A THERMAL AND ACID TREATMENT FOR CARBON EXTRACTION FROM CAST IRON AND ITS APPLICATION TO AMS DATING OF CAST IRON OBJECTS FROM ANCIENT KOREA

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ABSTRACT. A method of thermal and acid treatments was developed at the Archaeo-metallurgy Laboratory of Hongik University in Korea to extract carbon from cast iron, and carbon objects thus prepared from cast iron artifacts of ancient Korea were dated at the University of Arizona's AMS Facility. The thermal treatments consist of heating a specimen to ~1000 °C in a controlled environment with reduced oxygen potential, then cooling it rapidly to room temperature. The heating causes the cementite phase in white cast iron to be graphitized and the quenching suppresses pearlite formation. The specimen then consists of flakes of graphite embedded in a matrix of martensite. The next stage of the treatment is to dissolve the martensite matrix in a solution of nitric and hydrochloric acids to release the graphite as a powder. This material is then cleaned, dried, and pressed into target holders for accelerator mass spectrometry (AMS) analysis. The method was applied to a collection of artifacts from the Korean Three Kingdoms period (about AD 300–668) and the AMS results were compared with chronological estimates from other means.

INTRODUCTION

Cast iron is an important material, used continually in Korea for almost 2 millennia, from the rise of the first ancient states until quite recently. The frequent recovery of abundant artifacts relating to the smelting of cast iron and steelmaking indicates that varieties of cast iron technologies (Park 2005, 2008) came to be established by the beginning of the Korean Three Kingdoms period (about AD 300–668). Cast iron can therefore be regarded as a major archaeo-material bearing crucial information of the most important period in Korean history, not to mention its significance in historical iron technology. In particular, carbon in cast iron carries chronological information and provides a means for the age of artifacts and the date of the related historical sites to be scientifically determined. It is a rare occasion in Korea that no cast iron object is recovered from excavations of archaeological sites constructed in the Three Kingdoms period and afterwards. Nevertheless, the dating of most small-scale excavations in Korea depends on poorly defined artifact typologies (Taylor 1989), and the idea of using cast iron as a datable material is relatively new to Korean archaeologists. They make frequent use of radiocarbon dating, but primarily for organic materials and not for cast iron objects, most probably because of the difficulties encountered in the extraction of carbon samples from cast iron.

The Fe-C phase diagram presented in Figure 1 shows 2 different eutectic reactions, one at 1154 °C producing gray cast iron and the other at 1148 °C producing white cast iron. The method of carbon extraction from cast iron reported by Yoshida (1992) and also by Park (1990) can only be applied when carbon exists in the form of graphite as in gray cast iron, and is of little use in most historical cast iron objects containing no graphite. An attempt was made, therefore, at the Archaeo-metallurgy Laboratory of Hongik University in Korea to facilitate carbon extraction from any type of cast iron by modifying the method developed by Park (1990) for the extraction of graphite crystals from gray cast iron. This modified technique, to be described shortly, was applied to some cast iron artifacts recovered from sites of the Koguryo, Paekche, and Silla kingdoms of the Korean Three Kingdoms period. The resulting carbon samples were sent to the University of Arizona's AMS Facility for ^{14}C

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measurements and the results were compared with those of carbon samples extracted from the same artifacts, using the University of Arizona's AMS Facility's method.

