

Production of Radiocarbon by Neutron Radiation on Linen

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Abstract

Based on the hypothesis that the Turin Shroud received neutron radiation to produce contaminant radiocarbon that caused its 1988 radiocarbon dating to be in error by 1292 years, experiments were performed on modern linen. Radiocarbon was produced by neutron reactions with nitrogen indigenous to the linen. The amount of radiocarbon produced could be calculated from the neutron fluence and the nitrogen content of the linen. This radiocarbon was not removed by high temperatures or by the chemical cleaning treatments used in the 1988 tests. Spatial variations in linen nitrogen content caused radiocarbon age gradients as large as 261 yr/cm for the neutron fluence needed to reduce its age by 1292 years.

Keywords: Radiocarbon, neutron, radiation, nitrogen, linen.

1. INTRODUCTION

The 1988 tests determined that the Turin Shroud's radiocarbon date was approximately 1325 AD [1]. Radiocarbon dating is susceptible to error because of contamination, but the three laboratories used a number of standard chemical cleaning treatments to remove all usual types of contamination. Phillips [2] proposed a different type of contamination, nuclear radiation to produce unnatural radiocarbon that would artificially reduce the radiocarbon age of the Shroud. Hedges [3] stated that neutron reactions with trace nitrogen in the linen would be the principle mode for producing radiocarbon in the linen. Rinaudo [4], Moroni [5] and Barbesino [6] conducted experiments on a piece of 1st century Egyptian Lyra mummy linen that verified Hedges statement.

Riani [7] conducted a robust statistical analysis of 1988 data that rejected the null hypothesis that the ages measured by the three laboratories are homogeneous and suggest the presence of an important contamination in the 1988 Shroud samples. The effects of inhomogeneities had not been studied in the prior neutron experiments. This study supposed that neutron radiation can explain the erroneous radiocarbon date as well as the inhomogeneity and contamination of the Turin Shroud samples suggested by Riani [7], Walsh [8] and Van Haelst [9].

The three primary goals of these experiments were to (1) accurately predict the concentration of radiocarbon produced using the measured nitrogen content of the linen and the measured neutron fluence used during irradiation, (2) measure the loss, if any, of the produced radiocarbon as a function of various heat treatments and chemical pretreatments and (3) evaluate repeatability of the results.

2. THEORY

Carbon has two stable isotopes, ¹²C, which is 98.90% abundant and ¹³C, which is 1.10% abundant. Radiocarbon, ¹⁴C, is unstable and is only about 10⁻¹⁰ % abundant. ¹⁴C nuclei are continuously produced in the upper atmosphere by cosmic ray secondary neutron collisions with nitrogen to create ¹⁴C and a proton; this reaction is denoted by ¹⁴N(n,p)¹⁴C. This reaction is not constant, so the concentration of ¹⁴C in the atmosphere varies over time. In 1950 a standard concentration of ¹⁴C was defined as 100 percent Modern Carbon (pMC) when the ratio of the number of ¹⁴C nuclei to the number of ¹²C nuclei was equal to 10⁻¹² [10].

When living plants take in carbon dioxide for their growth, they take in some ¹⁴C and when the plant stops growing, this ¹⁴C slowly emits electrons to decay back to ¹⁴N with a half life of 5730±40 years. Thus, the percent Modern Carbon, $pMC(t)$, t years after it stops growing, is given by

$$pMC(t) = pMC_0 e^{-\lambda t}, \quad (1)$$

where pMC_0 is the percent modern carbon in the plant when it stopped growing and λ is equal to $1.2097 \times 10^{-4} \text{ yr}^{-1}$, which corresponds to its 5730 year half-life.

Equation 1 is solved below to yield the time, t , between the time the plant stopped growing and the time of measuring $pMC(t)$.

$$t = \ln[pMC_0 / pMC(t)] / \lambda. \quad (2)$$

Since pMC_0 is not constant, t must be corrected to obtain the true time by using measured historical values of pMC_0 from such things as tree rings.

Figure 3. Measured total nitrogen contents for all samples.

Figure 3 plots the results of all the nitrogen measurements. The normalized distributions of nitrogen weight fractions for samples plotted in Figure 3 are shown in Figure 4.

