A PUZZLING ^{14}C RESULT OBTAINED FOR A CARBONIZED WOOD SAMPLE EMBEDDED IN VOLCANIC LAVA

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ABSTRACT. It has been reported that the characteristics of a very old wood charcoal sample are different from those of modern wood charcoal according to its state of preservation (Cohen-Ofri et al. 2006; Rebollo et al. 2008). It can be assumed that these differences may lead to some difficulties when radiocarbon dating very old wood charcoal samples. To investigate this problem, we studied a carbonized trunk of *Prunus pendula for. acendens* tree buried in lava and found at the Hantan River lava plateau on the Korean Peninsula. The ^{14}C date of this sample was previously measured as >30,000 BP. However, separate ^{14}C results of its outer crust and inner wood showed a considerable difference, exceeding the estimated age differences by tree-ring counting. To study the reason for this discrepancy, optical microscopy and FTIR (Fourier transform infrared spectroscopy) were performed to examine the differences in the structural and chemical states of the samples. For reference data and to expand our understanding of very old wood charcoal, we applied the same analysis tools (AMS, FTIR, FE-SEM, EDS, and optical microscopy) to a variety of wood charcoals and original wood. From these analyses, we noticed considerable chemical changes in the outer crust sample, and this might explain the age discrepancy. Although it seems that the age difference might be due to the digestion of ^{14}C-free CO_2 from a volcanic environment, this explanation would not account for such a large value in the age difference.

INTRODUCTION

It has been reported that an accurate radiocarbon age determination for very old charcoal might be affected by its preservation state, and the difference in preservation state would indicate a chemical and structural change within the samples. Also, the change in chemical and structural state in poorly preserved old charcoal may cause higher overall weight losses upon chemical pretreatment and may increase the relative amount of contaminants in the sample (Braadbaart et al. 2006; Rebollo et al. 2008). In order to investigate this question, we studied an example discovered near Hantan River, South Korea, in 2004. A mass of volcanic lava containing a tree trunk is exhibited at the museum of the Jeongok prehistoric site, located in Jeongokri, Yeoncheon County. The lava was originally found at a construction site for an apartment building in 2004. The location is ~1 km from the prehistoric site and stands on a lava plateau beside Hantan River as shown at Figure 1. Even though the exact original location was not recorded, it seems that it was found near building #104 (38°00′54″N, 127°04′22″) shown in Figure 1, as inferred from Yi (2010). The lava was originally 1 whole chunk when it was discovered but it was broken and divided into 2 by construction workers and the charcoal embedded inside of the rock was found. There were 2 carbonized tree trunk pieces of ~10 cm diameter embedded in rock. As shown in Figure 2, some parts of the 2 trunks are preserved in the left rock (a) but most of these correspond to the outer crust, i.e. bark. Although there were more inner wood parts upon first discovered, some parts were removed before the samples were preserved by the local government. On the other hand, part of only 1 trunk is shown in the right-hand rock (b) and this part contains some inner wood parts of the tree as well. As shown in Figure 2b, the outer crust is not clearly seen because it is located in the right-lowest corner of the figure. A photograph of outer crust part could not be easily taken.

It is known that the lava plateau of this area was formed around 400–500 ka BP based on fission-track ages (Kim et al. 2010; Yi 2010). However, even though the effective age limit of ^{14}C dating

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Figure 1 Discovery location of the charcoal-embedded lava rock (Jeongokri, South Korea).



Figure 2 Charcoal-embedded rocks and the carbonized trunks at each side of the separated rocks. The parts of wood charcoal are shown at the dashed white squares of (a) and (b).