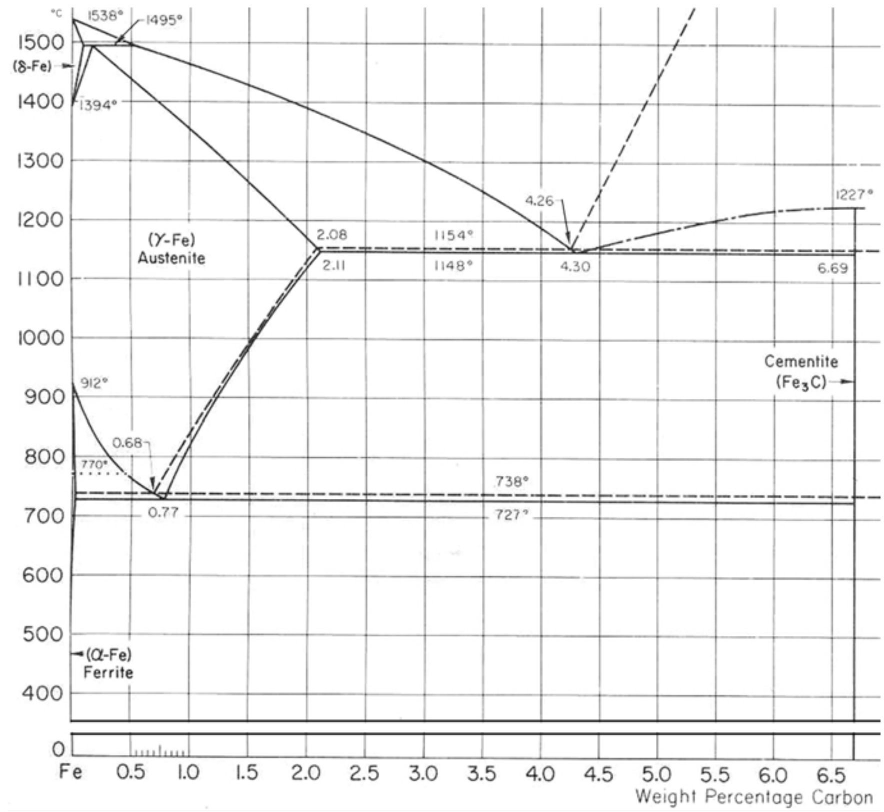

Figure 1 Fe-C phase diagram. Dashed lines represent the iron-graphite equilibrium diagram, except where coincident with the iron-cementite diagram (American Society of Metals 1970).

COMMENTS ON ARTIFACTS

Figures 2a, b, and c show the general appearance of the 3 cast iron objects from which carbon was extracted. The object in Figure 2a is an irregular piece ~5 cm across (Choi et al. 2001), and that in Figure 2b is a circular button ~6 cm in diameter and 1.5 cm in average thickness (Park 2003). The object in Figure 2c is a fragment broken off from a cast iron cauldron.

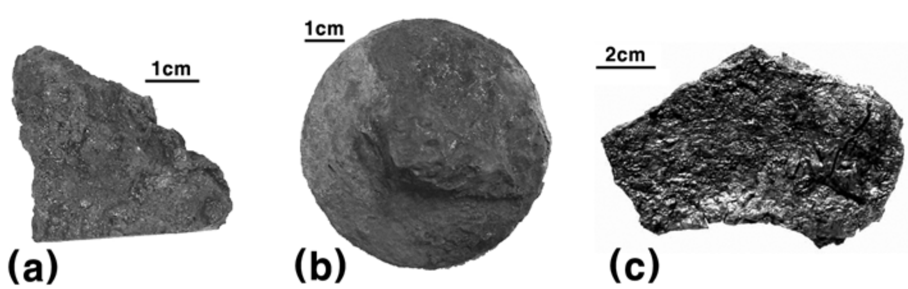

Figure 2 General appearance of cast iron objects examined: (a) piece from a Koguryo site at 1 in Figure 3; (b) a circular button from a Paekche site at 2 in Figure 3; (c) fragment of a cauldron from a Silla site at 3 in Figure 3.

The above objects originated from 3 different historical sites constructed during the Korean Three Kingdoms period, when there existed 4 kingdoms on the Korean Peninsula. These include the Koguryo state in the north including Manchuria, the Paekche state in the southwest, the Silla state in the southeast, and the Kaya state near the southern coast between the Paekche and Silla. Figure 3 is a map showing the approximate territories of the 4 kingdoms with their state capitals marked by arrows. Sites from which the objects in Figure 2 were excavated are labeled as 1, 2, and 3, respectively. Site 1, located in Seoul, was a military outpost used supposedly by the Koguryo state for the defense of its southern frontier until the allied forces of Paekche and Silla destroyed it in AD 551 (Choi 2000). No information on scientific dating is available for this site. Site 2, located in Puyo, the last capital of Paekche from AD 538, was a military fortress used for the defense of the capital city supposedly from the early AD 6th century until its fall in AD 660 (Park et al. 2003). The photoluminescence method applied to a ceramic tile from this site gave the date of AD 600 ± 120 (Hong 2003). Site 3, located in Kyongju, the capital during both the Silla and Unified Silla kingdoms, is a burial known as the Great Hwangnam Tomb (Kim et al. 1994), the largest of all Silla burials. The tomb consists of 2 mounds, one for a male and the other for a female. Its scale and the quantity and quality of relics from it suggest that it was constructed for one of the kings. The cast iron artifact was from the male portion of the site. The exact date of its construction, currently under hot debate, remains uncertain but is placed between the late 4th and early 6th centuries AD based on artifact typologies (Kim YS 2000; Lee 2000) and also on ^{14}C measurements of organic materials by conventional as well as AMS methods (Kim SB 2000).

