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Consolidation or initial design? Radiocarbon dating of ancient iron alloys sheds light on the reinforcements of French Gothic Cathedrals

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ABSTRACT

Large quantities of iron reinforcements, found in most Gothic monuments, are a data source for the interpretation of medieval architecture however their role both in contemporary engineering theory and the technical reality of construction yards has not yet been specified due to the difficulty of directly dating them. We present here an original radiocarbon dating methodology to date metal itself. Radiocarbon dates were measured for iron reinforcements used in specific parts of Bourges and Beauvais cathedrals, two iconic buildings in the development of French gothic architecture. Coupled with archaeometric and archaeological data, the new chronological results illuminate the major and active roles played by iron in the strategy of the building yards. At Bourges, iron was assimilated into the cathedral's construction strategy, whereas at Beauvais iron was integrated from the initial design, added to the monument following the vicissitudes of the building yard, and still used during the modern period. Thus, through decisive advances in radiocarbon dating of iron artefacts, the evolution of medieval architectural and engineering thought and action has been more reliably reconstructed.

1. Introduction

It is now currently understood that most gothic cathedrals and churches can no longer be considered as structures of purely lithic design. In addition to stone, the use of large quantities of iron or steel reinforcements, clamps as well as chains and tie-rods of substantial size has been brought to light by recent historical and archaeological researches (Chapelot and Benoit, 1985; Bernardi and Dillmann, 2005; L'Héritier et al., 2010, L'Héritier, 2007; Timbert, 2009). Thus, at Soissons, Paris, Rouen, Beauvais, and Bourges metal was potentially considered being part of the initial constructive design considering archaeological evidence from construction analysis (Erlande-Brandenburg, 1996; Taupin, 1996; Férauge and Mignerey, 1996) and archaeometry that brought light the use of ancient processes to produce metal components (Dillmann and L'Héritier, 2007; Dillmann, 2009; L'Héritier et al., 2010). Unfortunately, the history of medieval monuments beginning with their construction is often tumultuous, given the succession of building phases since the medieval period for the purposes of modification, repair and conservation. Each of these medieval, modern or contemporary building yards potentially used metal, thereby often making the archaeological interpretations of a building limited in this respect. At this stage, the absolute dating of these iron elements is essential for specifying their place both in medieval constructive thought and the technical reality of construction building yards. The aim of the present paper is to propose an original methodology for radiocarbon dating to examine reinforcing elements discovered in Bourges and Beauvais Cathedrals, two major monuments in the development of French gothic architecture in which ferrous alloy armatures of significant size (*i.e.* tie-rods and chains) have been identified.

The basic idea for dating ferrous alloys by radiocarbon is that the carbon contained in the steely zones of the ancient metal, coming from the charcoal used during ore smelting, can be extracted and its isotopic ratio determined, leading to a radiocarbon date. With the advent of accelerator mass spectrometry (AMS), dating of archaeological samples of a few milligrams has become technically feasible (Cook et al., 2003a). With uncertainties (see below), the

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radiocarbon dates correspond to the manufacturing date of the artefact. Nevertheless, only a hundred iron samples have been dated by radiocarbon and published to date (Van der Merwe and Stuiver, 1968; Cresswell, 1992; Kusimba et al., 1994; Beukens et al., 1999; Cheoun et al., 2001; Cook et al., 2001; Craddock et al., 2002; Hüls et al., 2004; Oinonen et al., 2009) and ~15% of the dates obtained seemed to be unreliable (Cook et al., 2003a). This discrepancy could be due to different factors: the age of the wood used to produce the charcoal (Forbes, 1955, 1963, 1964; Kusimba et al., 1994), potential contamination with the carbonates of the ore, recycling of older metals, cementing with other materials containing carbon. Another major limitation is related to the low carbon content of bloomery iron obtained in the Middle Ages, heterogeneously distributed within the metallic matrix. This stresses the necessity of having a good knowledge of the nature of the material prior to attempt dating. Another difficulty is linked to the carbon extraction from the sample. The protocols explored since the 1960's (Cook et al., 2003a) are based on a preliminary chemical cleaning or mechanical preparation to abrade, cut or mill the artefact (Cook et al., 2003b; Hüls et al., 2004; Oinonen et al., 2009). Various approaches for extracting carbon were then used based on acidic dissolution of iron (Nakamura et al., 1995; Scharf et al., 2004), and combustion without (Van der Merwe and Stuiver, 1968; Cresswell, 1992) or with acidic pre-cleaning (Cook et al., 2001; Scharf et al., 2005). Scharf et al. (2005) also proposed making a metal/carbon mix ready to be directly measured by AMS. This method is unfortunately not adapted to samples with relatively low C content such as ancient bloomery iron. None of these approaches consider the microscopic heterogeneity of bloomery iron and the fact that important zones of the artefact could contain very low C content, considerably lowering the chances of randomly sampling significant quantities of iron. Considering these different risks of misdating, we set up an adapted methodology for dating bloomery iron found in cathedrals following a detailed metallographic and Slag Inclusions (SI) study performed in transverse sections of the artefacts (Pagès et al., 2011). This approach allows for the determination of the chemical composition of SI entrapped in the metal providing information on the iron-making process and potential cementing and recycling of the archaeological object (Dillmann and L'Héritier, 2007; Fluzin et al., 2011). This methodology was validated on artefacts of known age from different periods and obtained with different kinds of ores including carbonated ones. We then examined the resulting ^{14}C data for iron reinforcements in Bourges and Beauvais Cathedrals, with regard to their location in the structure of the cathedrals.