(except for special installation) is known to be about 40 ka BP, i.e. 40,000 yr BP (Aitken 1999), the ^{14}C dating of the inner and outer parts of the charcoals was performed at 5 international AMS facilities to check whether the lava flow occurred earlier than the last 40 ka BP (Yi 2010). The results showed a conflicting result, as 7 out of 10 samples gave an age younger than 40 ka while 3 samples gave an age older than 40 ka. Moreover, the age difference between outer crust and inner part from all samples was greater than 950 yr and the outer crust age was older than that of the inner parts of the sample. In order to understand the possible reasons for these results and investigate any chemical and structural differences of these samples, we have employed many analytical tools such as optical microscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

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SAMPLE PREPARATION AND EXPERIMENT

Only 3 samples: SNU10-R050 (S-in: inner core charcoal), SNU10-R051 (S-out: outer crust charcoal), and a very old wood sample (SNU11-1093 or S-wood) were AMS dated in our laboratory. The third sample (S-wood) was added for the purpose of comparison in our other analytic studies of the Jeongokri sample. This very old wood that had undergone diagenesis and self-humification inside mud at the swamp area. The carbonized old wood was excavated at Dong-sam-dong, Pusan, Korea. Detailed sample preparation and experiment procedures for each analytic technique are provided in the following subsections.

Radiocarbon Dating

The standard acid-alkali-acid (AAA) treatment was performed as a preparation before ^{14}C dating the 2 samples (S-in and S-out), assumed to be charcoal, to remove carbonates and humic acids (Olssen and Possnert 1992). The old wood sample from Dong-sam-dong (S-wood) was immersed in 0.5M HCl at 80–85 °C for 30 min and washed to neutral pH. It was then subjected to 0.1M NaOH at 80–85 °C for 1 hr and washed to neutral pH. After that, it was treated by applying 4% $NaClO_2$ at 55–60 °C for 1 hr to extract α-cellulose and washed to neutral pH. It was again immersed in 0.5M HCl at 80–85 °C for 30 min to remove any CO_2 absorbed during the second and the third steps and washed to neutral pH. The residues from all 3 samples were dried in an oven at 120 °C for 8 hr. Dried residues were then combusted by an elemental analyzer and the produced CO_2 was trapped cryogenically. Conversion of CO_2 to graphite was thereafter conducted using H_2 and Fe powder. The resulting graphite was loaded to the ion source of the AMS (accelerator mass spectrometry) facility (Lee et al. 2000). ^{14}C dating of the samples (S-in, S-out, and S-wood) was done using the Tandetron 4130 AMS at Seoul National University. Oxalic acid II was used as a standard, and IAEA-C6, ANU sucrose (150.6 pMC, $\delta^{13}C = -10.8$) as a secondary standard. $\delta^{13}C$ values of the samples were estimated by assuming that the $\delta^{13}C$ of oxalic acid II is −18‰. The ^{14}C dates were corrected by $\delta^{13}C$ values relative to Belemnite Americana from the Peedee formation in South Carolina (PDB) (Park et al. 2010; Lee et al. 2013).

Optical Microscopy

To check the structural difference in appearance, detailed visual identification and optical microscopy in reflection mode were performed (Leica DM 750 P microscope). The samples S-in, S-out, and S-wood were cut to the proper size for optical microscopy. The approximate dimension values of each sample cut for visual inspections were (in mm) 13 × 14 × 10 (S-in), 16 × 12× 10 (S-out), and 12 × 12 × 10 (S-wood).

Field Emission Scanning Electron Microscopy (FE-SEM) and Energy Dispersive Spectrometry (EDS)

To check and compare the detailed microstructure and inorganic chemical elements from each sample, FE-SEM and EDS were performed using a JSM-6700F. To prepare the samples for measurement, they were manually cut at a dimension less than 5 × 5 × 2 mm and especially the top and bottom planes were cut as flat as possible for a better image acquisition. They were then dried in an oven at 60 °C for 8 hr to reduce the vacuum pumping time at SEM and EDS measurements. The prepared samples were attached to an aluminum stub with adhesive tape before installation.

Fourier Transform Infrared Spectroscopy (FTIR)

To investigate the chemical composition of the samples, FTIR measurements were performed. Before the measurements, each sample was transformed into powder form of <250 μm by crushing

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and grinding. Samples were then immersed in 0.5M HCl solution at 80–85 °C for 30 min and washed to neutral pH for simple cleaning. They were dried in an oven at 120 °C for 8 hr and pellets in disk form were prepared with the ground powders and dry potassium bromide (KBr) powder for installation in the sample holder of the FTIR apparatus. Scans were obtained with a resolution of 4.0 cm^{-1} in absorbance mode using a Nicolet 6700 spectrometer.

