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Factors Affecting the Apparent Radiocarbon Age of Textiles: A Comment on "Effects of Fires and Biofractionation of Carbon Isotopes on Results of Radiocarbon Dating of Old Textiles: The Shroud of Turin", by D. A. Kouznetsov *et al.*

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Introduction

In a paper published in this issue of Journal of Archaeological Science, Kouznetsov, Ivanov & Veletksy (1995) report on some ^{14}C results obtained by accelerator mass spectrometry (AMS) on a linen textile (En Gedi, Israel) which was exposed to a relatively mild procedure of heating to 200°C for 90 min in air. They report that the ^{14}C age of the textile, which was originally dated as about 2195 ± 55 years BP was changed by 1400 years to about 800 years BP, under these conditions. These authors make several claims about the veracity of radiocarbon dating of cellulose and cellulose-containing textiles. They include a statement that ^{14}C is not distributed uniformly in flax, and that isotopic fractionation of ^{14}C relative to ^{13}C and ^{12}C occurs in some way different than accounted for by the usual equations employed by radiocarbon laboratories, discussed by Stuiver & Polach (1977). Kouznetsov *et al.* (1995) have used results described in their paper to question the validity of radiocarbon measurements of textiles in general, and specifically to disparage results on the Shroud of Turin (Damon *et al.*, 1989).

In another result quoted in this paper, Kouznetsov *et al.* (1995) state that for textiles subjected to the heat treatment described above,

> "near IR spectra obtained from whole textile samples, subjected and not subjected to the gas/thermal treatment (FSM) indicates that the treatment introduced carboxyl groups into the molecular structure of the fibre (figure 2)"

and further

> "it is evident from the relative abundance of ratios of glucose to carboxyglucose CZE fractions (figure 3) and corresponding molecular ions (figure 4), that about 20% of the glucose residues have been carboxylated".

These statements are both made in support of the claim that 20% of the glucose residues are carboxylated, without any quantitative information from either method discussed.

We have attempted to reproduce the textile heating effect reported by Kouznetsov *et al.* (1995), without success. Because of their conclusions and also because this work is clearly flawed in several respects, we feel it is important to comment both on their results and interpretations.

Experimental

In order to check the assertion that heating a textile in an atmosphere containing CO_2 would change its $\delta^{13}C$ and radiocarbon age significantly, we performed an experiment similar to that of Kouznetsov *et al.* (1995) in our laboratory.

A sample of 3·6 mg of the En Gedi textile, from the same piece of material used for the original ^{14}C dating at Arizona, was put into a 9 mm Pyrex tube, and 1·9 atm cm^3 CO_2 at 25°C was cryogenically trapped into the same tube. The CO_2 had been previously prepared from combustion of NIST oxalic acid standard II (SRM 4990C). The tube was evacuated and sealed using a glass torch and placed in a muffle furnace and heated to 200°C for 15·5 h. After this time, the tube was placed in a cracking device, and the CO_2 in the tube was recovered. The gas sample was split into two fractions, one to make graphite for AMS analysis, the second for $\delta^{13}C$ measurements. The textile sample was also recovered. The textile sample was combusted to product CO_2, and this gas sample was also split into two fractions, one to make graphite for AMS analysis, the second for $\delta^{13}C$ measurement.

The samples of oxalic II CO_2 and textile CO_2 from before and after the heating experiment were analysed for $\delta^{13}C$ on a Fisons Optima stable-isotope mass spectrometer. The remaining samples of oxalic-II and textile CO_2 were converted to graphite, pressed into an accelerator target and measured for ^{14}C by AMS using the University of Arizona machine.

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Table 1. Results of ^{14}C and $\delta^{13}C$ measurements of En Gedi textile exposed to CO_2 gas at 200°C.

Sample	$\delta^{13}C$	Fm ^{14}C	^{14}C age*
Before heating experiment	−25·3‰	0·7609 ± 0·0050	2195 ± 55
After heating experiment	−25·9‰	0·7649 ± 0·0042	2153 ± 44
Net change	−0·6‰	0·0049 ± 0·0067	−42 ± 70

*corrected to $\delta^{13}C$ of −25‰

Results

Results of the study are given in Table 1. The radiocarbon measurements are reported as fraction of modern carbon (Fm), where "modern" is taken as 1950 AD carbon, and as a radiocarbon age in years before present (1950 AD). As can be seen from Table 1, there was a small change in the $\delta^{13}C$ value of the textile, due to removal of a small amount of organics by charring. The sample was slightly darker after the 200°C treatment than initially. This effect is in agreement with the pyrolysis treatments of Leavitt *et al.* (1982) on white fir cellulose, who observed a fractionation of −0·4‰ on heating this material to 200°C under vacuum. The change is caused by a small loss of volatile organics during the heating. Leavitt, Donahue & Long (1982) noted that the direction of the $\delta^{13}C$ change in the cellulose was negative, indicating that the volatiles are enriched in ^{13}C by a small amount.

