AMS RADIOCARBON DATING FROM THE NEOLITHIC OF EASTERN UKRAINE CASTS DOUBTS ON EXISTING CHRONOLOGIES

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ABSTRACT. The Seversky Donets River (Northern Donets) basin in eastern Ukraine and the Lower Don River valley in Russia were inhabited by populations that have been considered to be one of the earliest pottery-using cultures in Europe. The early pottery sites are all located on riverbanks and contain middens with many mollusk shells and fish bones. This suggests the intense exploitation of freshwater resources. The accuracy of radiocarbon dates obtained from these locations is of crucial importance for understanding the development of new technologies, diversification of the food consumed and its preparation strategies, as well as the degree of sedentism in this region, associated with the beginnings of pottery-making technology. The chronology of Neolithic sites in this region, however, was developed on the basis of ¹⁴C dates commonly obtained through the dating of freshwater mollusk shells, pottery with mollusk shell temper, or organic residue on pottery shards. Such samples are potentially affected by the freshwater reservoir effect, raising concerns about the accuracy of those dates. This paper presents accelerator mass spectrometry (AMS) ¹⁴C dates from a small pilot study from sites in eastern Ukraine in order to test for the presence of the reservoir effect in this region. The AMS ¹⁴C dates presented in this paper challenge the ¹⁴C chronology based on mollusk shell or organic residue, which appears to generate much older dates than those on wood charcoal or terrestrial animal bone.

INTRODUCTION

Geographically, the Dnieper River divides the territory of Ukraine along a north-south axis into east and west parts. It has been claimed that the Neolithic sites of eastern Ukraine (Donets River basin) have some of the earliest evidence of pottery use in Europe, dated to the 7th millennium BC (Manko and Telizhenko 2002; Manko 2006). The Neolithic populations in the eastern part of Ukraine are attributed to the Dnieper–Donets cultural region (Kotova 2003; Telegin and Titova 1998). The definition of the Neolithic in Ukraine is based on changes in material culture and the introduction of pottery-making technology, rather than any obvious economic change (Anthony 1995; Gronenborn 2003, 2008). The earliest “Pottery Neolithic” sites of eastern Ukraine, which have pottery but not food production (Motuzaite Matuzeviciute 2012), have been conventionally radiocarbon dated to the early mid-7th millennium cal BC (Manko and Telizhenko 2002; Manko 2006). The earliest pottery in eastern Ukraine is made of river marl with a crushed mollusk (Unio sp. and Viviparus sp.) temper.

While examining the ¹⁴C dates used in the construction of the chronology of these early pottery cultures, obtained from mollusk midden sites in Ukraine and southwest Russia (Lower Don River), it is evident that the oldest ¹⁴C dates were obtained from either pottery shards, mollusks, or organic residue on the pottery (Timofeev et al. 2004; Manko 2006; Tsybrii 2008; Aleksandrovsky et al. 2009). The authenticity of these dates have been questioned by Zaitseva et al. (2009) as the sources of organic carbon in pottery are unknown. Possible problems in the dating of such material include reservoir effects causing ¹⁴C age offsets in the dated sample (e.g. Fischer and Heinemeier 2003; Philippson 2013).

The aim of this paper is to present the results of a small pilot study, testing the ¹⁴C age of mollusk shells collected from two Neolithic sites in eastern Ukraine: Starobelsk-II and Novoselovka-III. These results should help improve the accuracy of the chronology of the Neolithic period in eastern Ukraine. Since a large number of Neolithic period dates in eastern Ukraine and neighboring regions...
of Russia have been obtained from mollusk shells, pottery shards, or organic residue on pottery from potentially aquatic sources, we aim to test whether the $^{14}$C dates from samples containing mollusk remains are different from those obtained from dating charcoal or bone. Mollusk, charcoal, and bone samples from the same archaeological context, an unstratified fireplace with pottery shards, were dated to assess the extent of the reservoir effect, the presence of which would suggest that the interpretation of a large majority of Neolithic period dates from southwest Russia and eastern Ukraine have to be reconsidered.

