AN EXPERIMENT TO REFUTE THE LIKELIHOOD OF CELLULOSE CARBOXYLATION[1]

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ABSTRACT. To test the hypothesis that cellulose in linen can be carboxylated at high temperatures in the presence of CO_2, water and silver, we heated two aliquots of cellulose extracted from old wood in glass ampoules, adding Ag powder to one to test its potential action as a catalyst for the carboxylation reaction. AMS measurement of the heated aliquots showed no statistically significant difference in ^{14}C content from the "uncarboxylated" cellulose. We conclude that carboxylation is not a systematic source of error in the dating of cellulose-containing materials such as the linen in the Shroud of Turin.

INTRODUCTION

Controversy has been recently created by the claim of Kousnetsov, Ivanov and Yeletsky (1996) that cellulose, in the form of a linen textile, can be carboxylated in the presence of carbon dioxide, water, and silver at elevated temperatures. This has obvious reference to potential systematic errors in the radiocarbon dating of the Shroud of Turin (Damon *et al.* 1989) since the Shroud was known to experience conditions that might have resembled those investigated by Kousnetsov, Ivanov and Yeletsky (1996). While it is not credible that carboxylation can occur to the extent that it would add or replace enough original carbon atoms of the Shroud to alter the question of its authenticity (*ca.* 50% of atoms would need to be replaced at the time of the Chambery fire to change the date from 600 BP to 2000 BP), the case that it might cause a significant systematic error, not necessarily with the Shroud date, but also with other dates on cellulosic materials, is worth consideration. The chemical processes proposed are not regarded by all chemists as infeasible. Therefore, we carried out the experiment described below to test as sensitively as possible whether carboxylation might be induced under the most favorable conditions we could contrive.

The experimental conditions are not a replication of those by Kousnetsov, Ivanov and Yeletsky (1996) because it is impossible to know how exact the replication must be. We have tried to carry out an experiment that would give a definite result on its own, but which is relevant to that of Kousnetsov, Ivanov and Yeletsky (1996). The experiment not only invalidates their claims with respect to the Shroud dating, but also makes a very strong case that the carboxylation mechanism, if it occurs at all, is very unlikely to make a significant change to the carbon composition of cellulose.

THE CARBOXYLATION EXPERIMENT

We took 5 mg of cellulose extracted from wood known to be growing >45 ka BP. Two aliquots were taken, one having added a few mg of Ag powder, since this is claimed to have catalytic properties for the carboxylation reaction. Both aliquots were sealed in glass ampoules in an atmosphere of

[1]This note was not presented at the Groningen conference, but the editors felt it was an appropriate complement to the preceding paper on cotton scorching by A. Long.

modern (Δ^{14} = 130 pc) CO_2 (2 bar pressure) and H_2O (1 bar), and kept at a temperature of 200°C for 24 hr. Slight charring took place. The ^{14}C content of the product was then measured by accelerator mass spectrometry (AMS), with the following results:

Sample 1: ^{14}C content = 0.33 ± 0.2 pMC
Sample 2 (including Ag): ^{14}C content = 0.41 ± 0.1 pMC

Previous dating of the extracted cellulose (*i.e.*, before "carboxylation") gives values of ^{14}C content = 0.2 ± 0.1 pMC. The dates of the treated samples are not younger in a statistically significant sense.

Discussion

Under these conditions, without any additional pretreatment of the "carboxylated" cellulose, the fraction of added or exchanged carbon content from the CO_2 was not detectable, the limit being *ca.* 0.2 pMC. These represent extreme conditions (certainly in terms of CO_2 concentration), so that more likely occasions when cellulose is liable to be in contact with hot CO_2 water vapor—with or without silver—would presumably be less liable to exchange carbon between cellulose and the atmosphere. It seems that the proposed mechanism can be entirely discounted as a detectable source of contamination and therefore a systematic error source in ^{14}C dating, not only for the Shroud, but, more importantly, for many other potential dating situations where cellulose and a degree of conflagration are involved. Similar results, albeit of less sensitivity, from experiments that are basically similar in their chemistry, have been reported by Jull, Donahue and Damon (1996).

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