-life of ^{210}Pb, and the ^{137}Cs activities in each sediment core are consistent with the historical trends of the annual fallout (National Institute of Radiological Sciences, 1963-1989), indicating that the ^{210}Pb ages after 1950 (Koike Pond and Nagasaki Bay) or 1970 (Huairou Reservoir) are very reliable. The sediments ages prior to 1950 were estimated by the extrapolation methods, because the ^{210}Pb profiles prior to 1950 are not fit to the decay curve.

Following the extraction method of Rose et al. (1994) and Murakami-Kitase et al. (2010), dry subsamples of 0.2–0.4 g were subjected to chemical digestion to remove all material except for SCPs. Digestion involved the sequential application of 60% concentrated nitric acid (HNO_3), 46% hydrofluoric acid (HF), and 6 M hydrochloric acid (HCl).

For analysis of vertical profiles of the number density of SCP in the sediment cores, we measured the number of SCPs per 1 g of dry sediment sample. After HNO_3 treatment, approximately 138,000 plastic microspheres (Ogden 1986) of 15 μm in size were added to facilitate the calculation of SCP concentrations. After chemical treatment, each subsample was mounted on a glass slide using glycerol jelly. The numbers of SCPs and microspheres were counted at 200× magnification under both transmitted light and incident light using an optical microscope. SCP selection was restricted to black, rounded particles with many pores and a characteristic glossy appearance when observed under incident light. We also measured the sizes of SCPs larger than 5 μm. The number and size of SCPs in each subsample were measured from at least 1000 microspheres. Using this method, we analyzed samples from 50 different stratigraphic levels within the Tokyo core, 40 different levels within the Nagasaki core, and 26 different levels within the Beijing core.

For analyses of surface morphology and chemical composition, the extracted SCPs were mounted on glass slides, coated with a thin layer of carbon, and observed using a JEOL JSM-5500 scanning electron microscope (SEM) equipped with an EDAX-EDS system (CDU-LEAP detector + Genesis software), housed at the Department of Geosciences, Osaka City University, Japan. The SEM was operated at an accelerating voltage of 20 kV and beam current of 500 pA. The obtained X-ray spectra confirm that the SCPs consist mainly of carbon. We used EDS to quantitatively analyze the concentrations of Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. The intensities of the characteristic X-rays were corrected using the ZAF method. Using the above method, we analyzed 139 particles from seven stratigraphic levels within the Tokyo sample, 129 particles from six levels within the Nagasaki sample, and 28 particles from two levels within the Beijing sample.

Results and Discussion

In the Japanese samples, SCPs are found in sediments prior to 1950, presumably dated back to 1930s (Fig. 3a, b). The concentration of particles increases between the 1940s and the 1970s, and decreases after the 1980s. Most of the particles are less than 70 μm in size; the mean particle sizes for the Tokyo and Nagasaki samples are 18 and 23 μm, respectively. These vertical profiles are similar to the profile for the sediment core from Osaka (Fig. 3d). These secular variations in SCPs in sediment from Japanese cities are comparable with temporal variations in the consumption of coal and oil in Japan (Fig. 4a). In the Beijing sample, the number of particles shows an abrupt increase in the 1990s (Fig. 3c). Most of the particles are less than 60 μm in size; the mean particle size is 21 μm. This secular variation in SCPs in sediment from Beijing is comparable with temporal variations in the consumption of coal and oil in China (Fig. 4a).

Three types of SCP surface morphologies were recognized from SEM observations: (i) smooth (Fig. 5a), (ii) rough and irregular (Fig. 5b), and (iii) convoluted and layered (Fig. 5c). According to the classification scheme proposed by Griffin and Goldberg (1979, 1981), the former two types correspond to coal-derived carbon particles, and the latter to oil-derived carbon particles. Hereafter, the former two types are referred to as 'non-convolute type' and the latter as 'convolute type.' The sediment core samples recovered from Japanese cities record a significant increase in the abundance of SCPs with convolute-type morphology in post-1940s sediments (Fig. 6). This finding suggests that the sources of convolute-type particles, such as oil carbon produced by industrial activity, grew dramatically in Japan from the 1940s. In contrast, the sediment core sample from Beijing contains no convolute-type SCPs (Fig. 6), probably reflecting the fact that in Beijing, industrial activity producing coal carbon particles far exceeds that producing oil carbon particles.

Among the Japanese cities, there exist differences in the ratio of the abundance of convolute-type to non-convolute-type SCPs. In Japan, coal- and oil-fired power stations are major sources of emissions of SCPs and IASs to the atmosphere. Figure 3b shows the annual combustion of oil and coal at power plants in three different districts in Japan for a period of 60 years: the Kanto district, including Tokyo; the Kansai district, including Osaka; and the Kyushu district, including Nagasaki. The combustion histories of power plants in these districts are similar overall : coal was the dominant fuel in all districts during the 1950s and 1960s, oil became the dominant fuel from the early 1970s, and oil consumption decreased from the late 1970s. However, the geographical origin of the consumed oil and coal differs among the districts (Kyushu Electric Power 1991; KEPCO 2002; TEPCO 2002).

