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Effect of HF leaching on ^{14}C dates of pottery

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ABSTRACT

This paper presents the experiments with ^{14}C dating of two potsherds, which contained carbon dispersed rather homogeneously in their clay fabric. After AAA treatment, the potsherds still appeared to be contaminated with young carbon, presumably connected with humic acids. To make removal of humic acids more effective, we treated the sherds with HF acid of different concentration. The ^{14}C results obtained demonstrate that HF treatment indeed helps to remove humic contaminants, but it also mobilizes carbon bound to raw clay, which may make ^{14}C dates too old. We conclude therefore, that using a simple combination of HF and AAA treatment seems insufficient in reliable ^{14}C dating of carbon homogeneously dispersed in the volume of potsherds.

1. Introduction

Pottery is one of the most important materials found in archaeological excavations, mostly because its typological features are usually characteristic for specific communities and cultures. Absolute dating of potsherds may give direct information on development of societies and their interrelationships. However, ^{14}C dating of pottery is difficult, and it is rather rarely performed. As shown e.g. by Hedges et al. [1], quite reliable ^{14}C dates can be obtained on organic-rich coating, such as from soot or food, preserved on the surface of ceramic vessels. Another possibility is to date large carbonaceous fragments found inside the sherds, like fibres of temper used during pottery manufacturing, or charcoals [2,3]. Probably the best material for ^{14}C dating is provided by specific lipids chemically extracted from the sherds and then isolated by gas chromatography [4,5], but this technique is complicated, and applicable only to pot fragments that were devoted to culinary use with a lipid-bearing food, and where lipids have preserved well.

In many cases, carbon is dispersed rather homogeneously inside the sherds, and no clear organic remains can be separated for dating. The carbon suitable for dating in such a sherds is that remaining from the organic temper [1,6], or originating from the fuel used during pottery production. However, the sherds usually contains also the carbon bound in the clay used by the potter [7], and also that of the humic acids fixed in a sherd during its burial in sediments [1]. The carbon in the raw clay makes ^{14}C dates too old [3,8], and in order to minimise its influence, combustion of sherds at low temperature has been proposed [7].

Humic acids, usually younger than the sherds itself, may also be clay-bound and thus difficult to eliminate by simple AAA (acid-alkali-acid) treatment. As noted by Hedges et al. [1] effectiveness of humic acid extraction in NaOH can be largely increased by the action of 40% HF. However, recently, Kovaljuch and Skripkin [9] described the procedure of combined treatment with weak (0.1 N) HF and AAA, claiming that it should be suitable for effective elimination of humic contamination from the dated sherds.

In this paper, we present results of ^{14}C dating of two potsherds from archaeological sites in Opatowice (Poland) and Kosice (Slovakia). In both cases, first attempts at ^{14}C dating, performed without HF treatment, gave dates clearly too young with respect to the archaeological expectations. Supposing that the wrong dates were produced by ineffectively removed humic acids, we performed some experiments on the influence of HF leaching on ^{14}C dates of the analysed sherds.

2. Material

2.1. Opatowice

In Opatowice, on the so-called Prokopiak's Mount (Kujawy region, central Poland), a large complex of settlements from the Late Neolithic and the Early Bronze Age was explored [10,11]. The investigation of the part designated as site Opatowice 42 [12], revealed at least 14 phases of occupation (3 settlement phases and traces of 11 short stays). All the settlement phases are linked to

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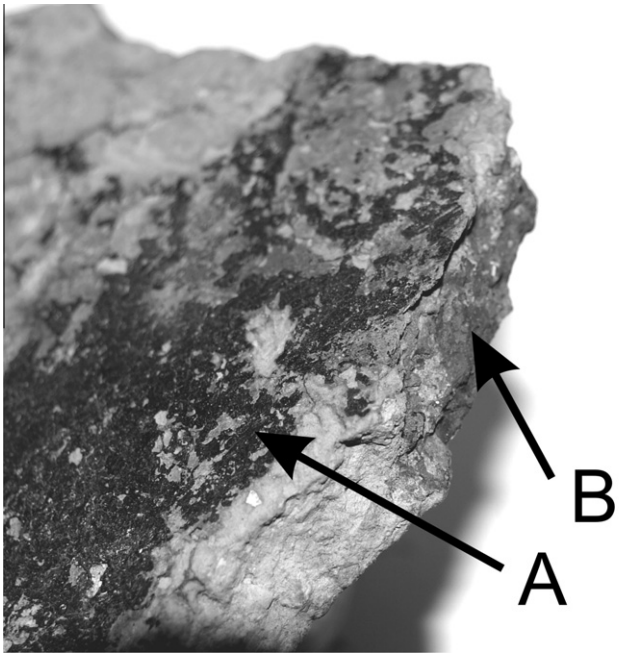

Fig. 1. Photo of the fragment of potsherds Opatowice 42/9213/C15, with places where the two types of material was collected. A – organic coating, B – volume.