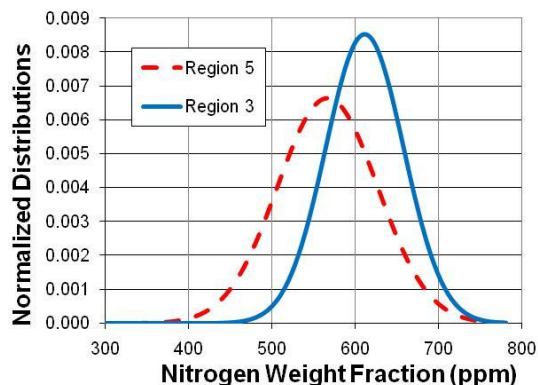


Figure 4. Normalized distributions of nitrogen weight fractions.

In the following, the measured radiocarbon that was produced by neutron irradiation was compared with the calculated amount using Equation 4. For this comparison to be valid, it is necessary to measure both the weight fraction of nitrogen, f_N , and the radiocarbon content, pMC, in the same sample. Unfortunately, both measurements are destructive and the nitrogen content varies significantly from place to place in the linen, so precise one-to-one comparisons were not possible. Fortunately, the Region 2 samples that were studied appeared to be fairly homogeneous because the measured results were consistent with a nitrogen weight fraction of 720 ppm.

Radiocarbon Measurements: [13, 14] All radiocarbon measurements had errors of about ± 0.75 pMC; none were larger than 1.1 pMC. The percent Modern Carbon of a virgin linen sample from Region 2 measured 107 pMC; this is larger than 100 pMC because of the remnants of radiocarbon produced in the atmospheric nuclear tests in the 1950's. A linen piece from Region 2 was neutron irradiated in carbon dioxide gas with a neutron fluence of $1.07 \times 10^{14} \text{ n}\cdot\text{cm}^{-2}$. Equation 4, using the average 720 ppm nitrogen content, predicted an increase of 27.55 ± 1.38 pMC which when added to the 107 pMC yields 134.55 ± 1.38 pMC. Errors of $\pm 5\%$ are included because nitrogen measurements had this accuracy. The measured value was 134.89 ± 0.76 pMC. This good agreement demonstrates the validity of Equation 4.

This good agreement is in contrast to the result obtained for linen irradiated with a fluence of $1.04 \times 10^{14} \text{ n}\cdot\text{cm}^{-2}$ in an air-filled 3 mL vial. The calculated value was 133.77 ± 1.34 pMC, but the measured value was 224.6 ± 0.9 pMC. Subtracting the baseline value 107 pMC from each of these indicates that the increase in radiocarbon when irradiated in air was 117.6 instead of the predicted 26.77 pMC, a factor of 4.39 times more than predicted. An approximate calculation indicated that this extra radiocarbon could be accounted for by the production of

radiocarbon in the 70% nitrogen in air that surrounded the linen and diffused into it.

Experiments were conducted to determine if the radiocarbon that was produced in the surrounding air would diffuse out at room temperature. After waiting 116 days, the measured radiocarbon content had dropped only 12.2 pMC to 212.4 ± 1.1 pMC, which was too slow to obtain an accurate rate at which the radiocarbon was diffusing from the linen. To speed the diffusion process as well as obtain temperature dependent diffusion data, elevated temperature diffusion experiments were conducted. Five samples were heated for 75 minutes at different temperatures, 130, 175, 200, 225, and 245 °C. Figure 5 shows these samples after heating along with a non-heated sample.

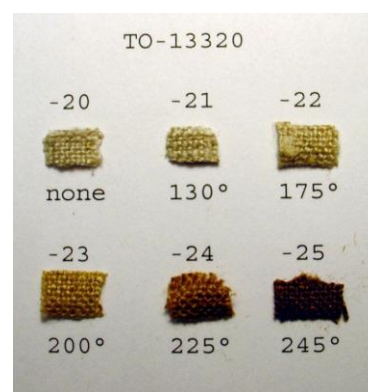


Figure 5. Appearance of six linen samples after heating for 75 minutes at indicated temperature.

The radiocarbon that remained after the heat treatments was measured and is shown in Figure 6; the extra points are for repeat measurements. The line at 133.77 pMC is the predicted value from Equation 4. If no points lie below this line, it indicates that only the radiocarbon produced from the nitrogen in the air diffused out of the sample and that the radiocarbon produced from the nitrogen within the linen did not leave the samples during heating at temperatures up to 245 °C for 75 minutes.