Figure 7 shows the relationship between the surface morphology and chemical composition of SCPs from Tokyo and Nagasaki; in the figure, SCPs derived from the combustion of oil plot near the S apex (the relationship for SCPs from Osaka Bay has been described by Murakami-Kitase et al. 2010). For the SCPs from Tokyo and Nagasaki, those with convolute-type surface morphology (suggesting an origin from oil-derived carbon) tend to plot near the S apex, close to the S–Si line, while non-convolute-type SCPs tend to plot away from the S apex.

Figure 8 shows S–Al–Si ternary diagrams for different age periods, showing the chemical compositions of SCPs obtained from sediment core samples from Tokyo, Nagasaki, and Beijing, along with data from Osaka Bay (Murakami-Kitase et al. 2010). For all age periods, the SCPs derived from Tokyo and Nagasaki sediments plot near the S–Si line, whereas those from Osaka have high Al contents (except for the 1990s and 2000s). The Beijing SCPs are different from the Japanese SCPs, plotting near the Si–Al line.

The profiles of SCP concentrations for the various Japanese cities are similar to each other, but are different from the profile for Beijing. Given that Japan and China have different histories of coal and oil consumption. The surface morphology and chemical characteristics of SCPs in sediments from different Japanese cities are somewhat different, suggesting that the chemical composition of SCPs may correspond to the fuel source (i.e., place of origin) consumed in a local area located at least ~500 km from other industrial cities. These differences in the chemical composition and morphology of SCPs among Japanese cities suggest that analysis of SCPs could be used to identify their sources, even in the case of different areas with similar combustion histories. Furthermore, the chemical compositions of SCPs from Japan and Beijing plot in different fields on ternary diagrams, indicating that SCPs transported from Beijing to Japanese cities were much fewer than those emitted and deposited nearby in Japanese cities.

The above finding is consistent with the results of Nagafuchi et al. (2009), who reported that most of the SCPs in a mountain lake in Japan originated from Japanese industrial activity. Although Rose et al. (2004) reported that SCPs are largely deposited within 70–100 km of their source, Bindler et al. (2001) discovered SCPs derived from Europe in lake sediments within Greenland, indicating the long-distance transportation (several thousand kilometers) of SCPs. Larsen (2003) suggested that very fine-grained SCPs (particle sizes of < 10 μm) could be transported for long distances in the atmosphere, although most of the SCPs emitted by industrial activity are 10–20 μm in size (Rose et al. 2002). Consequently, although some SCPs that originate from China may be transported to industrial cities in Japan by the monsoon and the temperate westerlies, like eolian dusts (e.g., Inoue and Naruse, 1986; Zhou et al., 1996; Ma et al., 2001), the number would be too small to identify them from among SCPs emitted by *in situ* industrial activity. This conclusion does not preclude the occurrence of long-distance transportation of ~20 μm SCPs; however, the dominant SCPs are derived locally, reflecting the local combustion history and geographic origin of oil and coal, which differ from that of other industrial cities.

The present results show that in order to reduce the influence on the distribution of SCPs of local industrial activity, SCPs should be investigated from lake sediments upon isolated islands or at sites located at least several hundred kilometers from the nearest industrial city. The morphology and chemical composition of SCPs are key factors in clarifying the source of particles in sediments.

Conclusions

We evaluated the abundance, surface morphology, and chemical composition of SCPs in sediment core samples recovered from industrial cities in Japan (Tokyo, Osaka, and Nagasaki) and China (Beijing). These cities are located at least ~500 km from each other. The vertical profiles of SCP concentrations in the sediment cores from Japanese cities are similar to each other, but different from the profile for Beijing, reflecting the contrasting industrial histories of the two countries. The morphological and chemical characteristics of SCPs differ among Tokyo, Osaka, Nagasaki, and Beijing, indicating that ~20 μm SCPs in sediments in industrial cities represent the local combustion history in the case that the city is located at least ~500 km from other cities where large amounts of SCPs are emitted.