EXPERIMENTAL RESULT

Radiocarbon Dating

Figure 3 and Table 1 show the dating results from the various laboratories (G: Geochron; B: Beta-Analytic; IAAA: Institute of Accelerator Analysis; W: Waikato Univ.; and S: Seoul National Univ.). If we exclude Geochron results, the discrepancies in ^{14}C results among different laboratories are not unreasonable, considering that the ages are near the limit of ^{14}C determination. The open circle symbol represents the measured ^{14}C dates of the samples and diamond symbols are $\delta^{13}C$ results. As shown in Table 1, there are large differences in ^{14}C ages between the outer crust (bark) and the inner part of the tree trunk, ranging from 950 to 13,800 yr. Moreover, in all measurements, the dendrochronological order is consistently reversed, with the outer crust being older than the inner part. In Figure 3, we added a result "S-wood" for a very old wood waterlogged at the Dong-samdong archaeological site. The $\delta^{13}C$ values give us a clue about this anomaly. While $\delta^{13}C$ values for all inner core measurements are well within the range of normal values for fossil wood and charcoal (–24 ± 4‰), those for the outer crust are erratic, particularly for measurements of B-out and S-Out.

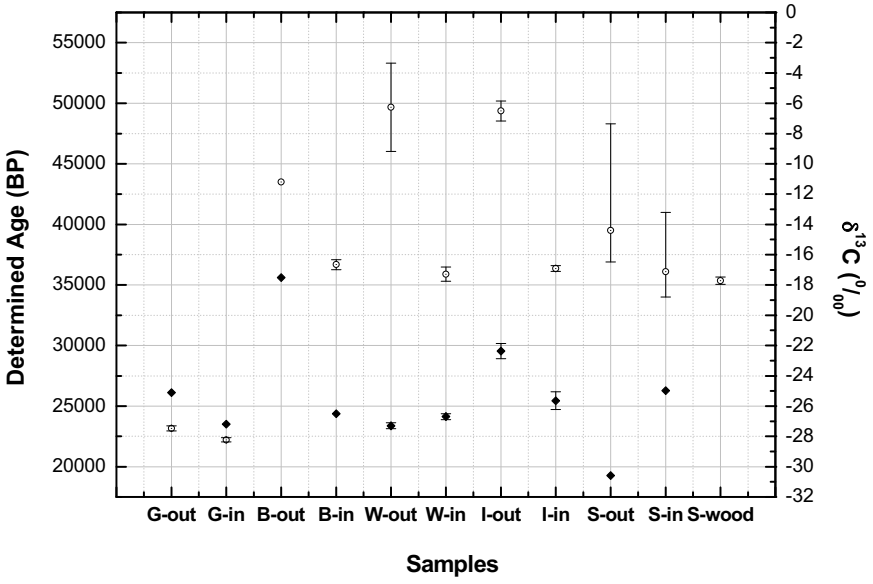


Figure 3 Determined ^{14}C age and $\delta^{13}C$ values of outer crust and inner core charcoal samples from 5 AMS facilities (G: Geochron; B: Beta-Analytic; I: Institute of Accelerator Analysis; W: Waikato Univ.; and S: Seoul National Univ.). "-out" means the outer crust and "-in" means the inner core. The open circle symbols are for the determined ^{14}C date and the closed diamond symbols for $\delta^{13}C$ values.

B-out and S-out are for the outer crust samples that were in contact with the lava. Thus, it is possible that they were mixed with other surrounding materials like peat ($\delta^{13}C$: –20 to –32‰) and straw ($\delta^{13}C$: –9 to –17‰) when they contacted the lava (Stuiver and Polach 1977). In addition, $\delta^{13}C$ vari-

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ations of charcoal and wood are within 0 ± 30‰ or −35 to −20‰ (Geyh and Schleicher 1990; Wagner 1998). For these cases, all $\delta^{13}C$ values from the samples fall within the range of variation and are therefore in agreement with reported characteristic values.