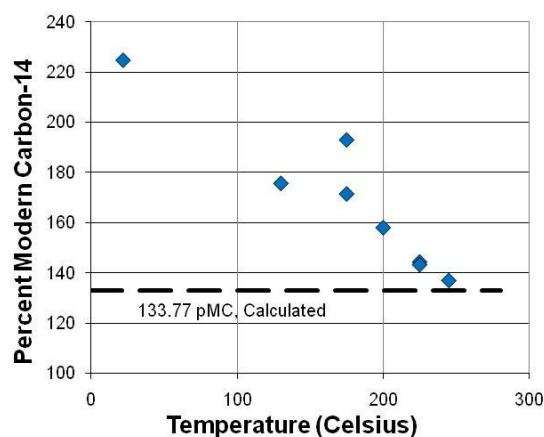


Figure 6. Measured radiocarbon remaining after 75 minute heat treatments between 130 and 245 °C.

The diffusion rates for the heated samples were computed using the unheated sample as the reference. Two room temperature diffusion rates were determined from room temperature measurements at times of 114, 294 and 410 days after irradiation. The diffusion rates are plotted in an Arrhenius format in Figure 7. It is important to note that in computing the diffusion rates, the diffusion was not assumed to be linear because it is actually exponential. Thus, more than two points are required to compute the exponential diffusion rate; the third point was the level to which the radiocarbon declined. The predicted value was 133.77 ± 1.34 pMC; other values were also tried and the value of 133.4 pMC gave the lowest R^2 value in the Arrhenius plot. This further verifies the validity of Equation 4. It also verifies that only the radiocarbon produced from the nitrogen in the air diffused out of the sample and that the radiocarbon produced from the nitrogen in the linen remained in the sample at temperatures up to 245 °C for 75 minutes.

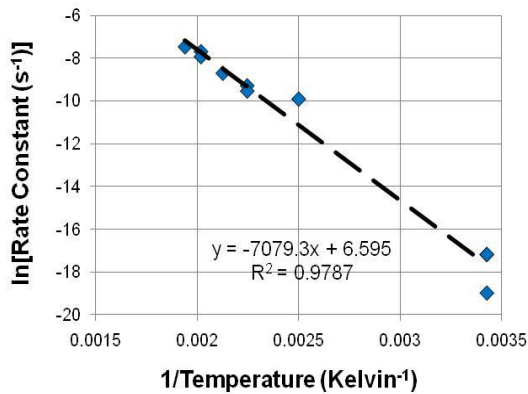


Figure 7. Least squares fit to Arrhenius plot of diffusion rates

The Arrhenius plot provides the rate constants $k(T)$ for the diffusion process for all temperatures, T , that lie on the straight line fit. The result is given in Equation 5.

$$k(T) = e^{6.595} \times e^{-7079.3/T} = 731.4 e^{-7079.3/T} \quad (5)$$

From Equation 5, the rate constant at room temperature (293 K) for diffusion of the radiocarbon produced from the nitrogen in the air is $2.34 \times 10^{-8} \text{ sec}^{-1}$, or 0.74 yr^{-1} . Thus, after 6 years the fraction of this radiocarbon remaining in the linen will be $e^{-0.74 \times 6} = 0.012$, or 1.2%. This is very slow for diffusion of gases in polymers. The quantity 7079.3 in the exponent of Equation 5 corresponds to an activation energy of 58.9 kJ/mole, which is not an uncommon value for diffusion of carbon dioxide or other gases through amorphous polymers. However, the pre-exponential factor of 731.4 is very small for diffusion in fibrous polymers. The reason is probably because flax fibers are highly crystalline and diffusion is virtually zero through crystalline material. Thus, the diffusion most likely occurs along the labyrinth of

amorphous material between the crystals that hold them together. This torturous path greatly slows the diffusion and could explain the very small pre-exponential factor.