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Table 1 Summary of description of the sediment core samples from the different localities

	Tokyo Koike Pond	Nagasaki Nagasaki Bay	Beijing Huairou Reservoir
Locality	35°35'57"N 139°41'51"E	32°44'35"N 129°51'44"E	40°18'18"N 116°36'39"E
Water area	6.0×10^3 m^2	1.1×10^7 m^2	6.6×10^6 m^2
Date of recovery	May, 2008	July, 2007	September, 2008
Length of core	1.7 m	1.6 m	0.52 m
Lithology (sample depth)	0–1.1 m: clay 1.1–1.25 m: silt 1.25–1.7 m : silt with very fined-grained sand	0–1.3 m: silt 1.3–1.6 m: clay	0–0.52 m: clay

Figure captions

Fig. 1 Locations of the sediment core samples recovered from industrial cities in Japan (Tokyo and Nagasaki) and China (Beijing). Shaded areas (Kanto, Kansai, and Kyushu districts) indicate regions where electric power is supplied by different power companies (TEPCO, KEPCO, and Kyushu Electric Power Co., respectively).

Fig. 2 Vertical profiles of ^{137}Cs and ^{210}Pb activities in the analyzed cores for dating.
(a) Koike Pond, Ota Ward, Tokyo. (b) Nagasaki Bay, Nagasaki. (c) Huairou Reservoir, Beijing.

Fig. 3 Vertical profiles of the number density of SCP in the analyzed sediment cores. (a) Koike Pond, Ota Ward, Tokyo. (b) Nagasaki Bay, Nagasaki. (c) Huairou Shuiku Reservoir, Beijing. (d) Osaka Bay, Osaka (data from Murakami-Kitase et al. 2010).

Fig. 4 (a) Secular variations in the consumption of coal and oil in Japan and China (BP Statistical Review of World Energy 2009). (b) Combustion history at power plants in three different districts in Japan: Kanto district, including Tokyo; Kansai district, including Osaka; and Kyushu district, including Nagasaki. Data sources: Kanto district, TEPCO (2002); Kansai district, KEPCO (2002); Kyushu district, Kyushu Electric Power (1991).

Fig. 5 Representative examples of three distinct SCP surface morphologies identified from SEM images. The left-hand images are enlargements of the areas indicated by rectangles in the right-hand images. (a) Smooth structure. (b) Rough and irregular structure. (c) Convoluted and layered structure.

Fig. 6 Percentage of SCPs with each morphology type at different levels within the sediments cores. (a) Koike Pond, Ota Ward, Tokyo. (b) Nagasaki Bay, Nagasaki. (c) Huairou Shuiku Reservoir, Beijing. (d) Osaka Bay, Osaka (data from Murakami-Kitase et al. 2010).

Fig. 7 S–Al–Si ternary plots showing SCPs from sediment core samples recovered from Tokyo and Nagasaki.

Fig. 8 S–Al–Si ternary plots showing SCPs from the main industrial cities in Japan and China. Data for Osaka Bay are from Murakami-Kitase et al. (2010).

Figure 1 (Hirakawa et al)