Consideration of Volcano Effect

It has been reported that ^{14}C-dated ages of plants present around volcano areas sometimes show much older ages than their actual ages because they capture volcanic CO_2 devoid of ^{14}C as well as atmospheric CO_2 (Sulerzhitzky 1971; Saupé et al. 1980). Also, it has been shown that the inner part of wood may not be affected by the volcanic CO_2. Thus, to check whether the age difference may be induced from volcanic CO_2, the ^{14}C dating results were investigated with Equation 1, from Sulerzhitzky (1971):

$$\mathrm{pMC}(\%) = 100 \times \exp\left(\frac{-^{14}C\,yr\,Gap}{8033}\right) \quad (1)$$

Table 1 shows the results from this study and also the calculated decrease in the specific activity of ^{14}C under the assumption that volcanic CO_2 induced the big age difference between the outer crust and inner part, and the inner part was not affected by volcanic carbon dioxide. Even though a difference in the value of up to 53% (V), i.e. a gap of 6000 yr, has been reported (Sulerzhitzky 1971; Bruns et al. 1980; Saupé et al. 1980), our results gave much larger percentages. Therefore, it may seem that the reason for the difference is not from volcanic CO_2 alone. We wondered if the structure or chemical composition of each trunk part would be so different, so we used analytical tools (optical microscope, FE-SEM, EDS, and FTIR) to examine them.

Table 1 Analysis and comparison for the volcano effect.[a]

Facility	Outer crust yr (BP)	Inner core yr (BP)	^{14}C yr gap	Calculation of volcano effect [V(%)]
GX	23,160	22,210	950	11.2%
Beta	43,500	36,680	6820	57.2%
Wk	49,668	35,855	13,813	82.1%
IAAA	49,366	36,368	12,998	80.2%
SNU	39,500	36,100	3400	34.5%

[a]V (%): Decrease in the specific activity of ^{14}C, V (%) = 100 – pMC (%)

Appearance and Optical Microscopy

Figure 4 shows the appearance and microscope images of the samples (outer crust and inner core charcoals from Jeongokri lava, and old wood from the swamp area in Dong-sam-dong). For the inner core charcoal and wood from Dong-sam-dong, they have a compact and hard appearance, and they show features of ordinary charcoals. The outer crust sample, however, shows a feature of tree bark mixed with gray-colored ashes. In microscopic images at both 40× and 100× magnification, the old wood (S-wood) shows a well-preserved cell structure. The inner core sample (S-in) is not very different from Dong-sam-dong old wood, but shows additional features of fine grains and an array of tiny pores. However, the outer crust (S-out) is very different and does not show any feature of laminated layers observed in the above 2 samples, but shows instead only irregular bubbles or a crater-like structure.

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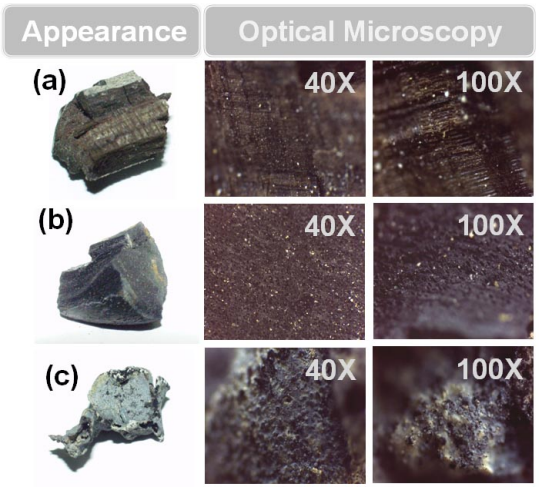


Figure 4 Appearance and optical microscopic images of samples: (a) the very old wood from Dong-sam-dong and the wood charcoals of (b) inner core and (c) outer crust from Jeongokri.

FE-SEM and EDS

Figure 5 shows SEM images from each sample and Table 2 shows the measured result of EDS. SEM images were taken at the 2 planes on the surface (horizontal direction to samples) and cross-sectional (vertical depth direction to them). The SEM images of the inner core sample show clear pictures of the cellular structure as seen in Hoyo et al. (2010), while those of Dong-sam-dong old wood show the cellular structure in a cross-sectional view. The 4× magnified images of X-section of these 2 samples are nearly identical. However, the outer crust sample shows only an amorphous pattern with small grains without any feature of cellular structure even at 4× magnification.

