

PRETREATMENT OF IRON ARTIFACTS AT SNU-AMS

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ABSTRACT. We present the current status of accelerator mass spectrometry (AMS) dating of iron artifacts at Seoul National University (SNU). In ancient iron production, charcoal was widely used as carbon for the smelting process, whereas coal is used in modern times. If reliable data could be obtained from carbon by using AMS, ancient iron artifacts could be traced to their production age. In normal acid treatment, it is not easy to extract carbon due to its colloidal property. The negative charge property of the carbon colloid, however, makes it possible for it to be precipitated with positive ions by dissolving the iron chemically. An extraction yield of the carbon incorporated in modern cast iron of about 70% is attained. More refined methods to increase the extraction rate are under progress for archaeological applications.

INTRODUCTION

Following the installation of accelerator mass spectrometry (AMS) at Seoul National University (SNU) in Korea (Kim et al. 2000), and success in pretreating wood and peat samples (Lee et al. 2000), we have begun to consider more difficult sample matrices such as iron. Ancient iron artifacts are believed to be made from ore, most of which is presumed to be iron sands, by smelting it in a furnace with charcoal, dung, peat, or coal. This procedure produces the high temperatures needed to smelt the ore, which are not attainable from a simple open fire. If it is presumed that charcoal is mainly used as the fuel in the smelting process, one can, in principle, determine the production age of the artifact. The usefulness of carbon dating in iron, of course, relies on the contemporaneity of that carbon with the time of its manufacture. Thus, the carbon source should have a radiocarbon content indicating the date of incorporation of that carbon into the artifacts. Until the Industrial Revolution, most smelting in China, apart from exceptional cases, was carried out using charcoal-fired furnaces (Beukens et al. 1998). Moreover, most old iron artifacts are believed to have been smelted from freshly cut wood. Therefore, results of ¹⁴C dating imply the age of manufacturing within the error in AMS analysis.

AMS has made it possible to carry out carbon dating on samples as small as 0.1 mg or less, so that 2 g of wrought iron (0.05% carbon content) or 5 mg of cast iron (2% carbon content) can be analyzed for dating if a 100% extraction yield is possible. Compared to conventional beta decay counting, the problems of sample size and poor precision are considerably lessened. This implies that carbon dating of precious ancient iron artifacts in archaeology is within reach of dating analysis.

Although in the Western world, the use of charcoal is generally assumed in old iron artifacts, the use of coal as a substitute for charcoal in Chinese steel making is often mentioned (Beukens et al. 1998). In the case of Korea, all evidence within a Korean context of the use of coal appears either anecdotal or indirect. However, the recent AMS dating of a Korean Iron Warrior on Horseback (Beukens et al. 1998), which was carried out at the IsoTrace Laboratory in the University of Toronto, yields 1.69 ± 0.14 pMC, corresponding to $32,780 \pm 670$ BP, clearly demonstrating that coal was used in the production of this object. This leads to one of the following conclusions: 1) the general belief of the Korean archaeological society that coal was not used during this era should be reexamined, 2) the object was imported from China where coal was often used in the smelting process of iron, and 3) some contamination from terrestrial native iron or meteoritic iron has occurred in the ore used.

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Extraction of Carbon from Iron Sample

Past carbon extraction techniques have usually been based on the method of van der Merwe (Cresswell 1992). In this method a finely divided sample, after physical treatments to remove corrosion, is heated to its melting point in a furnace. Carbon diffuses to the surface of the sample grains and is finally extracted in the oxidized form, CO₂, and trapped in liquid-nitrogen-cooled traps. This method is dubbed the dry method (Cresswell 1992) compared with the wet method used here. The wet method, originally developed at Nagoya University (Nakamura et al. 1996), involves dissolving the iron with acid. Since the carbon is dissolved in acid as a colloid, whose size is too small to be extracted (1 nanometer), it must be condensed for extraction. Fortunately, the carbon colloid is known to have negative electrical properties (Hurukawa 1997). It can thus be precipitated with the positive ion of the metal (Cu⁺ ion in this report).

Below we present a brief discussion of this chemical method for cast iron from modern times.

1. The sample of cast iron was divided into mm-sized fragments using a sawing or drilling machine. The fragments, which altogether weighed 80 mg, were cleaned by acetone to remove cutting oil, which could be a contamination source. Before this procedure, the content of the sample was analyzed by the element analyzer, which showed 2.7% carbon content. Thus, the carbon content in the cast iron sample is 2.2 mg.
2. We dissolved it in 0.015M CuCl₂ (about 300 mL) at room temperature for an hour. Then, the extracted carbon colloid, which is known to have a negative charge property (Hurukawa 1997), was precipitated with the positive charged Cu⁺ ion in CuCl₂.
3. The dark yellow precipitate was dissolved again in 2M HCl (about 300 mL) for 2 hr to remove Cu still remained in the extracted carbon colloid. This procedure was carried out in an oxygen (O₂) environment i.e., oxygen was bubbled into the container of HCl and the precipitate. We repeated this process 6 times until the precipitate began to turn black.
4. The final precipitate was washed with distilled water until neutral and dried in an oven at 120 °C. The final products weighed 2.02 mg and analyzed in the element analyzer. It showed a 75.7% carbon content yield. Most of the remainder was believed to be Fe. Therefore the extraction yield, which is calculated as follows,

$$\begin{aligned} \text{Yield (\%)} &= (\text{Weight of extracted carbon}) / (\text{Weight of carbon in sample}) \\ &= (2.02 \text{ mg} \times 0.757) / (80 \text{ mg} \times 0.027) \times 100 (\%) \end{aligned} \quad (1)$$

is 70%. This is similar to the 80% extraction yield reported at Nagoya University (Hurukawa 1997).

RESULTS

A modern cast iron sample, after the above pretreatments, underwent a standard combustion process and was finally reduced to a graphite target (Lee et al. 2000). The following table is the AMS dating result.

Table 1 AMS dating result for modern cast iron sample

Sample ID	Sample type	Weight (mg)	LAB #	δ ¹³ C (‰)	BP
S 15	Fe ^a	2.6	Fe	-43	21,500 ± 250

^aModern cast iron with 2.7% carbon content

As expected, the modern Fe sample shows about 20,000 yr, which is due to the coal used in the smelting process of Fe production. Archaeological artifacts, for example, an iron ax presumably produced in the Korea Dynasty (AD 500–600) and slag found in an old temple, are currently undergoing measurements. These forthcoming data would give an interesting result regarding the question of whether coal had been used in the production of ancient iron in Korean history. However, in the case of slag, the carbon extraction seems difficult due to its non-uniform carbon distribution.

SUMMARY AND CONCLUSIONS

The wet method for carbon extraction from iron is now well established in our SNU-AMS laboratory. It represents a very simple and economical method for AMS dating of iron samples and provides high carbon extraction yields.

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