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РАДИОУГЛЕРОД В АРХЕОЛОГИИ И ПАЛЕОЭКОЛОГИИ: ПРОШЛОЕ, НАСТОЯЩЕЕ, БУДУЩЕЕ

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Радиоуглерод в археологии и палеоэкологии: прошлое, настоящее, будущее. Материалы международной конференции, посвященной 80-летию старшего научного сотрудника ИИМК РАН, кандидата химических наук Ганны Ивановны Зайцевой. Под редакцией Н.Д. Буровой, А.А. Выборнова, М.А. Кульковой – СПб.: ИИМК РАН, РГПУ, Самара: СГСПУ/ООО «Порто-принт», 2020 – 123 с.

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Сборник содержит материалы конференции, связанные с радиоуглеродным методом датирования и включающие рассмотрение вопросов археологической хронологии, реконструкции палеогеографических условий антропогенеза Евразии, новые методы и подходы в радиоуглеродном датировании. Приводятся серии новых радиоуглеродных дат по отдельным памятникам от палеолита до средневековья. Корректируются хронологические рамки ряда культур.

and anthropogenic impact on formation of archaeological layers in lake area: case study from the Serteya II site,

Western Russia // *Geoarchaeology an Interdisciplinary Journal*. 2020 (submitted).

CHRONOLOGICAL TIMEFRAMES OF ARCHAEOLOGICAL COMPLEXES OF A MULTI-LAYER SERTEYA II SITE (BASED ON RADIOCARBON DATES)

A. Mazurkevich, P. Kittel, Y. Maigrot, E. Dolbunova, M. Krapiec, A. Ginter

Dr. Ganna Zaitseva participated a lot in researches conducted within the North-Western archaeological expedition of the State Hermitage Museum and elaborating the chronological timeframes for Neolithic in this region. Multidisciplinary investigations of the last five years changed a lot historical schemes and environmental reconstructions made for Serteya II site, located in Smolensk region. The Serteya II site is a multilayer complex used by hunter–fisher–gatherer communities in the 9th–8th mill. BC, and from the end of the 7th till the end of the 3rd mill. BC. Archaeological structures and horizons were developed in the palaeolake shore zone within changing water regimes and changes in the environmental conditions. Based on the most convergent dendrochronological sequences, two floating chronologies were compiled, for pine wood 53 years old and larch wood 54 years old. Finally five OSL dates have been obtained, but the acquired age of geological ones significantly exceeded expectations. Three dates indicate the Neolithic period (contrary to expected XVII century), and a chronological inversion of OSL dates can be seen. Surprisingly spectrometry measurements of gyttja sediments, despite of significant amount of organic matter allow as to calculate the dose rate and then to date one piece of Neolithic pottery. The obtained age perfectly corresponded to present state of knowledge.

Keywords: Mesolithic, Neolithic, multidisciplinary research, Serteya II, pile-dwelling settlements, radiocarbon dating, OSL dating.

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INTERPRETING ¹⁴C AGES OF THE TOTAL ORGANIC CARBON CONTENT OF PREHISTORIC POTTERY

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Archaeological chronologies in parts of Eastern Europe are based mainly on direct dating of pottery. Food crusts (FC) are dated if possible, but many more ¹⁴C ages have been obtained from the total organic carbon content (TOCC) of sherds. I discuss how to interpret TOCC ¹⁴C ages, based on how extraction methods concentrate or remove components with different ¹⁴C age offsets, and on comparisons of TOCC ¹⁴C ages and bone dates.

Keywords: the total organic carbon content (TOCC) of ceramics, AMS dating, direct dating of pottery.

Archaeological chronologies in parts of Eastern Europe are based mainly on direct dating of pottery. Food crusts (FC) are dated if possible, but many more ¹⁴C ages have been obtained from the total organic carbon content (TOCC) of sherds. I discuss how to interpret TOCC ¹⁴C ages, based on how extraction methods concentrate or remove components with different ¹⁴C age offsets, and on comparisons of TOCC ¹⁴C ages and bone dates.