**BACKGROUND**

The majority of the Neolithic sites are located along basins of the slow meandering steppe rivers of eastern Ukraine, such as the Aidar and the Seversky Donets. The Aidar River cuts its way through calcareous chalk outcrops (Figure 2). As previous studies have shown, alkalinity is one of the main indicators of the magnitude of the freshwater reservoir offset (Keaveney and Reimer 2012). The most common cause of reservoir effect in freshwater systems is the presence of dissolved inorganic carbonates, which form the base of the foodchain in most aquatic ecosystems and can cause an offset of thousands of $^{14}$C years (Clark and Fritz 1997; Fernandes et al. 2012; Philippsen 2013). Water rich in dissolved calcium carbonates of geological age causes a hardwater effect in aquatic plants and animals (Philippsen 2013), while terrestrial snails living in calcareous landscapes also ingest into their shells a substantial amount of calcium carbonate of geological age (Goodfriend 1987; Aitken 2001). Absorbed C ions are synthesized into CaCO$_3$ during mollusk growth, causing the so-called hardwater effect, making the apparent age of the dated material older (Goodfriend 1987; Aitken 2001).

As mentioned previously, the majority of $^{14}$C dates in both eastern Ukraine and southwest Russia, where the earliest European dates of pottery sites were found (Mazurkevich and Dolbunova 2012), were obtained either directly from shards of pottery or organic residue on the surface of the ceramic pot. A series of problems connected with the $^{14}$C dating of ceramic shards, resulting in dates that are too old, have been outlined by Bonsall et al. (2002). One of these issues is related to $^{14}$C dating of potshards that have absorbed organic carbon from fish and mollusks during the use of the pot, potentially incorporating a freshwater reservoir effect (see Philippsen 2013). The problem in dating will also occur if the dated material is an organic residue on pottery walls that is of freshwater/marine fish, shellfish or mollusk in origin (e.g. Goodfriend 1987; Fischer and Heinemeier 2003; Boudin et al. 2010; Philippsen 2013).

The sites chosen as a case study for this article (Starobelsk-II and Novoselovka-III) are located on the bank of the Aidar River, close to chalk cliffs, 7 km apart from each other (Figure 1). The Starobelsk-II site is located in the steppe zone of the easternmost region of Ukraine, on the western edge of Starobelsk city (49°17′52.3″N, 38°50′58.6″E) (Figure 1). The site is on the left bank of the Aidar River, about 70–80 m from the riverbank. Across the river from the Starobelsk-II settlement lies a steep chalk cliff (Figure 2). The Starobelsk-II site is located about 7 km south of the Novoselovka-III site (Figure 1). Starobelsk-II contains one of the earliest examples of pottery in eastern Ukraine (Manko 2006). After macrobotanical and zooarchaeological research, it was concluded that the site was a hunter-gatherer campsite with no evidence of food production (Motuzaite Matuzevičiute 2012). The cultural horizon is mainly formed by middens of freshwater mollusks, Viviparus sp. and Unio sp. Inside the middens, the remains of animal bones, pottery shards, and flint pieces were found. The fireplace was located a few meters away from the main accumulation of mollusk shells, but in the same lithological horizon. The Starobelsk-II site is up to 120 m$^2$ in size.

The Novoselovka-III site is located south of the Starobelsk settlement on the second terrace of
the Aidar River (49°17′9.79″N; 38°49′41.69″E) (Figure 1). The site is in an open field, which is presently ploughed and irrigated, within a large loop of the Aidar River. The cultural layer consists mostly of freshwater mollusk remains (*Unio* sp. and *Viviparus* sp.). Bone remains and pottery were mostly concentrated within the mollusk midden horizon, indicating that the calcareous environment created by the mollusk remains allowed for the preservation of some artifacts. A few kilometers to the west and northwest, steep chalk cliffs surround the site valley. The total area of the settlement is not known. However, mollusk clusters (“mollusk middens” or “kitchen middens”), representing a disturbed cultural layer, are distributed throughout the field over a few hectares, making Novoselovka-III potentially one of the biggest Neolithic sites in eastern Ukraine.

