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Identification of charcoal in Quaternary sediments and estimation of the charred temperature by reflectance measurements and H/C ratio analysis and observation through reflectance and scanning electron microscopy

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Abstract

Charcoal is a black, carbonaceous material obtained by heating plant material. Although black plant fragments are often found in sediments, we can't easily discuss whether or not they are charcoal formed by heating. Based on charring experiments in earlier studies (e.g. Jones et al., 1991; Sawada et al., 2000; Scott, 2000), chemical and physical specific changes of charcoal occur with heating. We examine the black plant fragments from the late Pleistocene to Holocene sediments and modern charcoal by reflectance and scanning electron microscopy, reflectance measurements and H/C ratio analysis, and confirm that the chemical and physical properties of charcoal in sediments are similar to modern charcoal. As a result, the cell walls of black plant fragments in sediments are well preserved and carbonized with a white shine similar to modern charcoal. The mean reflectance of each fragment is above 0.7% and H/C ratios are below 0.720. These values are indentical with modern charcoal. These black plant fragments must be charcoal. Therefore, these methods can be effective techniques in order to identify charcoal in sediments. Furthermore, there is a strong correlation between reflectance and H/C ratio, yielding the equation $H/C=0.34259\times(Ref.)^{-1.9224}$. Based on charring experiments in earlier studies (Jones et al., 1991; Sawada et al., 2000), we estimated the charred temperature from reflectance and H/C ratios, respectively. Charred temperatures estimated from reflectance are generally consistent with those estimated from H/C ratios and all temperatures are above 300℃. Therefore, H/C ratio analysis and reflectance measurements will be effective techniques for estimation of charred temperatures. Charring temperatures also yield useful information on past fires and these methods ought to be applicable not only to geology but also to archaeology and other fields.

Key-words : identification of charcoal, reflectance measurement, H/C ratio, charring temperature, Quaternary sediment

Introduction

Charcoal is a black, carbonaceous material obtained by heating plant material. It is generated mainly from burned plant materials in fire, such as forest fire. Therefore, the fire in the history can be studied by analysis of the charcoal preserved in sediments and soils. For studying the historical fire, charcoal is an important material to estimate fire in the paleoenvironment. On the other hand, plant fragments would be blackened like charcoal by diagenesis. Though black plant fragments are often found in sediments, we can't easily discuss whether they suffered heating or diagenesis exactly.

Several recent papers examined the charring process during heating. According to these papers, distinctive morphological changes, increasing reflectance and changes in C, H, N and O contents occur during heating (Scott, 2000). Cope (1979, 1981), Jones and Chaloner (1991), Jones et al. (1991), Scott and Jones (1991) and Scott (2000) observed charcoal by using reflectance and electron microscope. They noted that the degree of homogenization of the cell wall varied between 280℃ and 320℃ (Scott, 2000). According to Cope (1979), charcoal fragments have a well preserved cellular structure, while the coal fragments have compressed and fractured cell-wall structure. Several papers deal with reflectance measurements on modern charcoal, and establish that it has an increasing reflectance with increasing temperature (Jones et al., 1991; Jones et al., 1997; Guo and Bustin, 1998; Bustin and Guo, 1999). Jones et al. (1991) established a relationship between increasing temperature and reflectance for a range of modern woods. They devised a best-fit line from reflectance vs. temperature which allowed the estimation of the charring temperature of a fusain (fossil charcoal). On the other hand, elemental analysis on charred wood has been conducted by several authors (Cope, 1979; Jones et al., 1997). The results showed that an increased charring temperature results in a dramatic increase in carbon percentage. Cope (1979) carried out elemental analysis of both coal fragments and charcoal fragments, respectively. The results showed that charcoal fragments have lower H/C ratios in contrast to coal fragments by diagenesis. Recently, Sawada et al. (2000) performed charring experiments under various conditions and analyzed the H/C ratios of modern charcoal. They showed that H/C ratios are strongly correlated with the treatment temperature and arrived at the equation $\log T$ (℃) $= 2.50-0.530 \log (H/C)$ where the H/C ratios are <1.0 and T is >300℃. Based on this equation, Sawada et al. (2000) estimated the charring temperature of charcoals in pyroclastic flow.