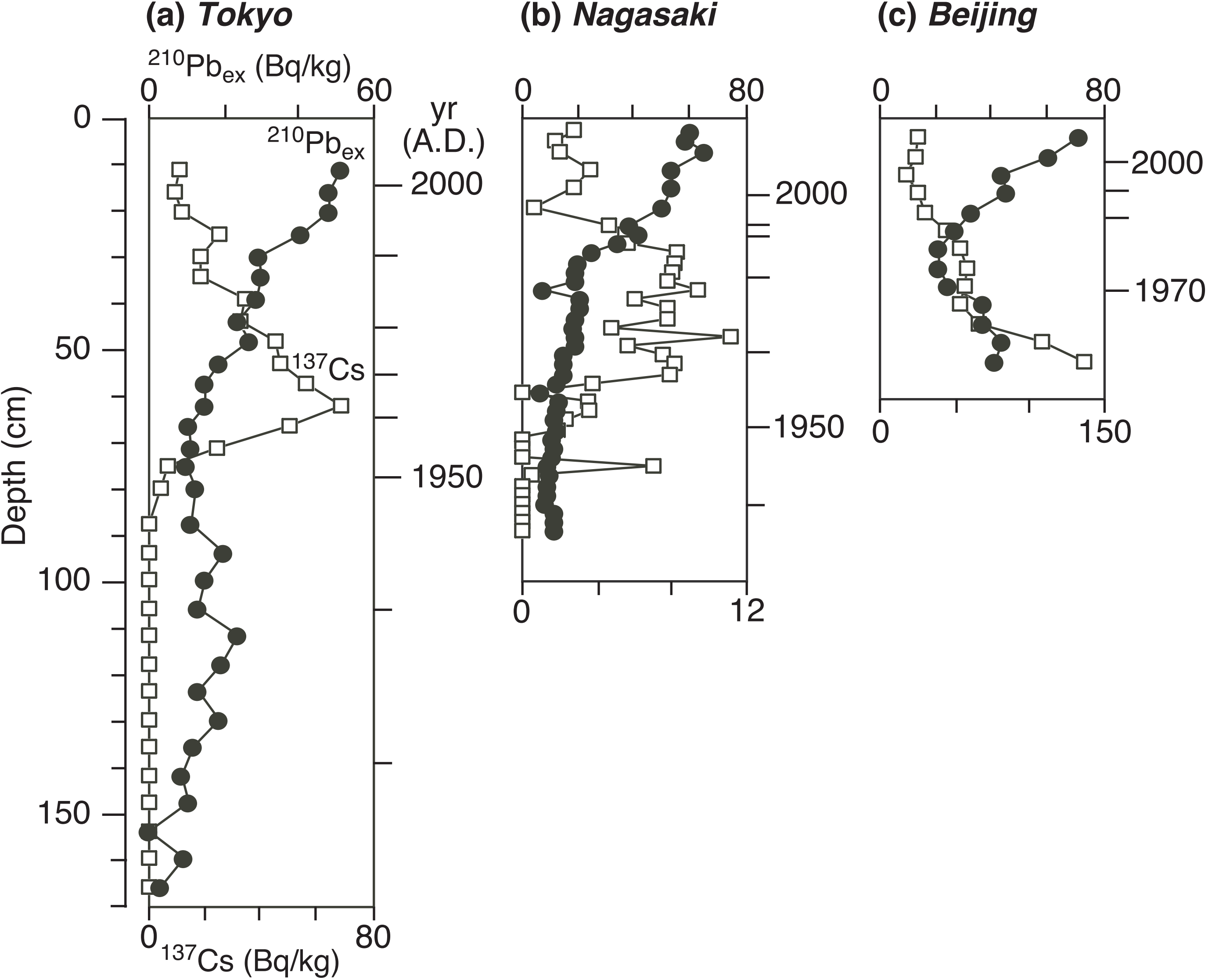

Figure 2 (Hirakawa et al)