We can also confirm that this mechanism (Leavitt *et al.*, 1982) is correct, as the CO_2 gas phase after the experiment had $\delta^{13}C = -17{\cdot}8‰$ and fraction modern carbon (Fm) = 1·30 ± 0·01, whereas the starting gas was characterized by $\delta^{13}C = -17{\cdot}8‰$ and Fm = 1·35 (Mann, 1982). A small amount (~80 μg C) of contamination of the CO_2 by the desorbed volatiles (of 2195 years BP ^{14}C age) from the textile can account for this effect. The weight of the textile recovered was about 300 μg less than the initial amount.

The results for ^{14}C show that there is no observable change in the ^{14}C age of the En Gedi textile under the conditions of our experiment. Any fractionation in ^{14}C composition is corrected by $\delta^{13}C$, to −25‰ which is the conventional practice (Stuiver & Polach, 1977). The results also indicates that there is no observable deviation from the assumption that a change in $^{14}C/^{13}C$ is approximately equal to a change in $^{13}C/^{12}C$ (Wigley & Muller, 1981).

The conditions of our experiment were that the experiment was conducted under pCO_2 of about 0·06 atm, compared to Kouznetsov *et al.* (1995)'s use of air, which has pCO_2 of 0·0003 atm. Additionally, we heated our sample for 10·3 times longer than the 90 min experiment of Kouznetsov *et al.* If we assume an approximation of a simple first-order process, the rate of our experiment should be 200 times faster than Kouznetsov's experiment. Our results show evidence neither for alteration of the age of the textile, nor for significant isotopic exchange of the textile under these conditions.

Discussion of Isotope Measurements

One may wonder why our radiocarbon measurements on the thermally-treated En Gedi textile differ so markedly from those of Kouznetsov *et al.* These authors report that they used a tandem accelerator mass spectrometer located at the Russian Academy of Sciences, Protvino. However, in their paper there are no citations to *any* published work from the Russian laboratory, or indeed any other AMS group. The only traceable radiocarbon date is one done on the original En Gedi textile in our laboratory (AA-12704). The remaining radiocarbon work was all performed at a laboratory which is new and not generally known to Russian scientists or the international AMS community. As this facility is new, and there are no published reports on its performance, the paper presented here by Kouznetsov *et al.* (1995) should contain AMS ^{14}C data on internationally-accepted standards, known-age samples and blank measurements. The operating conditions of the AMS equipment should also be discussed. For example, are data on ^{14}C measurements *before* the various corrections of the authors available?

Kouznetsov *et al.* (1995) include a series of radiocarbon measurements made on textile samples heated in air to various temperatures. In figures 6 and 7 of the Kouznetsov (1995) paper, these workers indicate that the ^{14}C activity of the textile, stated in dps g^{-1}, increases from 0·22 dps g^{-1} carbon to 0·33–0·34 dps g^{-1}. We point out that "modern" carbon contains ^{14}C with an activity of 13·5 dpm g^{-1}, or 0·225 dps g^{-1} (Stuiver & Polach, 1977). We also note the following:

(1) Kouznetsov *et al.*'s (1995) ^{14}C measurements indicate that the En Gedi textile had an initial ^{14}C age of approximately modern. The sample has been dated previously by our laboratory, and again reported in this paper to be approx. 2195 years BP.
(2) The samples which had been heated gave ^{14}C activities of up to 0·34 dps g^{-1}, equivalent to 150% of the value of modern, pre-bomb ^{14}C. This level cannot be achieved even by complete exchange with contemporary air, which has a ^{14}C level of 110% modern. This indicates that the treated samples contain artificial ^{14}C at a level higher than contemporary carbon. Further, it is impossible to derive an age of 700–800 years BP from the data, using any accepted calculation of ^{14}C ages, or even equation (4) presented by Kouznetsov *et al.* (1995) in this article.
(3) The results quoted in the captions of figures 9 and 10 (Kouznetsov *et al.*, 1995) are not consistent. Figure 9 shows that the untreated En Gedi linen has $\delta^{13}C$ of −25·6‰ and a radiocarbon age of

2175 ± 55 years BP. Figure 10 indicates that the heat-treated sample has $\delta^{13}C$ of −22·0‰ and a radiocarbon age of 800 years BP. Even assuming that an isotope correction was not applied, a change of 3·6‰ in $\delta^{13}C$ would result in a change of less than 60 years BP in radiocarbon age. Either the $\delta^{13}C$ or the radiocarbon age quoted in figure 10 (Kouznetsov, 1995) is incorrect. Considering that the measurement of radiocarbon age is completely undocumented, we would presume that it is that measurement which is incorrect.

(4) The section of calibration curve shown in figure 10 (Kouznetsov *et al.*, 1995) does not bear any relation to the curve published by Stuiver & Pearson (1986).

(5) Kouznetsov *et al.* (1995) exaggerate the small fractionation effects of stable carbon and ^{14}C. These effects are less than or equal to 9 ppm (i.e. 0·9%), accepting the value of −16‰ quoted by the authors for flax. Such a change would affect the radiocarbon age by less than 150 years BP. The authors fail to point out that ^{14}C dates are all normalized to a common $\delta^{13}C$ value, and that the equations of Stuiver & Polach (1977) cited compensate for even these effects.