As mentioned above, chemical and physical specific changes of charcoal occur with heating. We examine the black plant fragments from the late Pleistocene to Holocene sediments and modern charcoal from fire remains. These black plant fragments in sediments are black, completely opaque, angular fragments with diagnostic cellular features. These features are consistent with charcoal features (e.g. Rhodes, 1998). Therefore, we consider that these black plant fragments are probably charcoal. We examine these black plant fragments by reflectance measurements and H/C ratio analysis and confirm that chemical and physical properties of charcoal in sediments are similar to modern charcoal. When the chemical and physical properties of charcoal in sediment are well preserved, we can distinguish charcoal exactly from blackened plant fragments by diagenesis. We show that H/C ratio analysis and reflectance measurements are effective techniques in order to identify the charcoals in sediments exactly.

Furthermore, the method of estimating charred temperature has been used for estimating emplacement temperature of pyroplastic flows or making assumptions about types of past fire and other purposes. However, previous studies estimated the heating temperature of charcoal by either reflectance measurements or H/C ratio analysis. In our current study, we estimated the charring temperature by both reflectance measurements and H/C ratio analysis. We establish the connection between reflectance and H/C ratio of charcoal, and estimated temperatures by reflectance measurements and H/C ratio analysis are compared for the first time ever.

Method

We examined black plant fragments from the late Pleistocene to Holocene sediments and modern charcoal (Table 1, Fig 1). All samples were taken from sediments, except for sample No. 7, which was collected from burnt remains taken from a forest fire which took place in Sakai City in A.D. 2001. The significance of examining the modern charcoal from fire remains (No.7 charcoal) is in realizing how modern charcoal has value of H/C ratio and reflectance.

Black plant fragments concentrate was hand-picked under a binocular microscope or separated by flotation in a heavy liquid ($ZnCl_2$ liquor: Ca.1.7g/cm^3).

Reflectance microscopy and scanning electron microscopy

We observed the samples using polarizing reflectance (Leitz ORTHOPLAN) and scanning electron microscope (JEOL JSM-5500). For observation and reflectance measurements by reflectance microscopy, the samples were prepared and analyzed using procedures suggested by Jones et al. (1991) and Chijiwa et al. (1998).

Measurement of reflectance

For reflectance measurements, 'MPVGEOR' software for WINDOWS was used (Chijiwa et al., 1998).

Table 1 Location, occurrence and estimated age of charcoals used in this study. No. 3, 4, 5, 6 were collected from 141, 123, 63, 48 cm depths in moat sediments around Osaka Castle, respectively. Age of No.1 sample is based on Yoshikawa et al. (2003). Age of No.2 sample is based on Torii et al. (1998).

Sample No.	Location	Occurence		Size of sample charcoal	Age
1	Tsunan-cho, Niigata Prefecture	Uppermost part of Maibara loam formation	gravel bed	1-2 cm	Late Pleistocene (70,000 years ago)
2	Shinasahi-cho, Shiga Prefecture	Kuroboku soil	soil	250 μm-1mm	Holocene
3 4 5 6	Osaka Castle, Osaka City	Moat sediments around castle	clay or silt bed	1-2 cm	Several hundreds of years ago to present
7	Sakai City, Osaka Prefecture	———	———	1-5cm	A.D 2001

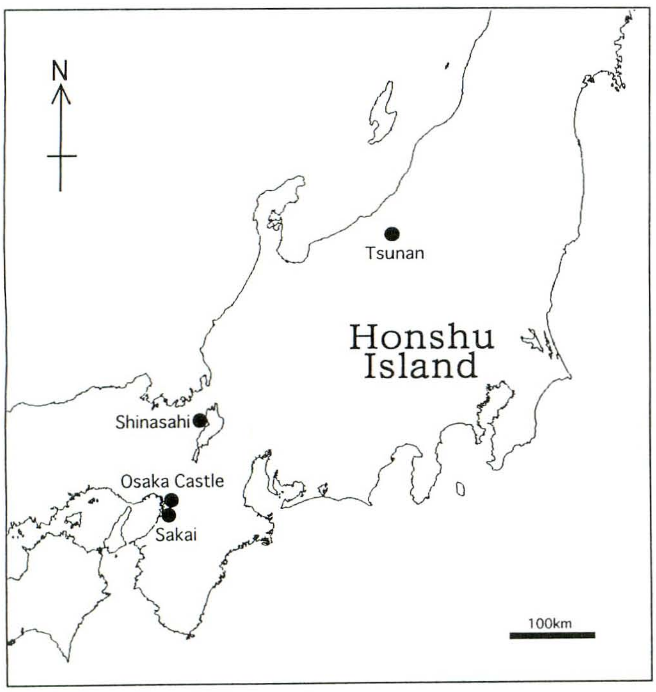

Fig. 1 Map of the central Honshu Island in Japan, showing the sampling location.