TABLE 1. Description of Chemical Treatments Used

Type of Pretreatment	Chemical Pretreatment
Arizona A	0.5% HCl for 2 hours at room temperature (RT) 0.25% NaOH for 2 hours at RT Dilute acid wash
Arizona B	Commercial detergent (1.5% SDS) for 1 hour at RT Wash with distilled water 0.1% HCl for 1 hour at RT Commercial detergent (1.5% Triton X-100) for 1 hour at RT Soxhlet extraction with ethanol for 1 hour Wash with water for 1 hour at 70°
Oxford A	Petroleum ether for 1 hour at 40° 1M HCl for 2 hours at 80° 1M NaOH for 2 hours at 80° Dilute acid wash
Oxford B	Oxford A followed by 2.5% NaOCl (pH=3) for 30 min at RT
Zurich A	Ultrasonic wash in distilled water for 1 hour at RT
Zurich B	Zurich A followed by 0.5% HCl for 2 hours at RT 0.25% NaOH for 2 hours at RT Dilute acid wash
Zurich C	Zurich A followed by 5% HCl for 2 hours at 80° 2.5 % NaOH for 2 hours at RT Dilute acid wash

Effects of Chemical Pretreatments: Neutron-irradiated samples from both Regions 2 and 4 were subjected to chemical pretreatments like those used in the 1988 radiocarbon dating of the Turin Shroud. Table 1 describes the chemical treatments that were used to duplicate those used by Oxford, Zurich and Arizona. Figure 8 shows the results of the chemical treatments for samples in Regions 2 and 4. The lower bounds marked in Figure 8 are explained as follows. The smallest nitrogen concentration measured in Region 3, which surrounds Region 2, was 528 ppm. From this and the neutron fluence of $1.04 \times 10^{14} \text{ n}\cdot\text{cm}^{-2}$ that this linen received, Equation 4 predicts that the pMC for Region 2 will not fall below 126.6 ± 0.98 pMC. If it falls below, then some radiocarbon that was produced within the linen is removed by the chemical treatment. Likewise, the smallest nitrogen concentration measured in Region 5, surrounding Region 4 and which received $1.07 \times 10^{14} \text{ n}\cdot\text{cm}^{-2}$, was 453 ppm; this results in a lower bound of 124.3 ± 0.87 pMC for Region 4. Only one sample falls below its lower bound and that is the Region 4 sample that received the Zurich C treatment, which actually was not as harsh as the Oxford B treatment.

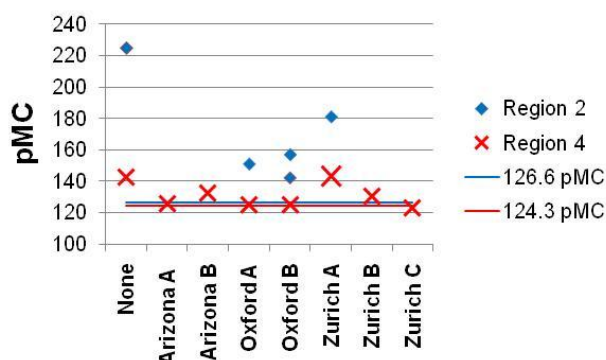


Figure 8. Percent Modern Carbon remaining in samples from Regions 2 and 4 after chemical treatments.

Effects of a Thermal Treatment followed by Chemical Pretreatments: Using some samples from the irradiated linen that was used in the chemical pretreatment experiments, similar experiments were conducted, but the samples were heated for 75 minutes at 175 °C prior to the chemical treatments. The temperature of 175 °C was chosen because Figure 4 shows that this heat treatment produces a small but noticeable color change, more than any change that was observed on the samples used in the 1988 tests. Figure 9 shows the results of these experiments. Region 4 samples Oxford A and B fall slightly below the lower bound for this region, but this is attributed to a large variation in nitrogen content. As an example of the inconsistencies caused by variations in nitrogen contents, notice that Oxford A is lower than Oxford B even though Oxford B is a much harsher treatment.

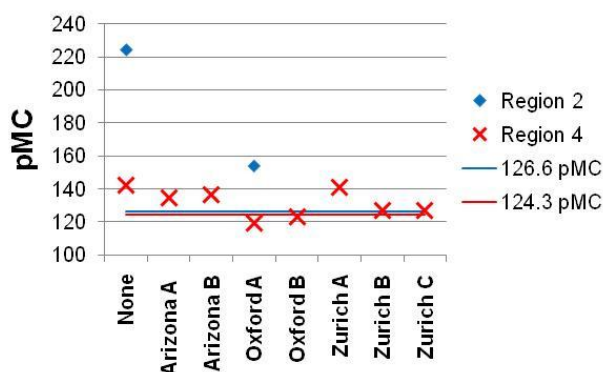


Figure 9. Percent Modern Carbon remaining in samples from Regions 2 and 4 after both thermal and chemical treatments.