2. Methods

2.1. Experimental procedure

All objects were cross-sectioned and polished to expose both the metallic matrix and the SI entrapped in the metal. By working on cross-sections, we excluded any pollution due to rust that could be a source of carbon contamination (Cresswell, 1992; Scharf et al., 2005). The procedure consists of first performing a metallographic observation of the matrix of the polished cross-section under an OLYMPUS light microscope (BX51 model) under reflected light to visualise the possible welding lines. This step was followed by analysis of SI entrapped in the metal to get information on the manufacture of the object, especially identifying use of metal pieces of different provenances (recycling) (Dillmann and L'Héritier, 2007). The chemical analysis of the SI is performed by X-rays Energy Dispersive Spectrometry coupled to a Scanning Electron Microscope. The SI analytical methodology will not be detailed here and can be found in Pagès et al. (2011), Leroy et al. (2012), Disser et al. (2014). A second metallographic etching was then done on the polished cross-section using Nital 4% to reveal the distribution of the carbon content within the metal allowing us to sample in the highest carburized zones for ^{14}C dating. It was also verified that no evidence of cementation could be observed. The chemical cleaning by nitric acid (HNO_3) also permitted removal of the outer surface and enhanced the elimination of possible carbon pollution that could have been added during cutting or polishing. Each cross-section was finally washed with de-ionized water, followed by ethanol washes and then dried to suppress any carbon contamination in an oven at 80 °C. The conditions required for each step of this preparation are described in Table 1.

Table 1
Sample treatment conditions used on the iron artefacts during the sampling procedure.

Step	Treatment	Remark
Cutting	SiC saw blade	Cross-section Exclusion of corrosion layer sampling
Polishing_1	SiC abrasive papers	
Polishing_2	Diamond paste	
Metallographic observation_1	4% HNO_3 etching	Revelation of metallic matrix microstructure + welding line location
Polishing_3	Diamond paste	
SI analyses		Information about manufacture of the object + identification of recycling case
Polishing_4	Diamond paste	
Cleaning_1	EtOH x2 + US 10 min	
Metallographic observation_2 (Cleaning_2)	4% HNO_3 etching	Revelation of the carbon distribution
Cleaning_3	H_2O	
Cleaning_4	EtOH	
Drying	80 °C	
Cleaning_5	Surface short abrasion + drill	In the highest carburized zones
Sampling	Ceramic/TiN or CoB coated drills	In the highest carburized zones

After this preparation, we collected samples in the highest carburized zones with ceramic, TiN or CoB coated drills of several millimetre diameters (Ø2 mm, Ø2.5 mm, Ø3.5 mm). Particles collected are under powder or shavings less than 1 mm thick. To ensure the elimination of potential carbon contamination, a first short abrasion with the drill was done to remove the outer layer of iron prior to the final sampling. The extracted particles were then picked up with a magnet. We finally sampled the weight required (a few hundred milligrams) to obtain up to 1 mg of carbon when

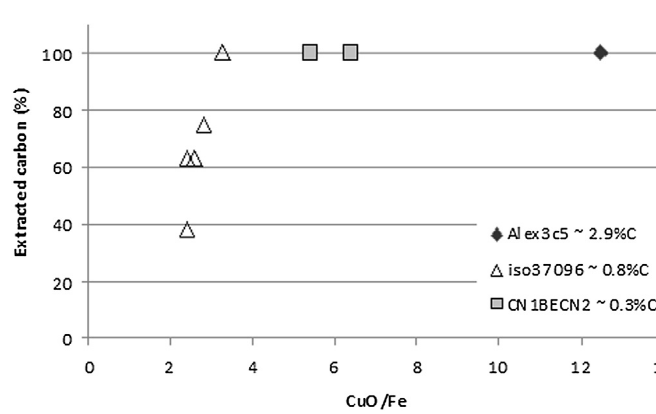

Fig. 1. Carbon extraction efficiency (%) as a function of CuO/Fe ratio values for samples with various carbon contents ($T = 850$ °C for 5 h).