Reflectance was measured by moving each specimen on a stage, so that the measuring point was centered on a cell wall. Fifty random readings were taken from each specimen under oil and the mean was calculated.

Carbon and Hydrogen analysis (Elemental analysis)

The preparation procedures and analysis are based on Sawada et al. (2000). Samples were repeatedly cleaned in NaOH (0.5 N) and HCl (1 N) solutions for removal of absorbed humic acid, fulvic acid and carbonate. Afterwards, they were cleaned again in distilled water and subsequently dried in an oven at 110℃. After crushing to a fine powder, the samples were again dried for several hours prior to H/C analysis. The carbon and hydrogen contents of the samples were determined by a combustion method using a FISONS (Carlo Erba) EA1108 elemental analyzer.

Results

Reflectance of microscopy and scanning electron microscopy

Reflectance micrographs and scanning electron micrographs of typical fragments used in this study are shown in Plate 1 and 2. Plate1and 2 show that fragments have well preserved cellular structure similar to photographs of charcoals in Cope (1980). Plate1 shows that cell walls are carbonized and have a white shine. Plate 1- A, B, C and D show that cell walls are homogenized and are similar to the charred wood samples heated above 300℃ shown in Scott (2000) and Jones et al. (1991). According to Scott (2000), homogenized reflectance of the cell wall occurred between 280℃ and 320℃, while inhomogenized cell wall occurred at lower temperature. Therefore it appears that charcoals showing homogenized cell walls will generally have been charred above 300℃. However, No.3 charcoal often has a lighter central cell wall and darker outer part (Plate 1- E, F). Thus, apparently, some portions of No.3 charcoal, those with inhomogenized cell walls, may also be charred at lower temperature.

Measurement of reflectance

Mean reflectance of each specimen is shown in Table 2. Based on the best fit line taken from the temperature-reflectance relation plotted by Jones et al. (1991), the estimated temperatures from mean reflectance are also shown in Table 2.

Carbon and Hydrogen analysis

Carbon contents (wt %), hydrogen contents (wt %), H/C atomic ratios and estimated temperatures of the seven charcoals studied are shown in Table 3. The estimated temperatures are calculated from log T((C) =2.50-0.530 log (H/C) (Sawada et al., 2000).

Discussion

As shown above, reflectance micrographs and scanning electron micrographs (Plate1,2) show that cell walls of charcoals in sediments are well preserved and carbonized, similar to modern charcoal. Mean reflectances of each charcoal in sediments are above 0.7% and maximum reflectances are above 1.1%. H/C ratios of each charcoal are below 0.720. These values are similar to modern charcoal (sample No.7 charcoal in this study; Sawada et al., 2000; Jones et al., 1991). From these results, charcoal in sediment seems to have chemical and physical properties similar to modern charcoal. The properties of charcoal in sediment would be well preserved for a long time. Therefore, reflectance micrographs and scanning electron micrographs, H/C ratio analysis and reflectance measurements can become effective techniques to identify the charcoal in sediment exactly. And we can estimate the charred temperature of charcoal in sediment based on charring experiments of modern charcoal (Jones etal., 1991; Sawada et al., 2000).

Table 2 H contents, C contents, H/C ratios and estimated temperatures of each charcoal. The estimated temperatures are calculated from log T((C) =2.50−0.530 log (H/C) (Sawada et al., 2000).

Sample No	C (wt%)	H (wt%)	H/C atomic ratio	Estimated temperature (℃)
1	60.0	2.7	0.536	440
2	55.7	2.2	0.471	470
3	67.9	4.1	0.720	380
4	85.8	2.0	0.278	620
5	88.7	2.4	0.322	570
6	67.0	3.0	0.534	440
7	70.4	2.9	0.491	460

Table 3 Mean and max reflectance of each charcoal. Fifty random readings were taken from each specimen and the mean calculated. The temperatures estimated from the mean reflectance based on best fit line of temperature vs. reflectance (Jones et al., 1991).