Visible residues usually consist of burnt food, perhaps with some soot from the cooking fire. An FC ¹⁴C date should thus correspond to the date of pottery production, but fish and other aquatic species (e.g. ducks) can have large ¹⁴C reservoir effects. Freshwater reservoir effects (FREs) in modern fish can exceed 1000 ¹⁴C years, so if half the carbon in an FC was from fish, its ¹⁴C age might be >500 years too old. Extraction methods are similar to those for charcoal. FC is treated with hot acid and alkali solutions, to remove inorganic carbonates and soluble organic compounds; the insoluble residue is then combusted to CO₂, which is converted

to graphite for AMS ¹⁴C dating (e.g. Possnert 1990) or benzene for radiometric ¹⁴C dating (e.g. Skripkin and Kovalyukh 1997).

There are many other sources of carbon in pottery (e.g. absorbed food residues, incompletely burnt plant temper, organic compounds absorbed during burial), with different relationships to the date of pottery production (Bonsall et al., 2002). The aim of TOCC extraction is to maximise the share of carbon from food residues, sooting and organic temper, which should be similar in date to the pot itself, and minimise the contribution of much older 'geological' organic carbon bound to silicates, and potentially much younger mobile organic compounds (Zaitseva et al., 2009; Kulkova 2014).

Most TOCC ¹⁴C ages in Eastern Europe were obtained by the Kiev laboratory (Ki-), where large sherds (200–400 g) are digested in hydrofluoric acid (HF), and the insoluble residue is combusted at 550–900° C to release CO₂ (Kovalyukh and Skripkin 2006). Before HF digestion, pottery is tested with HCl and acidified if carbonates are detected by effervescence (V Skripkin, pers

comm). HF digestion is designed to eliminate ‘geological’ organic carbon, by dissolving silicates (clay, silt and sand). Nearly all organic carbon bound to silicates in natural sediment may be removed by HF, but HF digestion seems not to dissolve unbound organics (Eusterhues et al., 2003). Thus HF should not dissolve organic temper, soot or food residues. A few TOCC dates were obtained at Herzen University, St Petersburg (SPb-), following acid-alkali-acid extraction (HCl-NaOH-HCl washes of powdered pottery) to remove carbonates and humics, the insoluble residue being combusted at up to 900° C to release CO₂ (Kulkova, 2014). HF digestion is sometimes used, but before the HCl wash (M Kulkova, pers comm).

TOCC yields from early East European pottery are typically 1–3 % (Vybornov et al., 2017; Zaitseva et al., 2009). Case studies in other regions (Thailand: Higham et al., 2010; Mongolia: Janz et al., 2015; France: Delqué Količ 1995) using HCl-NaOH-HCl extraction reported much lower yields (<0.5 %). These studies also recommend low-temperature combustion (≤400 °C) to minimise oxidation of ‘geological’ carbon. Nevertheless, carbon yields and ¹⁴C ages suggest that TOCC in East European pottery consists mainly of recent organics. TOCC ¹⁴C ages depend on differences in the carbon contributions and ¹⁴C ages of several constituents:

- *organic carbon in the clay, which was not eliminated by the original firing.* The amount remaining depends on clay source, addition of temper, and firing conditions; its ¹⁴C age cannot be younger than the pot itself, but may be much older if aquatic organisms, reworked

terrestrial plants, and/or ‘geological’ carbon are present. Vasilieva (2011) found that early pottery was made with silts naturally rich in plant debris, including aquatic species. Tsetlin (2018) proposed that firing was deliberately limited to avoid burning out the organic component. Natural or added organic temper, often with a significant FRE, is probably the main constituent of TOCC.

- *carbon absorbed during use (food ingredients, smoke and sooting).* These components can be too old, due to wood-age in soot and FREs in aquatic foods, but without visible crusts, they would contribute micrograms, not milligrams, of carbon per gram of pottery, and have negligible influence on TOCC ¹⁴C ages.