Comparing Figures 8 and 9, one might expect that samples both heat and chemically treated would have lower radiocarbon contents than those only chemically treated, but that is not true for all chemical treatments. This inconsistency is most likely caused by the variations in nitrogen content that occur throughout the linen. Within this error, it appears that no radiocarbon created within the flax fibers was removed by heat and chemical treatments.

Gradients of Nitrogen Inhomogeneities: While measurements of nitrogen concentrations at random locations in the linen confirmed that the nitrogen content is inhomogeneously distributed, it did not provide information on the spatial gradients of nitrogen variation and how this might affect the radiocarbon dating of closely-spaced samples. Therefore, closely-spaced samples were cut from 1 cm by 5 cm linen pieces obtained from Region 3 that surrounds Region 2, and Region 5 that surrounds Region 4, and their nitrogen contents were measured. Figure 10 shows how the samples were cut. The perimeters of the 1 cm×1 cm squares, which weighed 10 mg, were measured for nitrogen content. The centers, which weighed 15 mg, were retained in case additional measurements were required.

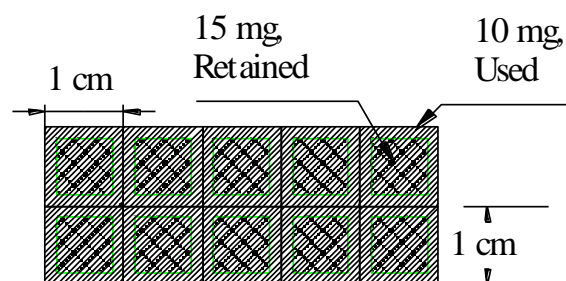


Figure 10. Samples for measuring gradients of nitrogen concentrations were cut from 1 cm×5 cm linen pieces.

The results are plotted in Figures 11 through 14. Figure 11 shows the nitrogen weight fractions for samples in region 3 and Figure 12 shows how these samples would radiocarbon date in 1988 if irradiated in 33 AD with a neutron fluence of $8.3 \times 10^{13} \text{ n} \cdot \text{cm}^{-2}$. Equations 3 and 4 were used to determine this neutron fluence to make the linen appear 1292 years younger if the nitrogen weight fraction was the average of all samples measured in this linen, namely, 569 ppm. The time period of 1292 years corresponds to the suspected age error in the 1988 radiocarbon dating of the Turin Shroud. Figures 13 and 14 are like Figures 11 and 12 except they are for samples taken from Region 5.

Figures 11 and 12 for Region 3 show nitrogen concentrations ranging between 528 and 653 ppm and the corresponding radiocarbon dates ranging between 1241 and 1502 AD instead of 33 AD. The gradients are as large as 125 ppm/cm and 261 years/cm.

Figures 13 and 14 for Region 3 show nitrogen concentrations ranging between 532 and 606 ppm and the corresponding radiocarbon dates ranging between 1241 and 1405 AD. The gradients are as large as 60 ppm/cm and 126 years/cm.

These gradients in radiocarbon dates calculated from the measured nitrogen concentrations in Regions 3 and 5 are comparable with the gradients of about 41 yr/cm observed for the 1988 radiocarbon results.

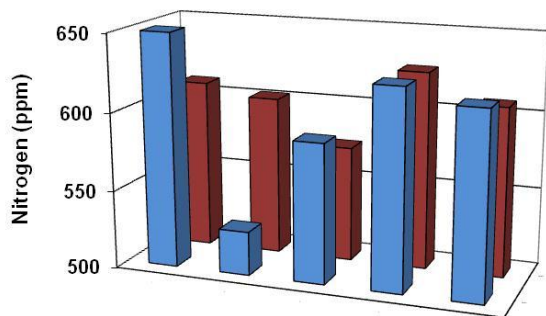


Figure 11. Measured nitrogen weight fractions in linen samples from Region 3. The bar locations correspond to the 1 cm spacing of the samples shown in Figure 10.