(6) In reference to the comments of Kouznetsov *et al.* (1995) on the dating of the Turin Shroud, we point out that if the Shroud sample were heated to 300°C, it would have charred significantly. We already observe darkening of the En Gedi textile at 200°C in the experiment reported here. However, the sample of the Shroud dated at Arizona (Damon *et al.*, 1989) showed no evidence of charring. Despite statements made by Kouznetsov *et al.* (1995), samples of the Shroud *were* measured for $\delta^{13}C$. The quoted values (Damon *et al.*, 1989) were within the usual range for cellulose textiles, and indeed cellulose in general, of about −23 to −25‰.

Comments on Kouznetsov *et al.*'s Chemistry

One of the results of Kouznetsov *et al.* (1995) is the report that samples of textile become carboxylated by the heating procedure used by these authors. Unfortunately, there is no quantitation of any of the techniques discussed. Figure 3 in Kouznetsov *et al.* (1995) shows a peak in the "heated" samples as opposed to the untreated samples. Neither in the text, nor in the figure legend is any information given about the temperature of heating, or other conditions of this particular experiment. The peak identified as 2-carboxy-β-D-glucose is stated in the text to be 20% of the total sample, yet the peaks for glucose are offscale, so that no quantitative comparison can be made.

For discussion purposes, let us assume that this estimate of 20% 2-carboxy-β-D-glucose is correct, and further than this contamination is *recent carbon (from 1994 AD)*. Then, 20% of the glucose from a textile dated to be 2195 years BP (76·1% modern, 0·761 fraction of modern C) are carboxylated at one OH location with a carboxyl group containing C of 110% modern (contemporary) carbon. Glucose contains six (6) carbon atoms. Adding one more as a CO_2H makes seven (7). The effect of this addition of one additional carbon to 20% of the molecules on the measured fraction of modern ^{14}C would be:

$$\begin{aligned}\text{Fm (heat treated)} &= 0{\cdot}20 \times 1/7 \times F_c \\ &\quad + 0{\cdot}20 \times 6/7 \times (F_{2195\ \text{years BP}}) \\ &\quad + 0{\cdot}80 \times (F_{2195\ \text{years BP}}) \\ &= 0{\cdot}7707\ (77{\cdot}07\%\ \text{modern}).\end{aligned}$$

In these equations, Fm is the fraction of modern carbon (taken as 1950 AD), Fc is 1·10, the fraction of modern carbon for contemporary (present-day) material, and $F_{2195\ \text{years BP}}$ is 0·7609, the fraction of modern for material of 2195 years BP radiocarbon age. The third term represents that portion of the sample unaffected by the treatment. For these values, the fraction of modern of the heat-treated sample would be Fm = 0·7707, and the radiocarbon age would be 2092 years BP.

Thus, even if the 20% carboxylation of Kouznetsov *et al.* were correct, a result certainly not demonstrated in their paper, a change in the radiocarbon age of about 100 years would result. It is not possible to generate an age of 800 years BP even if all glucose molecules became substituted with a carboxyl group of recent age.

In the thermal gas treatment experiment described, the textile is exposed to "an artificial atmosphere containing CO_2 (0·03%), CO (60 μg m^{-3}) and 20 g m^{-3} water". The size of the chamber in the "Thermogas Unit" was not given, but let us assume it was 100 l. This would mean there is 300 ppm volume of CO_2, or 30 cm^3. This amount of CO_2 contains about 15 mg of carbon at 25°C. The CO is very small and cannot account for much reaction. Even in the extremely unlikely event ALL the carbon in the gases exchanged at 200°C in 90 min with ALL the 2·0–2·8 g of textile stated to have been heated, the amount would be about 1·4% of the carbon being modern instead of 0·761 times modern, and this would only change the apparent fraction modern to 0·765, i.e. the apparent age would be 2150 years instead of 2195 years BP. One can perform similar calculations for other volumes.

Conclusion

In conclusion, we believe the ^{14}C methods described by the authors have not had appropriate control experiments performed. Additionally, the AMS ^{14}C measurements were done on an apparently untested piece of equipment with no reference to normal procedures of reproducibility, standards, control and blank samples.

With a similar experiment, we find no evidence for the gross changes in age proposed by Kouznetsov *et al.* (1995). These authors use a number of procedures on the samples, without any discussion of control samples, blanks or standards run through the same battery of treatments.

Finally, we have shown that even if the carbon displacements proposed by the authors during the heat treatment were correct, no significant change in the measured radiocarbon age of the linen would occur. We must conclude that the attack by Kouznetsov and his coworkers on measurements of the radiocarbon age of the Shroud of Turin and on radiocarbon measurements on linen textiles in general are unsubstantiated and incorrect. We further conclude that other aspects of the experiment are unverifiable and irreproducible.

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