- *carbon absorbed during burial.* Mobile organic compounds in the soil are continuously rejuvenated by breakdown of recent vegetation. Incomplete removal could produce misleadingly young TOCC ¹⁴C ages, particularly if contamination occurred recently. Bleaching to remove secondary organics has not always been applied, and may not be completely effective (Delqu Koli, 1995), but given the pattern of results, HF digestion appears to dissolve these compounds.

- *inorganic carbon.* Carbonates in minerals or shells in the clay, or in calcite precipitated during burial, are rapidly dissolved by HCl, but carbonates are not highly soluble in HF, and combustion at >700 °C would oxidise any undissolved carbonate. ¹⁴C age offsets due to undissolved carbonate are potentially unlimited, but in practice appear to be modest or negligible, probably due to HCl testing before HF digestion. If any undetected carbonate was present, some of it would have been dissolved by HF.

Figure 1: TOCC ¹⁴C ages and ¹⁴C ages of bones from early Neolithic cultural layers at four sites. Published results from Vybornov et al. 2016; Dolbunova et al. 2020; Tsybryi et al. 2017 (TOCC ¹⁴C ages on 7 sherds from a sounding by Telegin are not shown, as stratigraphic relationships between these sherds and samples from the Mazurkevich trench are unclear). Unpublished bone dates from the INDUCE project (INDUCE: the INnovation, Dispersal and Use of Ceramics in NE Europe, PI Carl Heron, 2016–2022).

TOCC is thus apparently dominated by detrital organic carbon already present in silty clay, or added as temper. If TOCC was dominated by 'geological' organic or inorganic carbon, TOCC 'dates' would usually have ^{14}C age offsets of thousands of years. However, 'geological' carbon representing <10 % of TOCC could lead to ^{14}C age offsets of several centuries. If TOCC also included detrital organic carbon from aquatic species, this combination of offsets could give ^{14}C ages that are >1000 years too old.

New ^{14}C dates at several sites with existing TOCC 'dates' seem to confirm the predicted pattern (Fig 1). At Kairshak III, in the Volga delta, TOCC samples are 0–900 years older than animal bones and charcoals. At nearby Baibek, 4 of the 5 TOCC ^{14}C ages agree with bone dates, with one c.300 ^{14}C years older. At Varfolomeevka in the Lower Volga basin, bone dates are scattered, but TOCC ^{14}C ages are 300–1000 years older than the oldest bone. Finally, at Rakushechny Yar, on the Lower Don, TOCC ^{14}C ages are 0–1000 years older than bone dates from corresponding layers. These 33 TOCC samples have average ^{14}C age offsets of $c.550 \pm 400$ years relative to contemporaneous bones, but there is a different pattern at each site, probably due to differences in clay sources, pottery

technology and extraction methods. Compared to Baibek, TOCC ^{14}C ages from Kairshak III and Rakushechny Yar are both older and much more scattered than bone dates, suggesting a relationship between consistency and accuracy. At Varfolomeevka, TOCC results are older, but not more scattered than bone dates. Elsewhere (e.g. Vybornov et al., 2018), TOCC ^{14}C ages for pots of the same type from multiple sites are so consistent that it is inherently unlikely that they incorporate large ^{14}C age offsets.

In conclusion, TOCC ^{14}C ages are not really 'dates', but do provide useful dating information. Many TOCC ^{14}C ages are probably much older than the pottery concerned, but not all. Different mechanisms contribute to ^{14}C age offsets in different situations. FREs, which cannot be eliminated by pretreatment, are probably more influential if low-fired pottery was made with organic silt from rivers and lakes than if aquatic species were cooked in the pot. Geological organic and inorganic carbon can be largely eliminated, if HCl-NaOH-HCl pretreatment is combined with HF digestion and low-temperature combustion of the insoluble residue, but this combination has not been applied routinely, and does not resolve the FRE problem.

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ИНТЕРПРЕТАЦИЯ РАДИОУГЛЕРОДНОГО ВОЗРАСТА ОРГАНИЧЕСКОГО УГЛЕРОДА, ИЗВЛЕЧЕННОГО ИЗ ОРГАНИКИ ДРЕВНЕЙ КЕРАМИКИ.