The Silla subjugated the Kaya first and, with the support of the Chinese Tang forces, conquered the other 2 states. The collapse of the Paekche in AD 660 and Koguryo in AD 668 marked the end of the Three Kingdoms period and the beginning of the Unified Silla, which was the first united kingdom in Korean history (Eckert et al. 1990).

EXAMINATION OF MICROSTRUCTURES

Small specimens were taken from the cast iron objects and were prepared following standard metallographic procedures. They were etched using a solution of 2 volume % nitric acid in methanol for microstructure examination under an optical microscope and a scanning electron microscope (SEM). Their chemical compositions were obtained using an energy-dispersive X-ray spectrometer (EDS)-equipped SEM.

Figures 4a, b, and c present optical micrographs showing structures of the cast iron objects in Figures 2a, b, and c, respectively. Figure 4a consists of dark flakes of graphite and white proeutectoid cementite crystals in the background of pearlite. This structure is typical of gray cast iron of near eutectic composition, i.e. containing ~4.3% carbon by weight. By contrast, the structure in Figure 4b is white cast iron of similar carbon content consisting of fine mixture of white cementite and dark pearlite. Figure 4c shows a mixed structure of gray and white cast iron, referred to as mottled cast iron. The structures in Figure 4 represent those that can form in the solidification of cast iron. Without the addition of silicon (Si), which is the case for most cast iron objects from ancient Korea including the present artifacts, the white structure constitutes the general mode of solidification, and the gray structure is rarely obtained unless a special measure is taken to keep the freezing rate extremely slow. The object of Figure 2a, a small piece with no specific purpose suggested in its appearance, must have resulted from slow cooling, most probably inside a furnace where it was left inadvertently. The mottled structure in Figure 4c suggests the use of a special mold allowing slower freezing rates than those producing white cast iron (Verhoeven 1975).