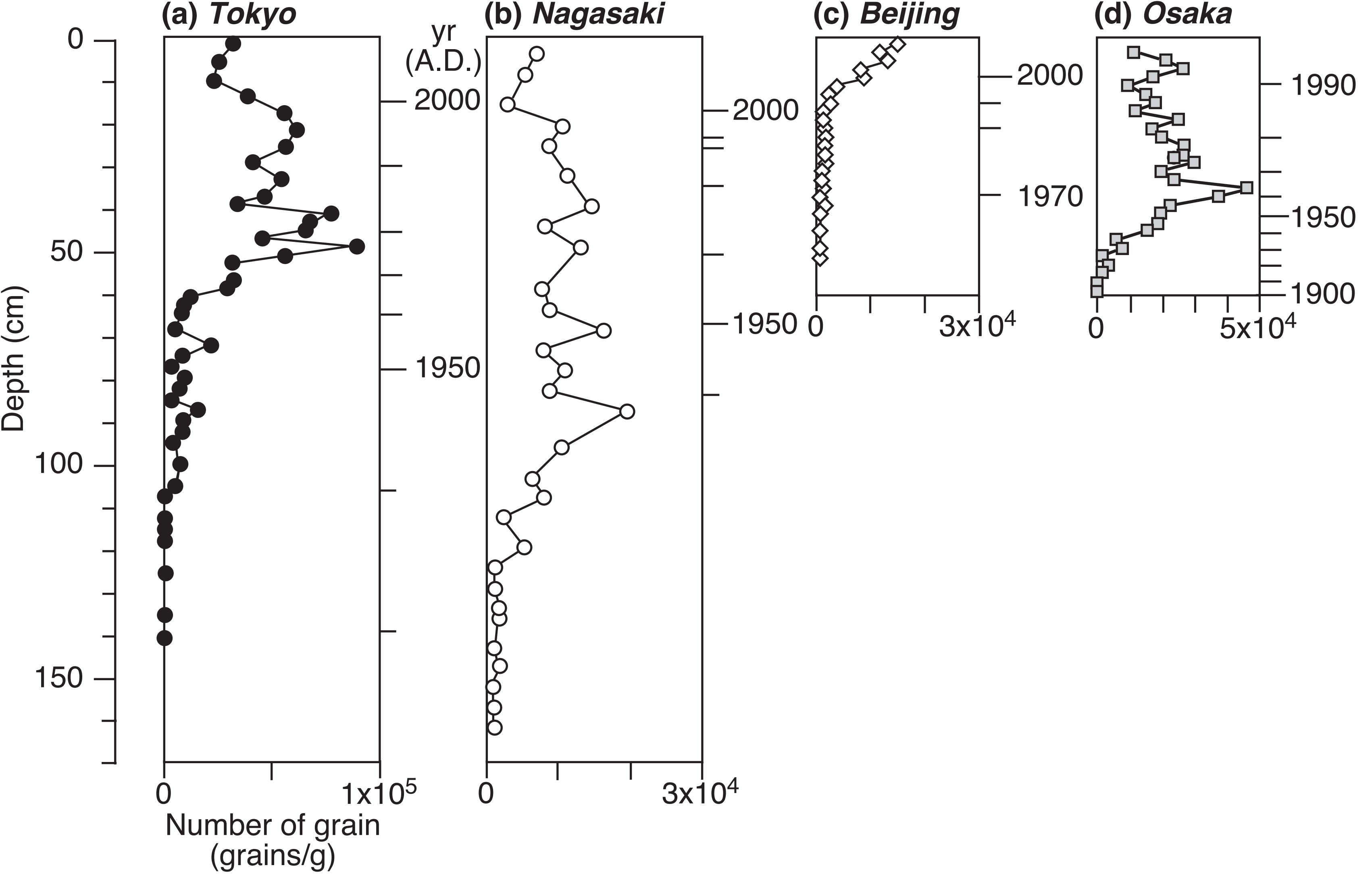

Figure 3 (Hirakawa et al)

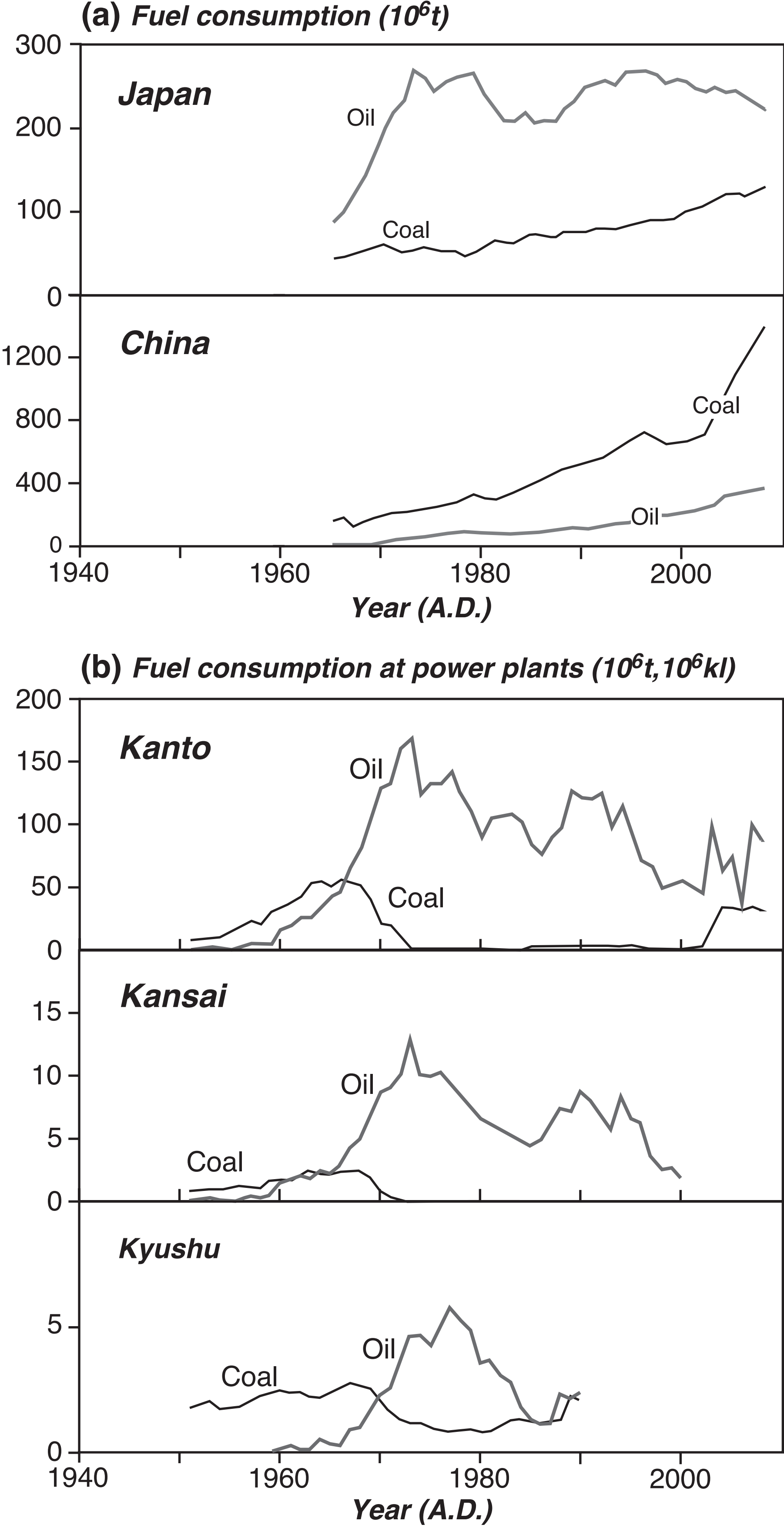

Figure 4 (Hirakawa et al)