Джон Медоус

Археологическая хронология для некоторых археологических памятников Восточной Европы основана в основном на прямой керамике. Датировки по пищевому нагару на сосудах также были получены, если это было возможно, но гораздо больше ^{14}C датировок было получено по общему содержанию органического углерода (ТОСС) в черепках. В статье обсуждается, как интерпретировать возраст ^{14}C ТОСС, основываясь на том, как методы пробоподготовки, экстракции концентрируют или удаляют компоненты, которые смещают значения ^{14}C возраста, а также проводится сравнение возраста ^{14}C (ТОСС) и дат, полученных по костной ткани.

Ключевые слова: общее содержание органического углерода в керамике, датирование AMS, прямое датирование керамики.

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ИСПОЛЬЗОВАНИЕ УСТАНОВКИ «УСКОРИТЕЛЬНЫЙ МАСС-СПЕКТРОМЕТР ИЯФ СО РАН» ДЛЯ РАДИОУГЛЕРОДНОГО ДАТИРОВАНИЯ КОМПЛЕКСОВ ЭПОХИ РАННЕГО НЕОЛИТА ПАМЯТНИКА ТАРТАС-1 (СРЕДНЕЕ ПРИОМЬЕ)

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Работа посвящена анализу радиоуглеродных дат, полученных на УМС, для раннеэнеолитической барабинской культуры, подтвердившие VII тыс. до н.э.

Ключевые слова: барабинская энеолитическая культура, стоянка Тартас I, УМС датирование.

На основе анализа материалов из двух жилых сооружений и серии ям для квашения рыбы с проявлением ритуальных действий человека (помещение в качестве прикладов трупов разнообразных животных: лиса, заяц, россомаха, собака и др., предметов из камня, кости и фрагментов керамики) памятника Тартас-1 выделена барабинская раннеэнеолитическая культура (Молодин, Райнхольд, Мыльникова и др., 2018). В Центре археометрии им. К. Энгельхорна (Германия) и на установке «Ускорительный масс-спектрометр ИЯФ СО РАН» (УНУ «УМС ИЯФ СО РАН») была получена серия радиоуглеродных дат. Дата самой древней находки, кости горностая (NSKA 01647) с глубины 320 см, – 7972 ± 70 л.н. Выше на 5 см залегали кости зайца. Их дата (NSKA 01650) – 7670 ± 73 л.н. Кость лисицы (NSKA 01648) происходит с глубины 304 см. Ее датировка – 7803 ± 66 л.н., т. е. эта находка древнее, чем предыдущая, как и дата, полученная по кости лисицы с глубины 302 см (NSKA 01649) – 7702 ± 71 л.н. Однако две последние даты относятся к одному периоду, а временные различия следует оценивать с учетом несовершенства метода. Дата ямы № 990 (NSKA 01644) – 7875 ± 81 л.н. – со-

падает с датой образца NSKA 01648 из ямы № 938 – 7803 ± 66 BP, что свидетельствует об одновременном их существовании. Абсолютно совпадают две даты из конструкции № 6: NSKA 01645 – 7532 ± 97 л.н. и NSKA 01646 – 7479 ± 91 л.н. Эти даты не вполне коррелируют с результатами датирования конструкции № 6, полученными в Центре археометрии – 7019 ± 23 л.н., они древнее последней почти на 400 лет, но общий разброс дат, полученных в этой лаборатории, достигает порядка тысячи лет.

Произведенная калибровка полученной серии дат по sigma 1 и sigma 2 демонстрирует полную корреляцию с датами, представленными лабораторией Гейдельбергского университета. При этом некоторые – тождественны.

Таким образом, корреляция дат, полученных в разных лабораториях, еще раз подтверждает правильность отнесения материалов памятника Тартас-1 к VII тыс. до н.э. Этим временем датирована и барабинская культура. Результаты опубликованы (Молодин, Ненахов, Мыльникова и др., 2019).

Работа поддержана Российским научным фондом, проект № 20-18-00111

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