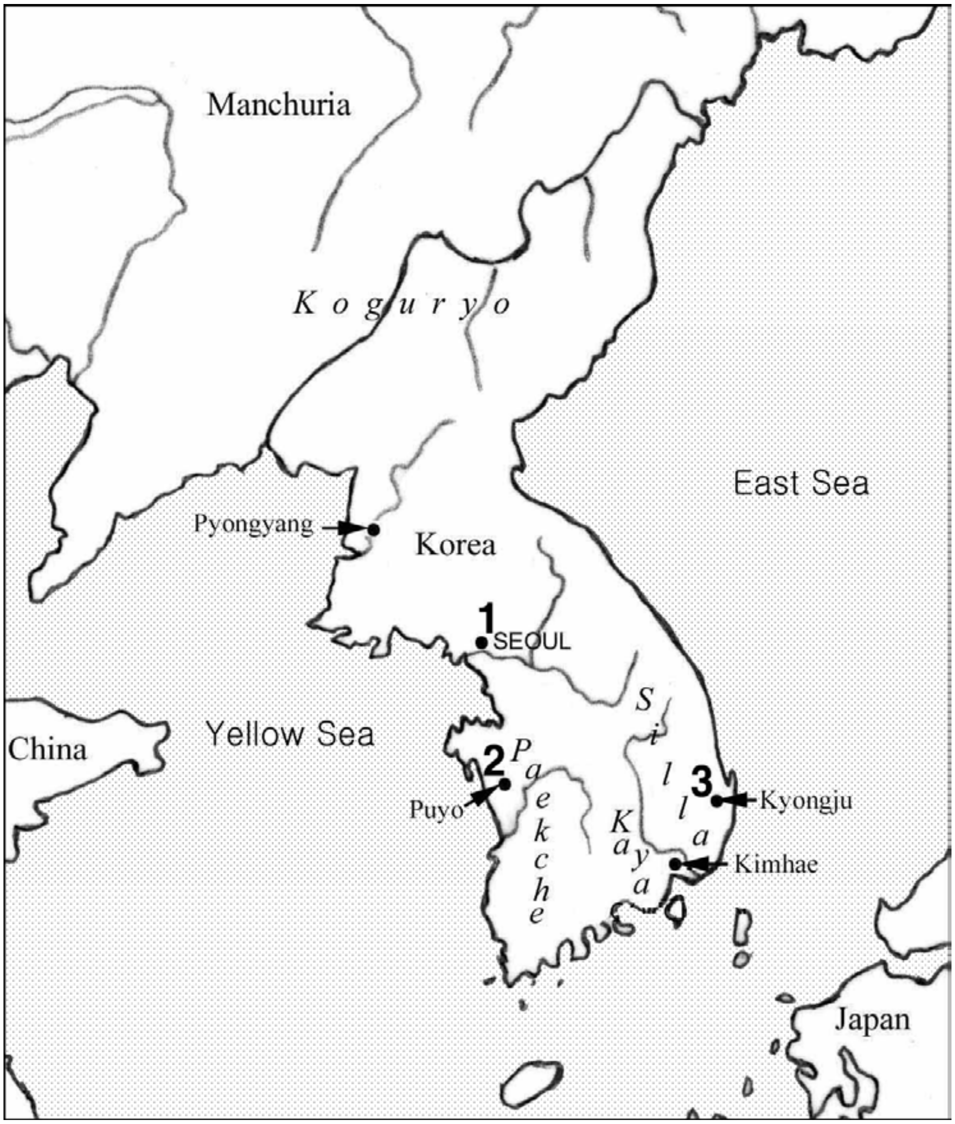

Figure 3 Map showing the Korean Peninsula and surroundings during the Korean Three Kingdoms period (about AD 300–668). Pyongyang, Puyo, Kyongju, and Kimhae were once the state capitals of the Koguryo, Paekche, Silla, and Kaya states, respectively. Numbers 1, 2, and 3 at Seoul, Puyo, and Kyongju locate the sites from which the cast iron objects in Figure 2a, b, and c were excavated, respectively.

THERMAL AND ACID TREATMENTS

Carbon is a component element in all of the phases in cast iron. The carbon extraction used in this study, however, can only be applied to the graphite phase, and begins with a thermal treatment to induce graphite. Specimens with gray structure as in Figure 4a need no treatment for graphitization, but those with white or mottled structures must be treated to transform the cementite phase into graphite. Graphitization of cementite is readily achieved in a prolonged heating at elevated temperatures. In the heating of cast irons containing little silicon, a specific measure needs to be taken to