Neolithic sites from the Donets and Don River basins contain abundant mollusk and fish bones, indicating specialized human exploitation of freshwater resources (Motuzaite-Matuzeviciute 2012). An abundance of bone harpoons and stone weights, probably used as net sinkers, along with tools made of mollusk shells, show that human activities were closely related to the exploitation of water

![Figure 1 Map of Ukraine showing the approximate locations of sites mentioned in the text](image1)

![Figure 2 The bank of the Aidar River and the chalk landscape in the vicinity of the Starobelsk-II site.](image2)
resources (Tsybrii 2008). Problems caused by the reservoir effect in human bones in central Ukraine due to the consumption of freshwater resources have been outlined by Lillie et al. (2009), who demonstrated that $^{14}$C dates of humans living along the Dnieper River during the Neolithic to Chalcolithic periods are strongly altered by the reservoir effect. The $^{14}$C dates of pendants made from fish teeth placed in human graves at the Dereivka and Yasinovatka cemeteries were on average ~400 yr older than the $^{14}$C dates from the human remains associated with those pendants. Differences in $^{14}$C age between fish teeth pendants and deer teeth pendants from the same archaeological contexts were ~700 yr (Lillie et al. 2009). Stable isotope analysis of carbon and nitrogen from the burials located along the Dnieper River has shown that those humans were highly reliant on freshwater fish as a major food source (Lillie 1996, 1998, 2001; Lillie and Richards 2000; Lillie et al. 2003, 2009; Lillie and Jacobs 2006).

Given that pottery in the Donets Basin in eastern Ukraine has produced some of the oldest Neolithic $^{14}$C dates in Europe, it is suspected that a freshwater reservoir effect could well be present in this region. This hypothesis, however, has not been systematically tested. The only known and $^{14}$C-dated Neolithic burial in eastern Ukraine is located at the site of Kleshnya. Here, a female burial was found within the Neolithic settlement site; the deceased was lying in a supine position, the body was covered with red ochre, and a pottery vessel was placed next to the head (Manko 2006). Two conventional dates from the same tibia of this female burial have been produced by the Kiev laboratory: Ki-6056: 7345 ± 60 BP (6235–6085 cal BC) and Ki-6057: 7405 ± 70 (6383–6119 cal BC) (Manko 2006). Unless the reservoir effect is present, the Kleshnya date suggests that the pottery-making traditions at the Kleshnya site might indeed be among the oldest in Europe.

MATERIAL AND METHODS

At the Starobelsk-II site, three samples were taken for $^{14}$C dating from a hearth feature where animal bones, mollusk shells, flint tools, and some pieces of pottery were found in the same context, indicating that those artifacts should be of the same age. The samples chosen for dating included freshwater mollusk (Unio sp.), a Bos taurus (cow) tarsal bone fragment, and tree/shrub charcoal. The wood species was not identified, but a fragment of a twig was chosen in order to avoid dating problems often occurring due to the “old wood” effect (Aitken 2001). At the Novoselovka-III site, two samples from the same mollusk midden were taken for AMS $^{14}$C dating. The samples included a fragment of Sus sp. (boar) tarsal bone and a Unio sp. mollusk. The samples from both sites were AMS $^{14}$C dated at the Oxford Radiocarbon Accelerator Unit (ORAU). All $^{14}$C dates were calibrated using the calibration program OxCal v 4.2.3 (Bronk Ramsey and Lee 2013) and the IntCal13 data (Reimer et al. 2013).

Brock et al. (2010:109) outline the ORAU pretreatment procedures for carbonate samples such as shells and cremated bones. The samples are extracted by reaction in vacuo with phosphoric acid. Brock et al. (2010) provide a detailed explanation of treatment protocol for carbonates as well as freeze-drying, combustion/recycling, and graphitization of the carbonate samples; therefore, this methodology is not repeated in full here. Measurement was undertaken by accelerator mass spectrometry (AMS) using a HVEE Tandetron with two recombinators (Bronk Ramsey et al. 2004a).