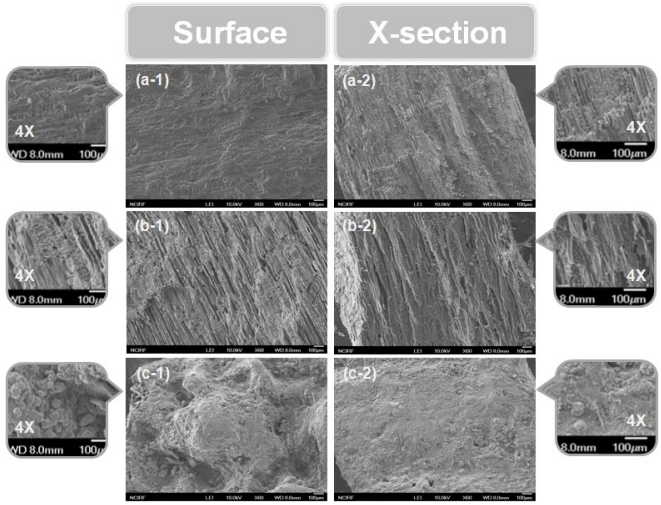


Figure 5 SEM images at surface and cross-sectional planes and their respective 4× magnified partial images: (a-1 and a-2) wood from Dong-sam-dong, (b-1 and b-2) inner core charcoal from Jeongokri, and (c-1 and c-2) outer crust charcoal from Jeongokri.

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Table 2 EDS results of each sample in weight (wt) and atomic (at) percentages.[a]

Element	wt %						at %					
	w-1[a]	w-2[a]	i-1[b]	i-2[b]	o-1[c]	o-2[c]	w-1[a]	w-2[a]	i-1[b]	i-2[b]	o-1[c]	o-2[c]
C K	61.31	61.66	62.93	67.31	41.20	21.87	69.58	70.01	74.46	77.17	76.09	33.33
O K	33.52	32.95	22.41	21.91	—	41.48	28.56	28.08	19.90	18.86	—	47.44
Mg K	—	—	0.62	—	—	1.15	—	—	0.36	—	—	0.87
Al K	—	—	0.44	0.58	—	3.70	—	—	0.23	0.29	—	2.51
Si K	—	—	4.44	2.39	0.93	15.40	—	—	2.25	1.17	0.74	10.03
S K	3.30	3.28	—	0.67	—	—	1.40	1.40	—	0.29	—	—
K K	—	—	—	—	—	2.09	—	—	—	—	—	0.98
Ca K	—	—	4.60	4.66	—	1.15	—	—	1.63	1.60	—	0.53
Cr K	—	—	—	—	6.46	—	—	—	—	—	2.75	—
Fe K	1.87	2.11	4.56	2.48	51.41	13.16	0.46	0.51	1.16	0.61	20.42	4.31
Totals	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a]w-1[a] and w-2[a] represent Dong-sam-dong wood, i-1[b] and i-2[b] are inner core charcoal, and o-1[c] and o-2[c] are outer crust charcoal from Jengokri.

EDS results show the chemical element and their relative quantity in the ratios of atomic percentage (at %) and weight percentage (wt %) on each sample. EDS measurements were performed at 2 different positions on the respective samples. As expected, for most of the measurements carbon was most abundant. But even though most of the measurements show carbon quantity over 69% in atomic ratio, the measurement for the o-2 position gives a lower carbon quantity of 33.33%. Also, for this o-2 position of the outer crust sample, the quantity of Si is above 10%, the highest among all measurements. The measurement for the o-1 position of the sample gives the highest Fe quantity, 20.42% in atomic ratio. Our results suggest that Si and Fe have replaced some of the C in the outer samples.