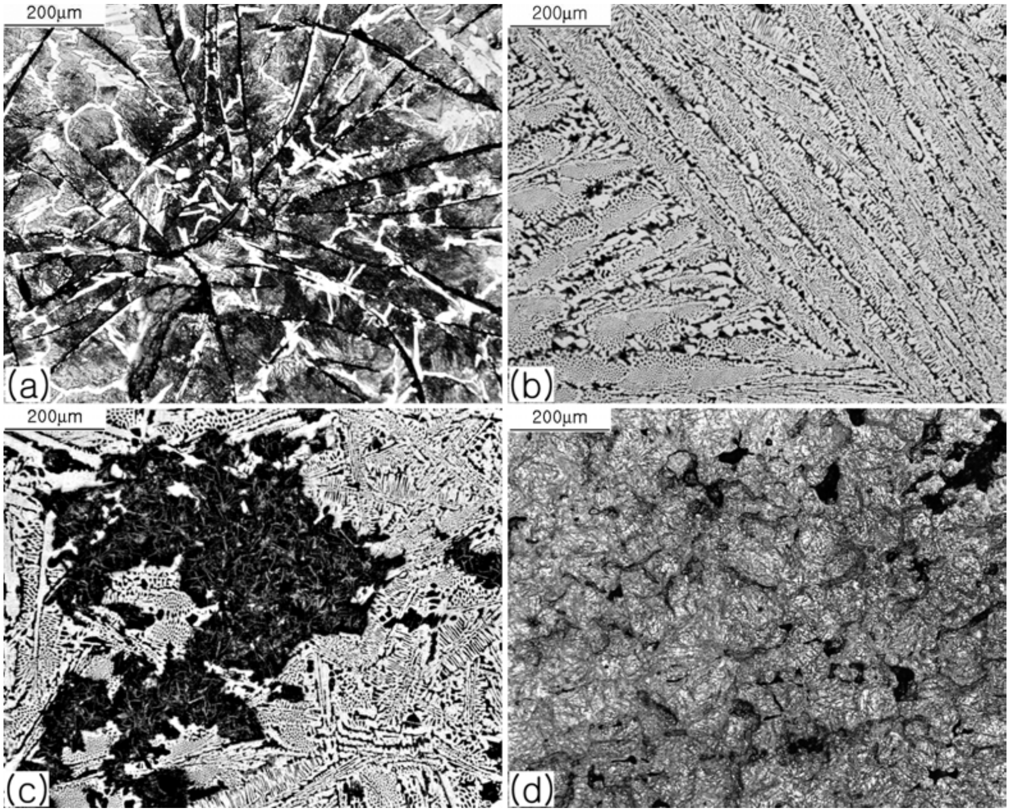

Figure 4 Optical micrographs showing structures of the cast iron objects examined: (a) gray cast iron, (b) white cast iron, and (c) mottled structure observed in the objects in Figure 2a, b, and c, respectively; (d) structure obtained after the thermal treatment of (b).

reduce the oxygen potential in the heating environment. Otherwise, specimens are decarburized rather than graphitized (Park 2008). The control of environment is necessary not only to promote graphitization but also to avoid the loss of iron and carbon atoms by oxidation. In this work, specimens of about 5–10 g are heated at 1000 °C in a vacuum environment provided by a commercial rotary pump, where it takes ~4 hr for full graphitization. Specimens are then quenched in water to suppress the formation of pearlite and thereby to improve the dissolution rate of iron in the following acid treatment. Figure 4d shows the microstructure resulting from the thermal treatments given to the specimen of Figure 4b. The dark curved flakes correspond to the graphite phase and the iron background consists of martensite and retained austenite.

Extraction of graphite after the thermal treatments takes place at room temperatures in a solution of nitric acid and hydrochloric acid commercially available. The acid treatment usually begins with specimens placed inside the solution of nitric acid (60%) only, which in many cases provides a sufficiently high rate of iron dissolution as inferred from the amount of bubbles produced from the reaction occurring at the specimen surface. Hydrochloric acid is added when the rate seems too low, up to 25–50%. In about 12–24 hr, the background iron dissolves almost completely and the graphite phase is collected at the bottom of the solution if it is in the form of isolated particles or floats on the top if it forms an aggregate. In principle, the acid treatment can recover all carbon atoms that form graphite, but not those in martensite, which are lost when the iron phase dissolves in the acid solution. The amount of carbon recovered from specimens of 5–10 g was sufficient for a number of AMS measurements, although the rate of carbon yield cannot be accurately predicted or measured. The graphite phase is then cleansed in distilled water and dried before it is sent to the AMS laboratory where it is made into graphite targets for ^{14}C measurements with no further treatment. The whole process including the heat and acid treatments is free from contamination by modern carbon atoms except by those existing in the environment. Figure 5a is a SEM micrograph showing flakes of graphite extracted from the specimen of Figure 4a. Figure 5b, an EDS spectrum taken from the flakes in Figure 5a, contains no other elements than carbon. Figure 5c, a SEM micrograph of the graphite phase from the specimen of Figure 4d, shows a number of individual blocks each of which consists of stacks of plates roughly hexagonal in shape. These hexagonal plates, reflecting the hexagonal structure of graphite crystals, result from the unique mechanism of graphite growth during the thermal treatment. The flakes in Figure 5a, when highly magnified, are also found to have similar hexagonal structures on the surface. Figure 5d, an EDS spectrum from Figure 5c, shows noticeable peaks at calcium (Ca), iron (Fe), and chlorine (Cl) in addition to the major carbon peak.