Sample No	Mean Reflectance (%)	Max Reflectance (%)	Estimated temperature from mean reflectance (℃)
1	1.100	1.418	380
2	1.196	1.824	390
3	0.706	1.118	320
4	4.098	4.947	630
5	3.162	3.572	540
6	1.016	2.183	360
7	1.629	2.381	440

Higher reflectance charcoals generally have lower H/C ratios (Fig 2). Fig 2 shows a strong correlation between reflectance and H/C ratio, but relationship between reflectance and H/C ratio is not linear, yielding the equation $H/C=0.34259\times(Ref.)^{-1.9224}$ with correlation coefficient at 0.9817, where Ref is reflectance (%) and H/C is atomic ratio. Furthermore, temperatures estimated from mean reflectance are generally consistent with those estimated from the H/C ratio within 80℃ difference. The charred temperatures of No.4 and NO.5 charcoals are above 600℃ and 500℃ respectively, estimated from both H/C ratio and mean reflectance. Additionally, No.3 charcoal, with lowest temperature estimated from H/C ratio, also has the lowest temperature from mean reflectance. In this way, the estimated temperatures from H/C ratio and mean reflectance are generally similar. Therefore, charred temperature estimated from H/C ratio or mean reflectance seems to possess higher reliability with the error ranging from 10℃ to 80℃. Especially, the charcoal samples showing lower temperatures (sample1,2,3 and 6) have a large margin of error. This may be derived from the difference of heating experiments by Jones et al. (1991) and Sawada et al. (2000).

H/C ratio analysis and reflectance measurements will become effective techniques for estimation of the charred temperature. Charred temperature provides useful information on past fire and others, because different fires have different temperature. For example generally grassland fire has lower temperatures and forest fire has higher temperatures.

Conclusion

We have examined some charcoals found in Quaternary sediments by reflectance microscopy, scan-

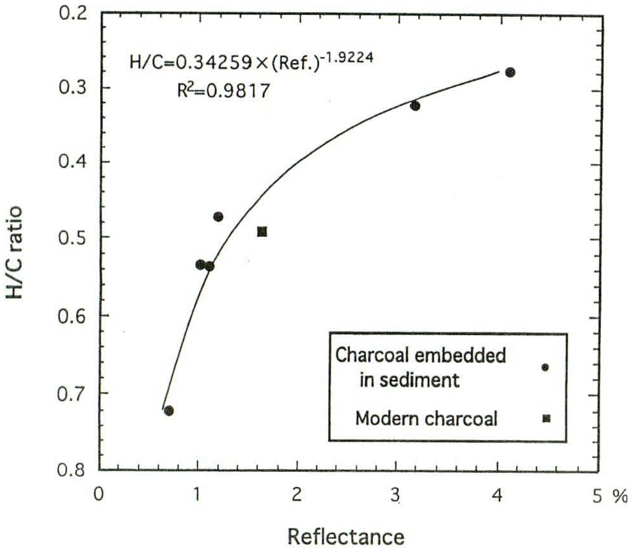

Fig. 2 Graph of H/C ratio vs. mean reflectance of each charcoal. There is a strong correlation between reflectance and H/C ratio, yielding the equation H/C=0.35259×(Ref.)$^{-1.9224}$, with correlation coefficient at 0.9817.

ning electron microscopy, reflectance measurements and H/C ratio analysis. Charcoal in sediments have chemical and physical properties similar to modern charcoal.

We estimated the charring temperature by reflectance and H/C ratio based on charring experiments in earlier studies. The estimated charring temperatures from H/C ratio and mean reflectance are generally similar. And there is a strong correlation between reflectance and H/C ratio, yielding the equation H/C=0.34259×(Ref.)$^{-1.9224}$. These techniques are effective for identification of charcoal in sediments and estimating the charred temperature. These methods provide useful information on past fires.