For dating animal bones, the protocol as described in Brock et al. (2010:106–7) was followed. A routine pretreatment procedure involved a simple acid-base-acid (ABA) treatment followed by gelatinization and ultrafiltration. Full details of the cleaning and quality assurance procedures applied to the ultrafiltration step are given in Bronk Ramsey et al. (2004b) and Brock et al. (2007). The assessment of samples’ suitability for dating after the evaluation of collagen yield and during the conversion of the sample to CO$_2$ was conducted as described in Brock et al. (2010).
For $^{14}$C dating of wood charcoal, the standard ABA method was applied as described in Brock et al. (2010). ABA was followed by freeze-drying, combustion, and graphitization of the sample. The resulting graphite was pressed into aluminum targets for AMS $^{14}$C dating.

RESULTS AND DISCUSSION

The dates obtained from Starobelsk-II and Novoselovka-III are listed in Table 1. At Starobelsk-II, a very distinct difference can be seen between the samples from the same archaeological context. As seen in Table 1, the $^{14}$C date of the mollusk shell is ~2700 yr older than the date from a terrestrial animal bone. Obviously, the dates from cattle bone and wood are very close (Table 1). At Novoselovka, the river mollusk sample and terrestrial animal bone sample taken from the same context also exhibit a significant difference in $^{14}$C ages: the mollusk appears to be almost 3000 yr older than the bone of $Sus$ sp. (Table 1).

Table 1 AMS radiocarbon determinations from the Neolithic sites of eastern Ukraine (Starobelsk-II, Novoselovka-III), and conventional dates from a Neolithic burial at Kleshnya (Manko 2003). Radiocarbon data calibrated against the IntCal13 calibration curve (Reimer et al. 2013).

<table>
<thead>
<tr>
<th>Site name</th>
<th>Dated material</th>
<th>Lab nr</th>
<th>$\delta^{13}$C</th>
<th>$^{14}$C age BP</th>
<th>Calibrated date (95% probability) cal BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starobelsk-II</td>
<td>$Unio$ sp. mollusk</td>
<td>OxA-22272</td>
<td>–8.19</td>
<td>9405 ± 40</td>
<td>8787–8572</td>
</tr>
<tr>
<td>Starobelsk-II</td>
<td>$Bos taurus$ (tarsal bone)</td>
<td>OxA-22278</td>
<td>–20.40</td>
<td>6950 ± 39</td>
<td>5971–5736</td>
</tr>
<tr>
<td>Starobelsk-II</td>
<td>Wood charcoal</td>
<td>OxA-22279</td>
<td>–24.36</td>
<td>6954 ± 35</td>
<td>5968–5741</td>
</tr>
<tr>
<td>Novoselovka-III</td>
<td>$Unio$ sp. mollusk</td>
<td>OxA-22280</td>
<td>–10.94</td>
<td>8928 ± 35</td>
<td>8246–7967</td>
</tr>
<tr>
<td>Novoselovka-III</td>
<td>$Sus$ sp. (tarsal bone)</td>
<td>OxA-22281</td>
<td>–18.13</td>
<td>6297 ± 34</td>
<td>5341–5214</td>
</tr>
<tr>
<td>Kleshnya</td>
<td>Human (female) (tibia, same as below)</td>
<td>Ki-6056</td>
<td>Not provided</td>
<td>7345 ± 60</td>
<td>6368–6073</td>
</tr>
<tr>
<td>Kleshnya</td>
<td>Human (female) (tibia, same as above)</td>
<td>Ki-6057</td>
<td>Not provided</td>
<td>7405 ± 70</td>
<td>6423–6098</td>
</tr>
</tbody>
</table>

AMS $^{14}$C dating of two Pottery Neolithic sites in eastern Ukraine suggests that the earliest site in the region is the Starobelsk-II settlement, dated to the beginning of the 6th millenium cal BC. The Novoselovka-III site represents a slightly later stage of the Pottery Neolithic, dated to the second half of the 6th millenium cal BC. It is important to note that the $^{14}$C dates of wood and animal bone from Starobelsk-II are ~400 $^{14}$C yr younger than the dated Neolithic individual from the Kleshnya site described earlier. This casts some doubts on the accuracy of the calibrated $^{14}$C date of the Kleshnya human.