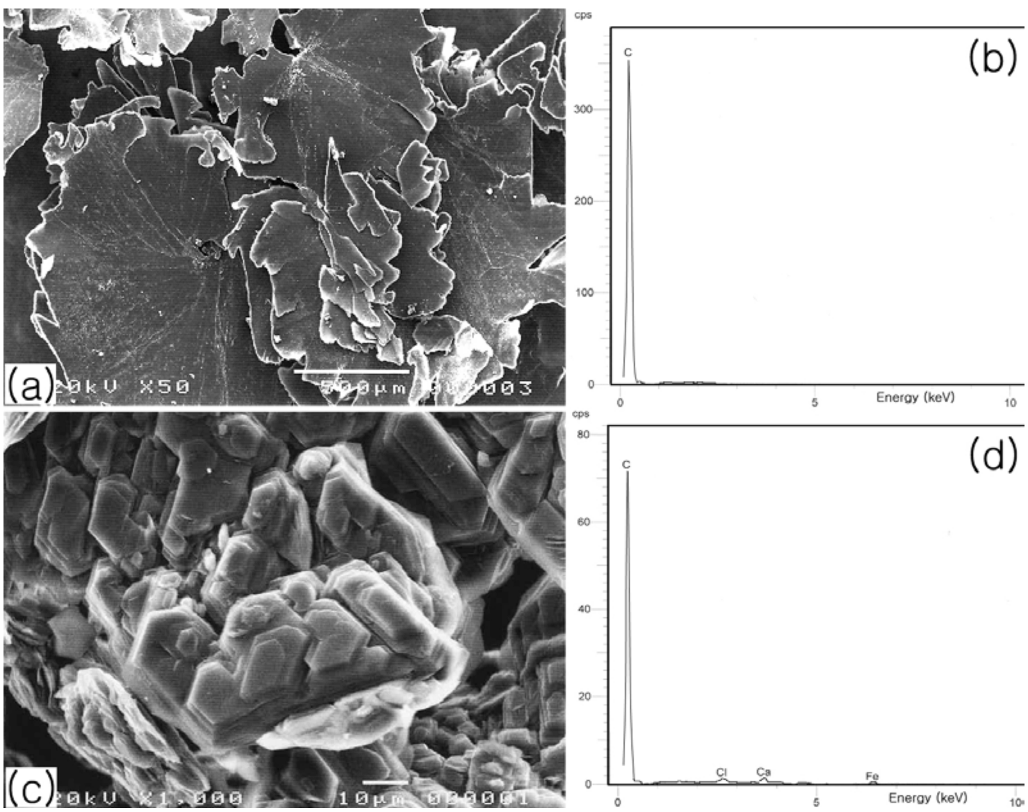

Figure 5 Secondary electron micrographs and EDS spectra: (a) general appearance of graphite flakes extracted from the specimen of Figure 4a; (b) EDS spectrum taken from (a); (c) general appearance of graphite extracted from the specimen of Figure 4d; (d) EDS spectrum taken from (c).