FTIR

Figure 6 shows the measured spectra from the samples compared to those from the literatures, which had treated the FTIR measurement of modern wood charcoals by carbonization temperature and the fossil charcoals (Nishiyama et al. 1988; Cohen-Ofri et al. 2006; Rebollo et al. 2008). It shows that the spectrum of Dong-sam-dong wood has the most absorbance peaks and shows O-H stretching vibrational mode peak (~3300 cm^{-1}), corresponding to H_2O molecules or hydration, even though all samples were dried in the oven before measurement. Also, Dong-sam-dong wood shows 2 peaks for the carboxylate group (COO-: 1650–1540 cm^{-1} of asymmetric CO_2 stretch; 1450–1360 cm^{-1} of symmetric CO_2 stretch), which implies diagenesis with oxidation. Also, 3 peaks for COOH carboxylic acid (1714, 1263, 1216 cm^{-1} of C-O stretch) and 2 peaks of C-O-C bond (890–820 and 1210–1070 cm^{-1}) are observed (Smith 1999; Cohen-Ofri et al. 2006). As shown in Figure 6, the spectra from the inner and outer crust charcoal are much different. The spectrum of the inner core charcoal shows a peak at 1570 cm^{-1}, which might correspond to the carboxylate group (COO-: 1540–1650 cm^{-1}) or aromatic ring stretching mode (C=C: 1510–1600 cm^{-1}) and there is no other carboxylate group peak. The peak at 1570 cm^{-1} is also found in modern charcoals (Smith 1999; Cohen-Ofri et al. 2006). Therefore, the peak may not be from the carboxylate group. Consequently, it is inferred that the inner core part is well preserved by being enclosed in the lava and its isolation from the outer environment helped prevent diagenetic change. The spectrum of the outer crust shows peaks at 426, 579, 777, 1050, and 1150 cm^{-1}. Small peaks at 426, 579, and 777 cm^{-1} may be from the mineral phase of quartz, -SiH_2- twisting mode, and metal-oxygen bond in the brucite-like lattice (brucite: $Mg(OH)_2$), respectively (Dean 1987; Smith 1999; Rebollo et al. 2008; Wang et al. 2009). The peaks

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at 1050 and 1150 cm^{-1} are probably attributed to the Si-O-Si asymmetric stretch bond in silica (1000–1200 cm^{-1}) (Higgins et al. 1961; Smith 1999) rather than the 1025 and 1060 cm^{-1} peaks associated with cellulose β molecules, since it is not expected that these molecules survive the extensive lava heat.

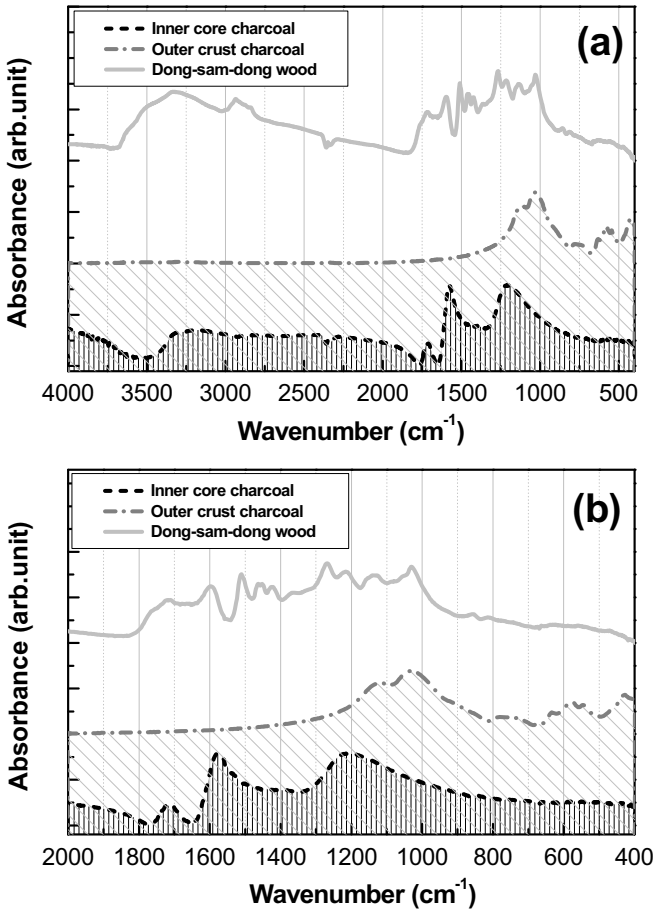


Figure 6 FTIR absorbance spectra from the samples: (a) spectrum at the wave number range 4000–400 cm^{-1}; (b) spectrum at the wave number range 2000–400 cm^{-1}.