The $^{14}$C determinations received from freshwater river mollusks, terrestrial animal bones, and wood charcoal have revealed that mollusk samples are affected by a freshwater reservoir effect, resulting in an offset of the actual date, when compared to terrestrial samples of animal bone or charcoal, of up to 3000 yr. These results make us question all the existing $^{14}$C dating results from eastern Ukraine that were received from mollusk shells, or pottery with organic residue that could be of aquatic origin (Manko and Telizhenko 2002; Kotova 2003; Timofeev et al. 2004; Manko 2006).

Many regions of northeastern Ukraine contain chalk and limestone outcrops exposed at the surface. Therefore, freshwater bodies may contain varying concentrations of carbon of geological origin. Systematic dating of freshwater mollusks and fish alongside terrestrial fauna and plant materials
should be undertaken, as it is anticipated that the majority of \(^{14}C\) dates from mollusks and pottery might well be older than the dates obtained from terrestrial sources.

The Donets River basin was inhabited by Early Neolithic populations of the Rakushechny Yar culture, which also occupied the Lower Don River valley. The earliest Neolithic dates from the Lower Don region fall in the 8th millennium BC (Timofeev et al. 2004). The river network in eastern Ukraine played an important role in the interaction between populations of the Lower Don River in southwest Russia and the Donets River in eastern Ukraine, manifest in a close resemblance in material cultures (Motuzaite-Matuzeviciute 2012). Early pottery in the Neolithic sites of eastern Ukraine is technologically and stylistically similar to that found in the Rakushechny Yar culture of southwest Russia (Tsybrii 2008). According to Davison et al. (2009) and Dolukhanov et al. (2005), pottery technology spread into Ukraine from the east westwards. Therefore, we may expect that Neolithic sites in southwest Russia might be very similar in date to those in eastern Ukraine. However, the \(^{14}C\) chronology of the southwest Russian sites is ~500 yr older than the earliest dates from the Neolithic period of the eastern Ukraine. As mentioned earlier, such differences in chronology could also be due to the fact that in southwestern Russia more dates have been obtained on samples that have a potential reservoir effect than in eastern Ukraine, thus causing problems in interpretation. For example, one of the most famous sites in Neolithic Russia (Rakushechny Yar) has 29 \(^{14}C\) dates in total (produced until 2004), but only four of these were from terrestrial animal bone. The rest of the dates were obtained by dating charcoal-rich sediments, mollusk shells, pottery shards, or organic residue on pottery walls (Manko and Telizhenko 2002; Timofeev et al. 2004; Manko 2006; Motuzaite Matuzeviciute 2012). Furthermore, most such dates have a very high uncertainty (1σ). For example, the date (Le-5344) received from dating aquatic turtle shell from layer 9 of the Rakushechny Yar site contained an error of \(\pm 250\) yr (7180 \(\pm 250\) BP) (e.g. Manko 2006). The presence of a reservoir effect in the Donets Basin could mean that chronological periodization of the populations in the Lower Don River region is also affected by a freshwater reservoir effect. Consequently, it is apparent that a systematic investigation, aimed at identifying the potential for a reservoir effect, should be undertaken not only in eastern Ukraine but also in the Lower Don region.

**CONCLUSIONS**

An assessment of the available \(^{14}C\) chronology for southeastern Ukraine and the new AMS determinations obtained from the sites of Starobelsk-II and Novoselovka-III suggests the following:

- Molluscan carbon is strongly affected by calcareous chalk-rich landscapes. The mollusk shell \(^{14}C\) dates are up to 3000 yr older than animal bones or charcoal from the same contexts.

- The abundance of mollusks and fish bones from the Neolithic sites of eastern Ukraine indicates human consumption of riverine resources. This will most likely have an effect on the \(^{14}C\) dates retrieved from dating pottery, organic residue on pottery vessels, and humans and animals consuming freshwater resources in this region.

- The dated Neolithic burial from Kleshnya represents one of the oldest examples of pottery in Europe, raising the suspicion that the human \(^{14}C\) age could have been affected by a dietary reservoir effect, as freshwater resources were a main food source for the Neolithic populations of eastern Ukraine.

- AMS \(^{14}C\) dates challenge the \(^{14}C\) chronology based on measurements of aquatic resources. A systematic sampling strategy and dating program needs to be conducted on the Neolithic sites in eastern Ukraine in order to evaluate more precisely the reservoir effect in the region.
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REFERENCES