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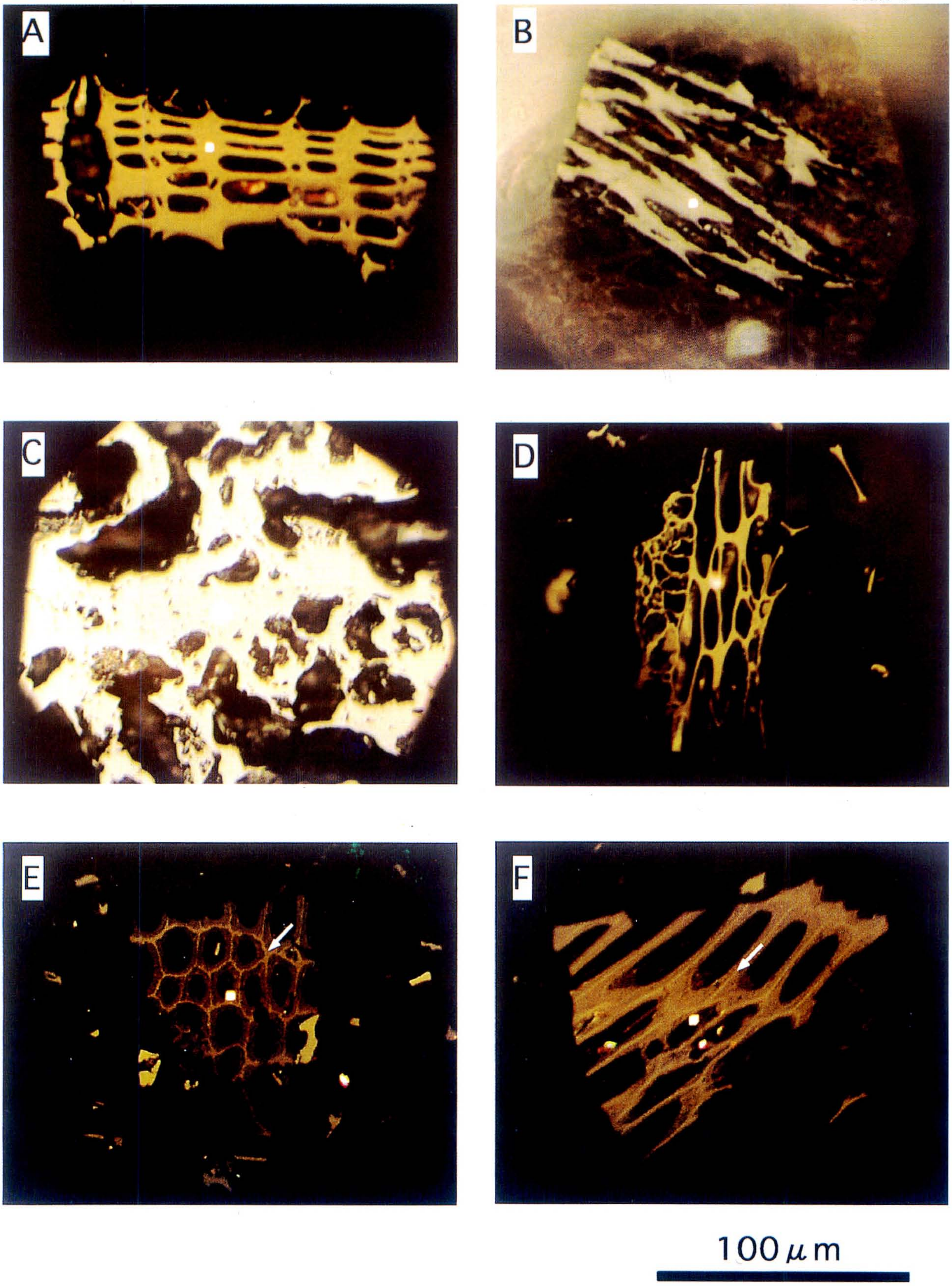
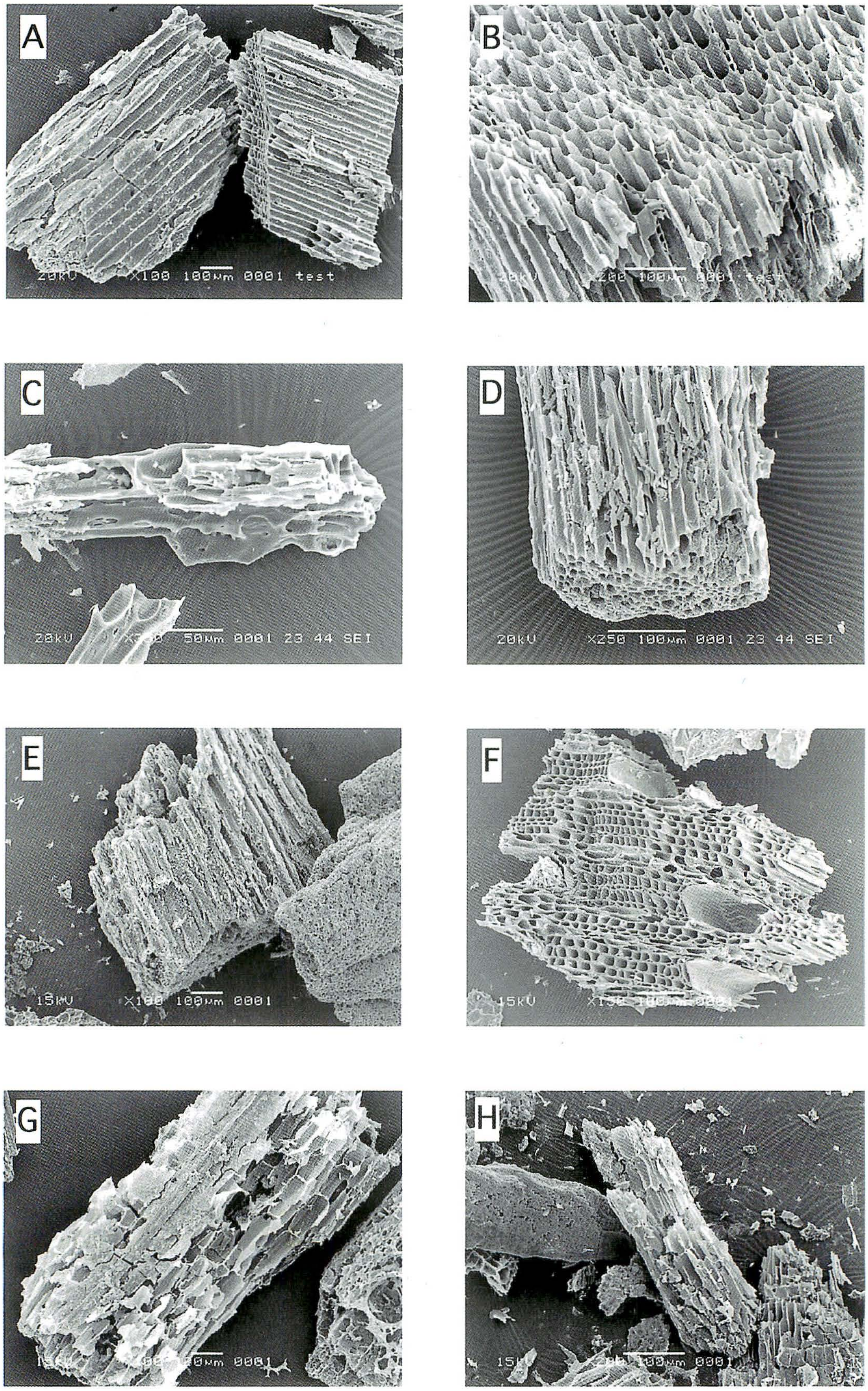
Plate 1



Reflectance micrographs of charcoals. A: Charcoal 1, Tsunan-cho, Niigata Prefecture. B: Charcoal 2, Shinasahi-cho, Shiga Prefecture. C: Charcoal 4, Moat sediments, Osaka Castle, Osaka City. D: Charcoal 7, Sakai City, Osaka prefecture. E, F: Charcoal 3, moat sediments around Osaka Castle. The lighter parts of cell walls are indicated by arrows.

Plate 2



Scanning electron micrograph of charcoals. A, B: Charcoal 1, Tsunan-cho, Niigata Prefecture. C, D; Charcoal 2, Shinasahi-cho, Shiga Prefecture. E, F, G: Charcoal 3, 4, 5, moat sediment around Osaka Castle respectively. H: Charcoal 7, Sakai City, Osaka prefecture.