Figure 7 also shows spectra of the modern wood charcoals as they undergo various carbonization temperatures (Nishiyama et al. 1988) and the spectra of Figure 6 for comparison. It also shows that the spectrum for the inner core is similar to the spectrum for the carbonized charcoal at 300 or 600 °C. Dong-sam-dong wood, which we assume has undergone self-humification in the swamp area over a very long period, is also similar to the charcoal spectra of 300 °C, i.e. the lowest carbonization temperature. Figure 7a shows that the peak at ~1100 cm^{-1}, which is due to wood cellulose β molecules, disappears in charcoals produced at higher temperatures. Thus, it is clear that the peak observed at ~1100 cm^{-1} in the outer crust sample is not associated with cellulose molecules.

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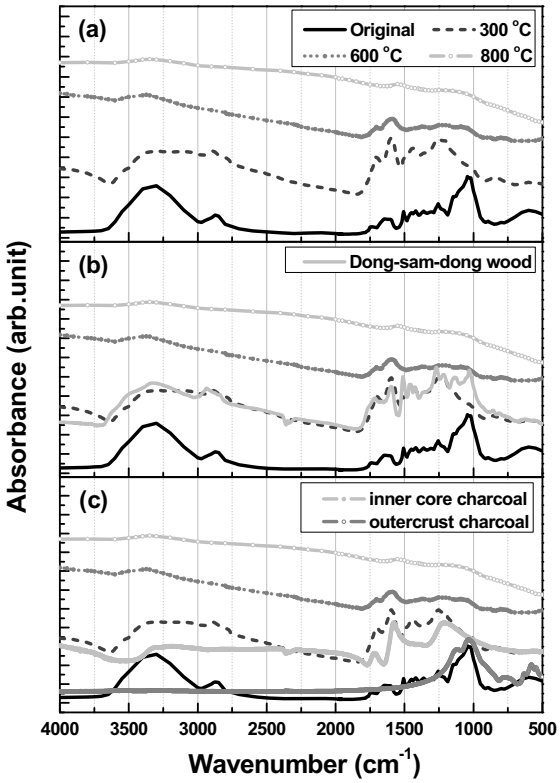


Figure 7 FTIR absorption spectra (a) from Nishiyama et al. (1988) showing the respective spectrum of the modern wood charcoals by carbonization temperature and their comparisons, (b) to Dong-sam-dong wood and (c) to charcoals from Jeongokri, to the measured spectra from samples in Figure 6.

DISCUSSION AND CONCLUSION

The ^{14}C dating results of Jeongokri samples from 5 AMS facilities showed that the range of the determined ages ranges from 49.7 to 22.2 ka BP. The results for the inner core samples, which are below 40 ka BP, seem more reliable than the results for outer crust samples. The volcano effect by the absorption of ^{14}C-free volcanic CO_2 gas around a lava flow cannot account for the large age difference between the inner core and outer crust ages. Although EDS measurements show that carbon exists in the outer crust samples, the quantitative amounts measured by EDS are relatively lower than other samples, and the FTIR spectrum for the outer crust does not show any carbon-related FTIR signal. These observations indicate that the outer crust sample is not in a well-preserved charcoal state, but underwent a considerable modification both chemically and structurally from its interaction with the surrounding lava, resulting in a loss of original carbon material. In fact, we started out this study hoping to see more stably structured charcoal in the tree bark portion of the Jeongokri tree trunk imbedded in volcanic lava. This way, the result would be fitting the archaeological assertion (Kim et al. 2010) that the overlaying layer is formed long before 40 ka. However, the results turned out were the reverse of what was expected. We have not observed any charcoal-like structure in the outer crust; instead, we see an amorphous structure depleted in carbon content. On the other hand, the inner core sample shows characteristics of modestly well-preserved charcoal in

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all analytic methods applied in our present study. Moreover, comparing the FTIR spectrum with that of the other carbonized old wood sample of Dong-sam-dong indicates that the inner core sample of Jeongokri was free from diagenetic changes. Therefore, we conclude that the inner sample may be better for ^{14}C dating. For the carbon-containing material in the outer crust that produced a ^{14}C date older than the inner core, we speculate that acidic carbon soaked up by the tree bark and hot temperature in direct contact with lava flow prevented the original tree bark from transforming to charcoal. However, further study is needed to clarify the nature of this material.

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