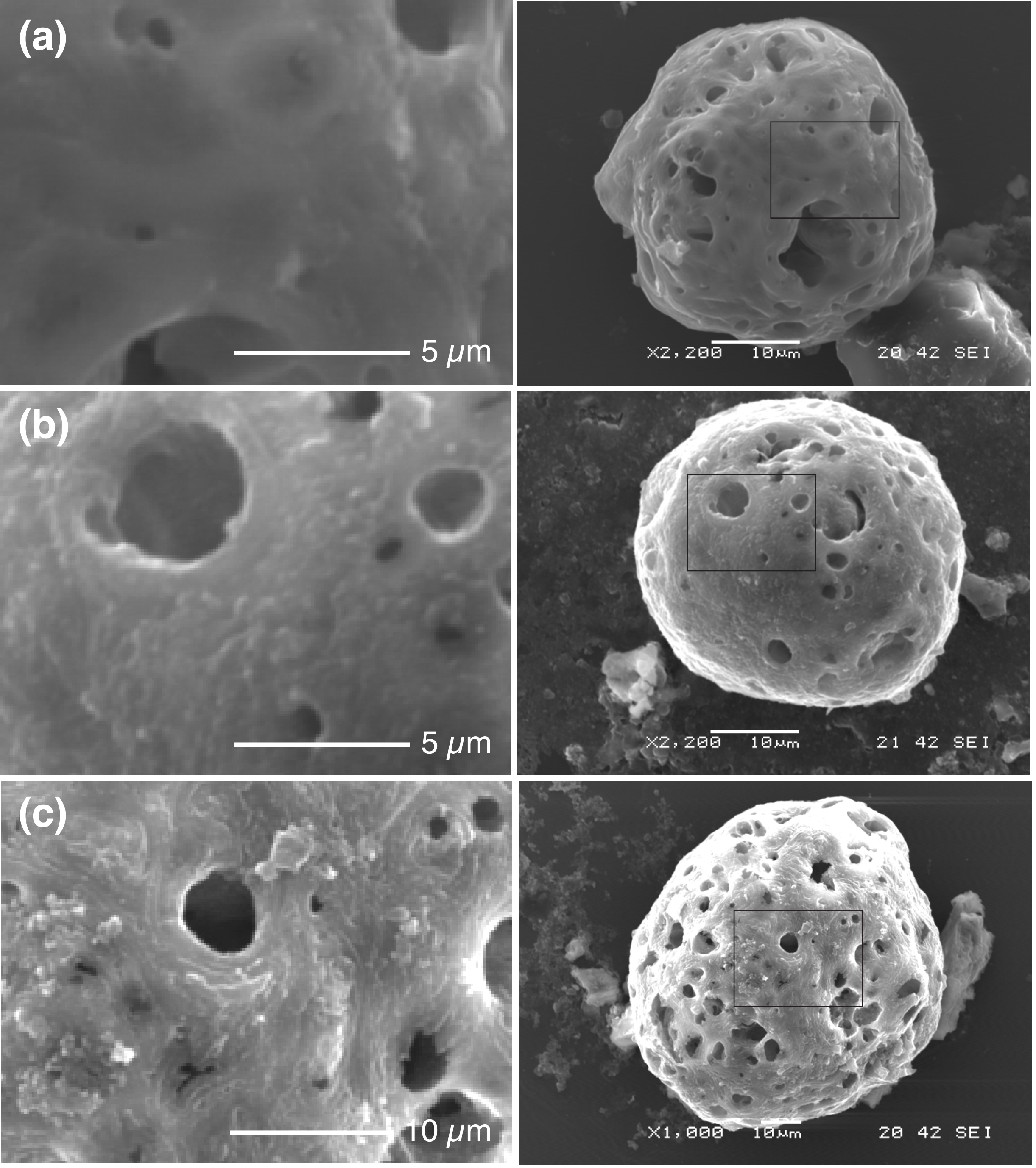

Figure 5(Hirakawa et al)