AMS EXPERIMENTS AND RESULTS

Table 1 summarizes the results of 8 AMS measurements on the 3 cast iron objects. The results given under the lab code with the prefix NUTA2 were obtained at the AMS facility installed in the Center for Chronological Research at Nagoya University before the present technique for carbon extraction was initiated. Carbon was then extracted using the so-called dry method (Enami et al. 2004), where the carbon in iron is first converted to CO_2 gases by combusting iron samples under a controlled atmosphere provided by a quartz chamber of an induction furnace. The CO_2 is then singled out at the liquid nitrogen temperature from the combustion gases to be reduced into graphite, which is then made into a target for the spectrometer. The Koguryo and Silla objects were first chosen to test the reliability of the present technique for carbon extraction. Graphite samples extracted using this new technique were sent to the University of Arizona's AMS Facility along with pieces of cast iron from which carbon were to be extracted in the lab using its own method. The iron artifacts were processed at Arizona with a modified RF melting procedure, used to measure ^{14}C in meteorites (Jull et al. 1989). About 100 mg of iron was mechanically cleaned, etched, rinsed, and dried. The sample was then placed in an RF furnace and heated to its melting point in an oxygen atmosphere. Oxygen was flushed through the system to collect CO_2. The CO_2 was then reduced to graphite for AMS analysis. The interlaboratory results were in agreement and another object from the Paekche site was chosen for an additional test to see if the result agreed with a date already available. From this object, carbon samples were not extracted at the Arizona AMS facility.

Table 1 Eight AMS ^{14}C measurements on 3 cast iron artifacts from sites of the Korean Three Kingdoms period (about AD 300–668).

Artifact	Site of recovery	Kingdom	Lab code	Sample type	$\delta^{13}C$ (‰)	^{14}C age (1 σ) (yr BP)	95.4% cal AD (2 σ) age ranges
Anonymous object	Seoul	Koguryo	AA64756	graphite	–25.0	1484 ± 52	434–493 (14.4%) 506–520 (2.4%) 527–653 (83.1%)
			AA64755	gray cast iron	–25	1486 ± 35	443–451 (0.9%) 462–483 (3.0%) 533–648 (96.1%)
			NUTA2-4239		–29.5 ± 0.1	1396 ± 31	599–671 (100%)
Anonymous object	Puyo	Paekche	AA70424	graphite	–25	1448 ± 44	541–660 (100%)
			NUTA2-9144	white cast iron	–30 ± 1	1461 ± 24	561–645 (100%)
Cauldron	Kyongju	Silla	AA64758	graphite	–25.0	1617 ± 53	262–279 (1.9%) 327–564 (98.1%)
			AA64757	mottled cast iron	–25	1668 ± 35	256–304 (12.4%) 313–435 (84.7%) 491–508 (1.9%) 518–528 (0.9%)
			NUTA2-4233		–29.3 ± 0.1	1619 ± 24	392–472 (60.3%) 476–534 (39.7%)

The 1-σ ^{14}C ages of the Koguryo object measured at the University of Arizona using 2 different graphite samples from it are shown in Table 1 to be 1484 ± 52 and 1486 ± 35 years before present (yr BP), where the present year is taken as 1950. Those of the Silla object are 1617 ± 53 and 1668 ± 35 yr BP. These results are almost equivalent within a 1-σ probability range, and generally overlap the ranges measured at Nagoya University, 1396 ± 31 and 1619 ± 24 yr BP for the Koguryo and Silla objects, respectively. There is some discrepancy noticed, however, in the ages of the Koguryo object. The ages of the Paekche object measured at the 2 AMS facilities, 1448 ± 44 and 1461 ± 24 yr BP, are also in agreement. There is a substantial difference, however, in the $\delta^{13}C$ values. The data from the University of Arizona fall consistently around –25‰ while those from Nagoya University are in the vicinity of –30‰. Calendar age ranges in Table 1 were calculated using CALIB Rev 5.0.1 (Stuiver and Reimer 1993; Stuiver et al. 2005) in conjunction with the data set IntCal04.14c (Reimer et al 2004).

DISCUSSION

The feasibility of using the present thermal and acid technique as a reliable method of carbon extraction from cast iron is evident in Table 1, especially in the 2 pairs of data given under lab codes AA64755 and AA64756 for the Koguryo artifact and AA64757 and AA64758 for the Silla artifact. The 1-σ ^{14}C ages of the former are almost identical in both measurements and those of the latter also show fair agreement and substantially overlap within a 1-σ probability range. The measurements made at Nagoya University produced almost identical results, particularly for the Paekche and Silla objects. The deviation, noticed in the ^{14}C ages of the Koguryo artifact and also in the $\delta^{13}C$ values for all the objects, reflects the difference between the 2 laboratories and may not undermine the reliability of the present method of carbon extraction.