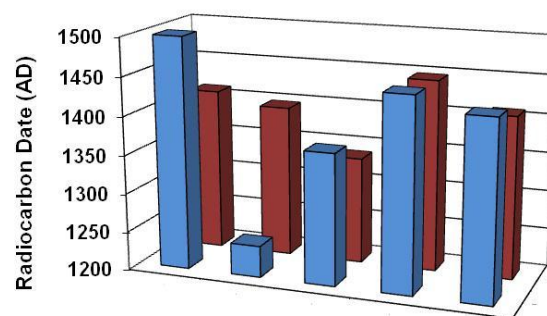


Figure 12. Calculated radiocarbon dates of the samples from Region 3 shown in Figure 11; see text.

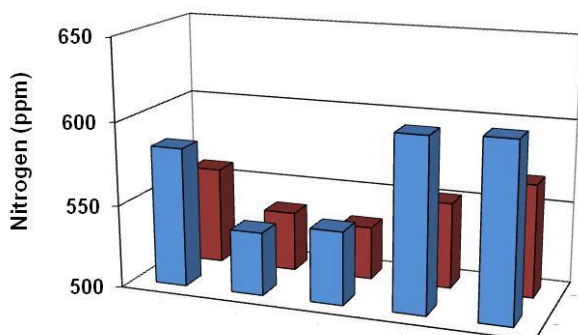


Figure 13. Measured nitrogen weight fractions in linen samples from Region 5. The bar locations correspond to the 1 cm spacing of the samples shown in Figure 10.

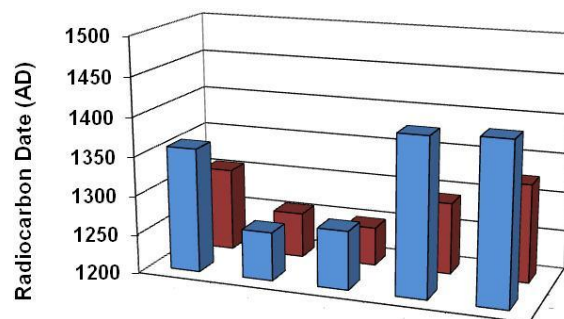


Figure 14. Calculated radiocarbon dates of the samples from Region 5 shown in Figure 13; see text.

4. CONCLUSION

Neutron irradiation of flax linen increases the radiocarbon content by two distinct modes. The first mode is by nuclear reactions with nitrogen indigenous to the flax. Within the uncertainties caused by variations in nitrogen content of the linen, the amount of radiocarbon produced by this mode can be calculated from the neutron fluence and the nitrogen content of the linen. This radiocarbon was not removed by high temperatures or by the chemical cleaning treatments used in the 1988 tests. Thus, this radiocarbon acts as a contamination that is indistinguishable from the natural radiocarbon in the linen and it will act to reduce the radiocarbon age of the linen.

The second mode of generating radiocarbon is by nuclear reactions with the nitrogen in the air that surrounds the linen and then enters the linen. These experiments have shown that the amount of radiocarbon produced by this mode and which enters the linen can be estimated if the linen is of known volume, is in a closed container of known volume, and it remains there for many days. Experiments were not conducted to determine how much radiocarbon produced by this mode enters the linen if the linen is not in a closed container or if it is removed

from the container soon after irradiation. The most important finding of this research concerning radiocarbon produced in the air surrounding the linen is that it is not permanently bound to the linen and 99% of it diffuses out in about six years at room temperature. Furthermore, virtually all of this radiocarbon can be removed in minutes by exposure to elevated temperatures or by the chemical cleaning treatments used in the 1988 tests.

Thus, if the Turin Shroud received neutron irradiation, its carbon-14 content would increase, causing its radiocarbon age to be younger despite experiencing thermal heating greater than it received in the 1532 Chambery fire and by the pretreatment cleaning procedures employed in the 1988 tests.

In addition, significant spatial variations of nitrogen were measured in the modern linen used in these experiments. Calculations showed that these variations would cause radiocarbon age gradients as large as 261 yr/cm if it received the neutron fluence needed to reduce its age by 1292 years. If the Turin Shroud had received neutron irradiation and the Shroud's natural variations of nitrogen content were similar to these found in the linen used in this study, these radiocarbon age gradients could explain Riani's [7] conclusions that the Shroud's radiocarbon dates were inhomogeneous.

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13. Neutron irradiations were performed at the University of Missouri Research Reactor in Columbia MO.
14. Radiocarbon measurements, sample heat treatments and chemical treatments were performed at IsoTrace Radiocarbon Laboratory, Accelerator Mass Spectrometry Facility at the University of Toronto.