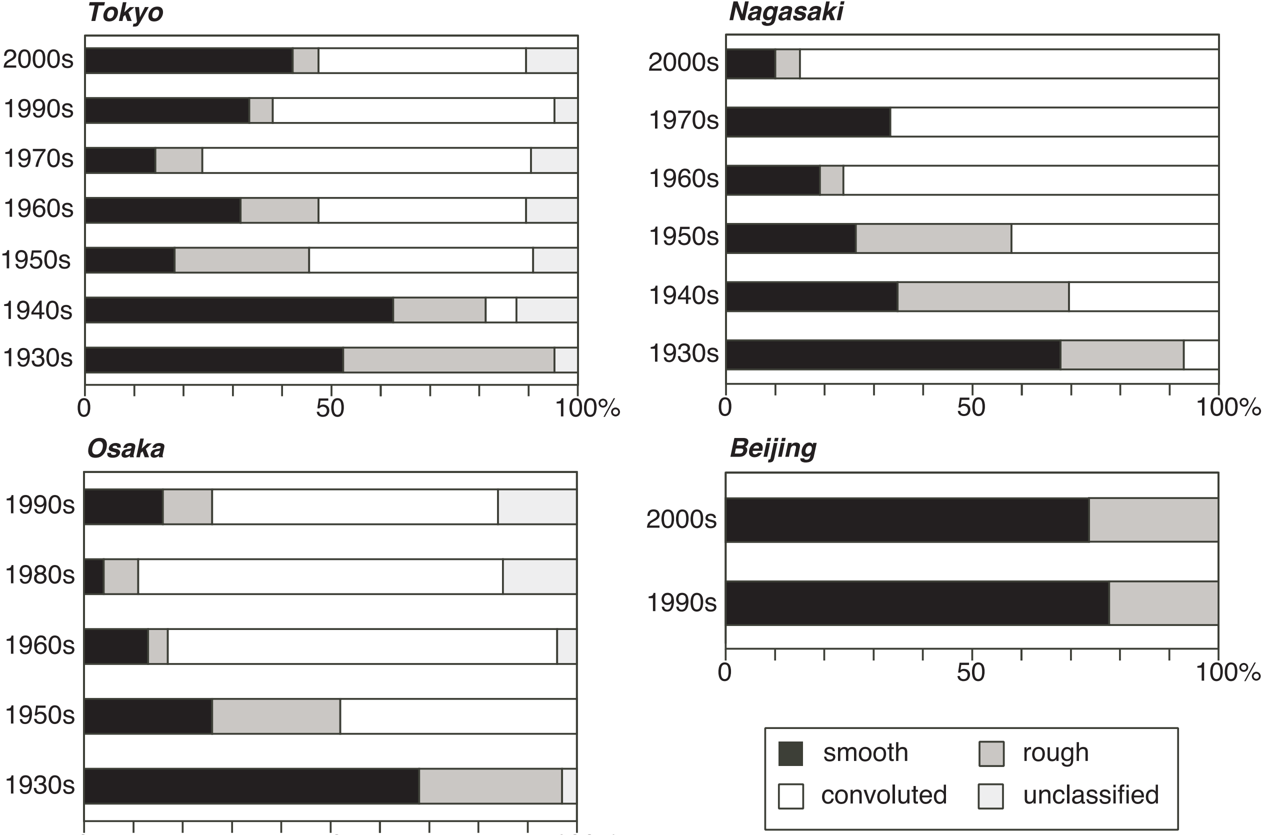

Figure 6 (Hirakawa et al)