Cast iron cannot serve as a practical dating material unless it is free from contamination that may occur in smelting or remelting by the use of ores, fuels, and fluxes originating from sources having widely different ages, as described in detail by Craddock et al. (2002). Little information is available on the engineering processes used in the production of the cast iron objects under consideration, and it is difficult to know how their ^{14}C ages relate to their real dates. This problem, however, should not cause one to overlook the valuable information that can be drawn from ^{14}C measurements on cast iron when used in conjunction with other information. All the sites in Table 1 were well dated based on various sources of information. Because of its historical importance, the Silla tomb has been dated in a number of studies as summarized by Kim (2000). The relative chronology inferred from typology by both Korean and Japanese scholars is placed between the late 4th and late 5th century AD (Kim 1998). The first scientific dating experiment, performed at the Korea Atomic Energy Research Institute (KAERI) in 1976 by applying the conventional ^{14}C method to 7 wood samples (KAERI135–137, -140, -141, -151, and -152), placed their ^{14}C ages in a range from 1540 ± 100 to 1772 ± 120 yr BP. In 2000, samples of wood, fabric, and lacquered vessels were dated using both the conventional and AMS technique. The 5 results (GX27209–27213) from β-ray counting at the Geochron Laboratory in the USA range from 1720 ± 120 to 1870 ± 130 yr BP, and the 3 AMS measurements (SNU00117–00119) made at the Seoul National University's AMS Facility in Korea were 1530 ± 40, 1570 ± 40, and 1730 ± 40 yr BP. Most of the results obtained at KAERI and Seoul National University substantially overlap with the ages of carbon samples from cast iron presented in Table 1 under the lab codes AA64757–AA64758 and NUTA2-4233. There is, however, too much uncertainty in the data measured with conventional techniques, and the calibrated ages, mostly placed around the mid-2nd century AD with substantial uncertainties, can hardly be compared or contrasted with those estimated on typological grounds. By contrast, there is fair agreement between the relative chronology and the age ranges inferred from the AMS measurements either on carbon samples from cast iron or on objects of wood and fabric. It is significant that the results from the other 2 cast iron objects are mostly in agreement with the ages estimated from other sources.

In Korea, little archaeological or documentary evidence has been reported on the use of mineral coal in ancient as well as medieval periods. Excavation of iron smelting sites always comes up with a number of fresh or burnt charcoal pieces and frequently locates facilities for charcoal making in their neighborhood. In their AMS and thermoluminescence (TL) experiments on samples from an iron site near a mining field located close to the Silla capital Kyongju, Park et al. (2005) found that it was run at around AD 1700 on the basis of charcoal. This mining field is famous for its long history of exploitation as a major iron source for nearly 2000 yr and also for its arsenic-rich magnetite ores found nowhere else in Korea. In view of the historical and geographical importance of this site, it was suggested that charcoal had dominated the local iron industry until quite recently. This premise is also supported by the AMS experiment Park and Nakamura (2004) performed on a cast iron object from the Kaya capital Kimhae, shown in Figure 3. Its ^{14}C age was 1776 ± 23 yr BP, which, when calibrated, predicts the 3rd century AD as the most probable date, in agreement with the relative age estimation. It is interesting to notice that the high arsenic content measured in the object was taken as strong evidence that it may have been imported from the Silla Kingdom.

CONCLUSION

A method of thermal and acid treatments was applied to cast iron for the extraction of carbon samples to be used in AMS ^{14}C measurements. The thermal treatments consist of heating for graphitization in a reduced oxygen environment, and a quench treatment to avoid pearlite formation during cooling. The subsequent treatment in nitric and hydrochloric acids successfully dissolves the iron matrix to release graphite in the form of powder, which can then be made into graphite targets for AMS with no further treatment. This method and others well established at the AMS facilities of the University of Arizona and Nagoya University were applied to artifacts from the Korean Three Kingdoms period (about AD 300–668), and the AMS results confirm the reliability of the present method. In addition, the ^{14}C ages, in general agreement with the estimated chronology from other sources of information, suggest that iron smelting in ancient Korea was primarily run on the basis of charcoal with little possibility of incurring carbon contamination leading to unpredictable errors.

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