the Funnel Beaker Culture. The sample labelled Opatowice 42/9213/C15 was one of six potsherds from the site which were submitted for ^{14}C dating in the Poznań laboratory. All these potsherds had thick organic coating (Fig. 1), identified as wood (mainly birch) tar [13] probably used as a seal of culinary pots, which offered good opportunity for reliable ^{14}C dating. Indeed, ^{14}C dates of these samples clustered in two short periods: around ca. 4750 ^{14}C BP (4810 ± 40, 4770 ± 40, 4710 ± 40) and around 4500 ^{14}C BP (4590 ± 50, 4540 ± 35, 4475 ± 35), in agreement with the dates of bones collected at the same levels (4700 ± 35 ^{14}C BP and 4515 ± 35 ^{14}C BP, respectively). However, the stratigraphic position of the sample 42/9213/C15 (dated at 4710 ± 40 ^{14}C BP) suggested that it could also belong to the younger period. This could be the case if the fragment of coating sampled for ^{14}C contained an admixture of material taken from the wall of the potsherds, which could be contaminated with older carbon bound to raw clay. The control sample of the volume of the potsherds, however, gave much younger ^{14}C dates, i.e. 4130 ± 40 ^{14}C BP (Poz-15502) and 4240 ± 40 ^{14}C BP (Poz-17483), suggesting contamination with humic acids rather than with clay carbon. To gain closer insight into the problem, we decided to analyse ^{14}C in several fractions, collected using different methods of sample pretreatment.

2.2. Kosice

Sample Košice-Červeny Rak 07/1 was one of the thick walled, undecorated sherds from pit 2 at this site, situated in the middle Hornad valley (Eastern Slovakia) and excavated by L. Kaminska [14]. It is attributed to the transitional phase between the Körös and the Eastern Linear Culture, described as the Protolinear Phase [15]. This sherds did not have organic coating, and the only available carbon was dispersed fairly evenly in the groundmass of the sherds; its origin was mostly the organic temper used in the preparation of the ceramic mass. The ^{14}C date obtained with no HF treatment (5660 ± 40 BP) was clearly younger than expected.

The age of the site is particularly important because it is one of the northernmost sites with distinct Körös Culture tradition in pottery technology and decoration (particularly relief decoration – e.g. Fig. 13 in [15]), situated in the Hornad basin far to the north of the Körös sites in the Upper Tisza basin, and north of the Central European agro-ecological barrier [16]. Additionally, pit 2 in Košice-Červeny Rak furnished some fragments of pots with linear decoration (zigzags, wavy lines), which suggest the transition to the Eastern Linear Culture (AVK) (Fig. 14 in [15]).

While the classical phase of the Körös Culture in the middle Tisza valley was radiocarbon dated at between 7000 and 6800 BP [17], the transition towards the Eastern Linear Culture in the Upper Tisza basin was dated to the period between 6800 and 6300 BP. The latest Körös sites in the Upper Tisza basin can be placed in this time span (i.e. Nagykörű-Cooperative Orchard – 6751 ± 40 BP (VERA-3051) and 6890 ± 35 BP (VERA-3474), Kötelek – 6630 ± 60 BP (BLN-1677) and 6780 ± 35 BP (VERA-3478), the Méhtelek type sites (6835 + −60 BP (Bln-1331), 6665 ± 60 BP (Bln-1332), and 6625 ± 60 BP (GrN-6892)) and the earliest Eastern Linear sites (i.e. Füzesabony-Gubakút from phase 1 – 6660 ± 55 BP (Fg-135) to phase 4 dated at between 6345 ± 75 BP (Fg-131) and 6252 ± 58 BP (Deb-4852); Mezökövesd-Mocsolyás) [18,19].

Taking into account the dynamics of cultural processes and the First Temperate Neolithic (FTN) settlement spread from the Upper Tisza basin, the expected date for Košice-Červeny Rak pit 2 would fall in the middle of the time span in question, i.e. about 6500 BP. Indeed, exactly this date (6520 ± 50 ^{14}C BP, Poz-22131) was obtained on another sherds (also undecorated) from pit 2, technologically and typologically similar to sherds no 1. This is further evidence to suspect that the young ^{14}C date of sample KČR 07/1 was caused by contamination with humic acids not efficiently removed by the AAA treatment. To increase efficiency of humic acid removal, we performed several tests with leaching the sherds with HF.

3. Methods

Before sampling, the surface of available sherds was washed with warm deionised water, using a soft brush, with care to not to destroy the organic coating. Slices of organic coating (1–2 mm wide, up to 0.5 mm thick) were carefully split out of the ceramic wall with a knife ("coating" samples in Table 1). To take "volume" samples (Table 1), whole sherds (after removing any traces of coating) were gently crushed with a hammer into grains of ca. 1 mm.

All the samples were treated with 1 N HCl for 12 h (room temperature), and then, to dissolve humic acids, with 0.1 N NaOH for 12 h (room temperature). The insoluble fraction was treated again with HCl and labelled as RES. In order to increase the effectiveness of humic acid extraction, before the AAA steps the sample was treated with HF of different concentrations. The treatment with HF took 3 h and during the last 10 min of that stage, the effectiveness of HF dissolution was stimulated by using an ultrasonic bath. After the chemical treatment, each fraction was combusted, graphitised and forwarded for AMS ^{14}C measurement. In addition, we determined the yield of chemical preparation (using dry-mass weight) and also the content of carbon (by measuring amount of CO_2 obtained after combustion).

In the first series of experiments, samples were combusted at 900 °C. In this series, if appreciable amount of humic acids was dissolved in NaOH, they were precipitated with HCl, and collected for ^{14}C analysis as the SOL fraction.

In the second series of experiments, samples were first combusted at 400 °C (labelled "400" in the sample name), and the material remaining after that step was combusted again at 900 °C (labelled "400 res"). Using such two-stage combustion, we tried to distinguish the effects of HF-leaching on carbon bound in organic compounds from those on carbon bound in clay [4]. In this series of experiments, only the NaOH-insoluble (RES) fraction was analysed.