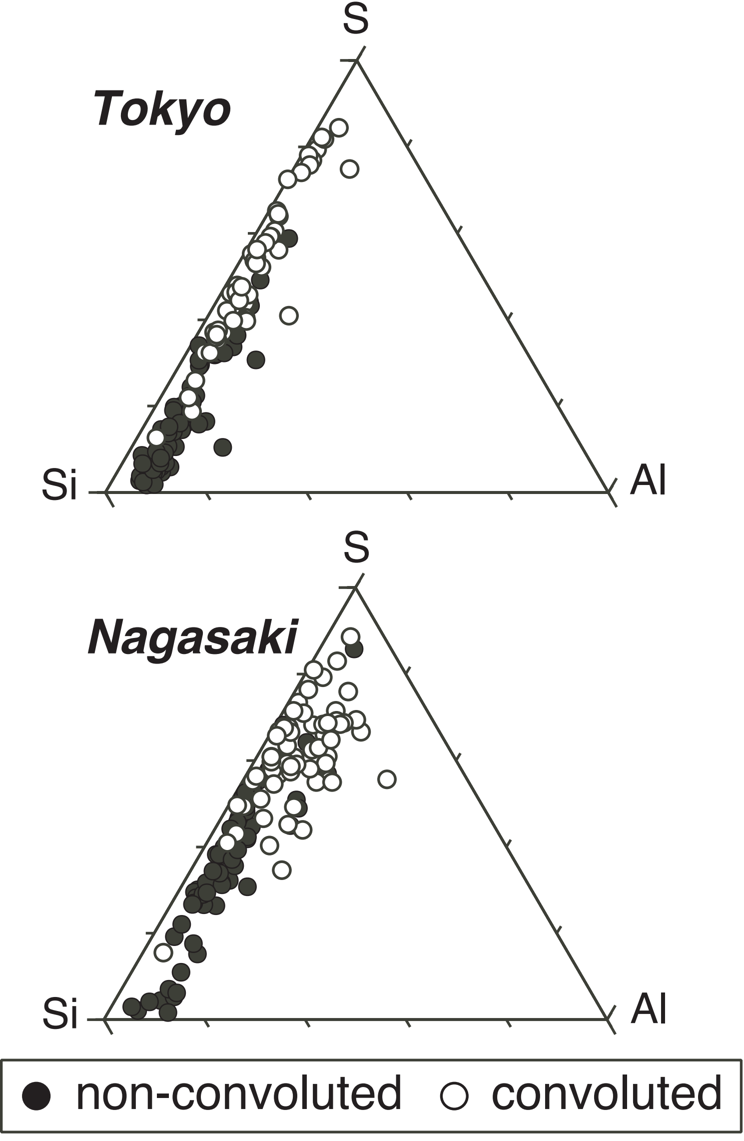

Figure 7(Hirakawa et al)

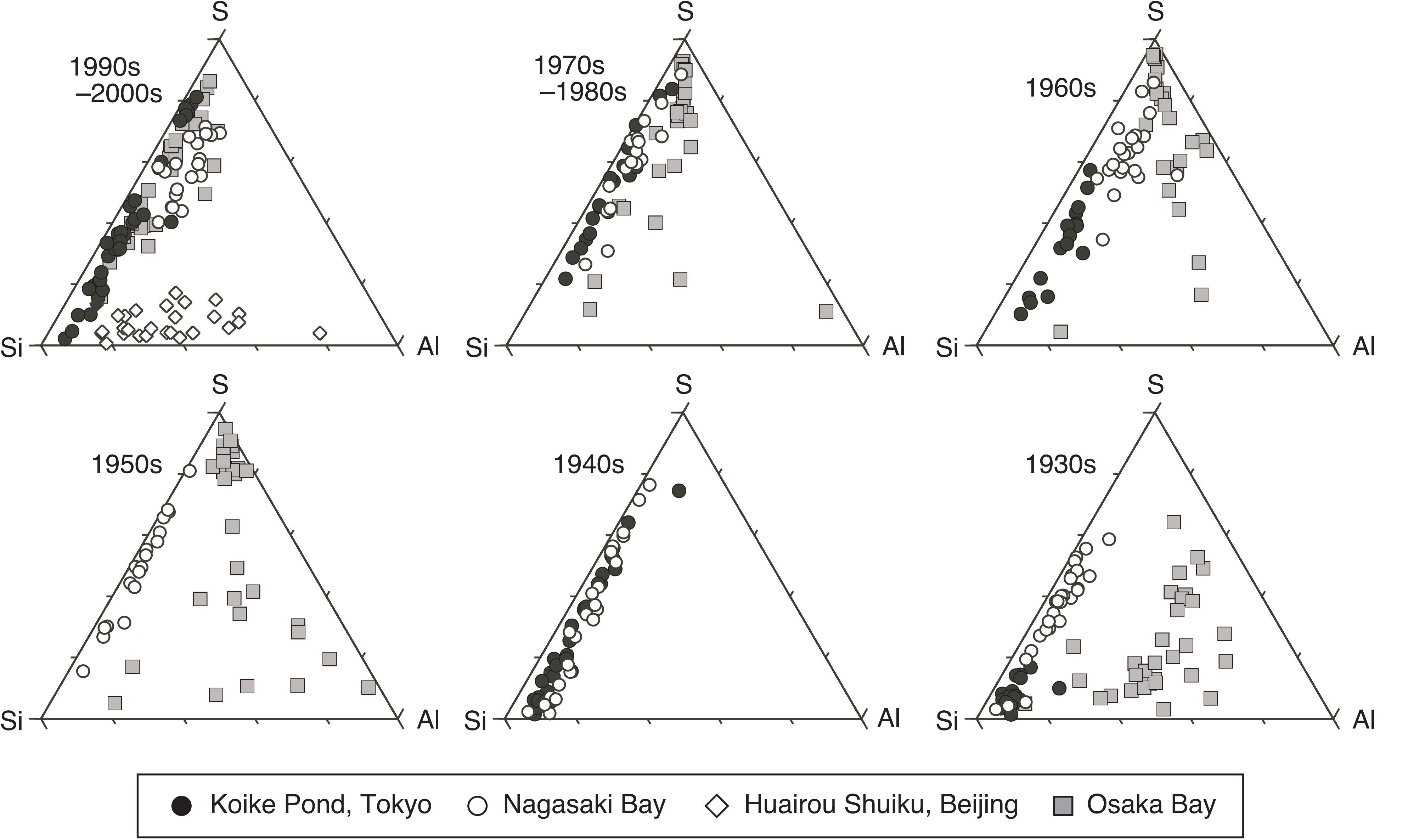

Figure 8 (Hirakawa et al)