LETTERS TO THE EDITOR

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On behalf of myself and my Russian co-workers **Drs. Ivanov and Veletsky** I would like to respond to the criticisms of one of our papers concerning the accuracy of the radiocarbon dating of the Shroud, as reported in your last Newsletter [`Dr. Kouznetsov's Claims attacked in leading U.S. Scientific Journal' BSTS Newsletter no. 41, pp.10-11]. In fact, I am very well aware of the Arizona laboratory's criticisms. Dr. Ivanov and I met Arizona's **Dr. Jull** at the American Chemical Society meeting held last April, during which we reported our findings as part of the Archaeological Chemistry session. I personally gave our Arizona colleagues a complete copy of our calculations re-evaluating the Shroud dating. Moreover, the manuscript of our paper, which has now been accepted for publication in the *Journal of Archaeological Science* [January 1996 issue], also the proceedings of the American Chemical Society Symposium, had been sent by it to the Arizona laboratory even before these papers had been peer-reviewed and accepted. So the Arizona team had our data well in advance of our publication, our only aim being to stimulate the most productive discussion. This is the background to the Arizona team's response as expressed in their article, **A.J.T. Jull, D.J. Donahue & P.E. Damon** "Factors which Affect the Apparent Radiocarbon Age of Textiles", University of Arizona, Arizona 85721. 'They claim to have shown our Fire Simulating Model (FSM) experiment, promoting, in our view, marked changes in a linen textile's carbon isotope content, to be `irreproducible'. However, careful study of the procedure they used reveals that this lacked the necessary precision to reproduce what we found. Thus although they incubated a two thousand year old sample (from En Gedi, Israel), in the same carbon dioxide/monoxide environment that we used, and at the same temperature (200 degrees centigrade), this was at a pressure of 0.06 atm, not the 0.0003 atm which we recommended. They argued that this pressure difference would enable the reported isotopic exchange processes to work 200 times faster (i.e. 0.06/0.0003). And since Jull et al. ran their incubation process ten tines longer than we did, they argue that the lack of isotopic exchange indicated by their experiment meant that ours was of a poor quality.

To us, however, their argument is far too simplistic. The radiocarbon exchange that we noted is a *complicated function of time* (see fig. 7 of our paper). As we showed in the very work that Jull et al. attack, there is a rise of C14-specific activity, followed by a *slow, and consistent decrease* in that activity with time. To our regret (because we had only a very limited amount of ancient textile fabric to experiment with), we could not extend these findings far enough to determine either the final equilibrium value reached, or when it might occur. So we are unclear how our opponents can claim that our findings are inconsistent with theirs, given the possibility that the C14 level ultimately returns back to values which their experiment lacked sufficient precision to detect.

To clarify this important point, we can linearly extrapolate the C14-specific activity curve (dependent on time at the fixed temperature), up to the very point at which it reaches the initial value of about 0.22 decays per second per grain of material. The estimated time for this is approximately 22 hours. We can follow Jull et al's logic that their experiment should have progressed 200 times faster than ours. So we estimate that in the context of Arizona's experiment the characteristic time for decrease of C14 should have been approximately equal to 22 hours

(200 equals 6.6 minutes). In their attempt to reproduce our findings Jull et al. ran their incubation for more than 15 hours, i.e. roughly 140 times longer than this tine, assuming that their experiment was well into the fall-of region implied by our findings.

This means that a proper comparison between the Arizona experiments and ours involves knowing quantitatively the behaviour of the reported radiocarbon exchange processes in late times. Conceivably Jull et al. failed to detect the isotopic changes we observed not because the effect does not occur, but because the characteristic time for these changes to manifest, and to diminish to some level of equilibrium, was much less than the run time of their incubation experiment. The chemical conditions chosen by Arizona to reproduce our data look strange to us. We did not describe anything like that! Thus the number of carbon dioxide molecules available for reaction in their experiment can be calculated from the ideal gas law, N=PV/kT. In the Arizona experiment, P=0.006 atm (see above), V=1.9cm^3, T=200 C, which yields N=1.8 x 10^{18}, the number of C-atoms in the surrounding atmosphere. Taking then $(C_6H_{10}O_5)n$ as a formula for dehydrated cellulose, the number of C-atoms in their 3.6 mg En Gedi simple is 8.0 x 10^{19} (i.e. mass fraction of carbon to cellulose = (72/162) x (3.6 x 10^{-3} g) x (6 x 10^{23} /12g) = 8.0 x 10^{19}). This means that the ratio of the number of C-atoms in the atmosphere to that in the textile cellulose is equal to 1/44. This simple conclusion can help to calculate the fraction of modern carbon that could arise in the liven sample if 100% of the air carbon were exchanged into the textile structure after heating by using the formula $^{F}FSM = (1/144)F_c + (43/44)F_{219SBP} = 0.7686$, where F_c=1.10 and F_{2195BP}=0.7609 - according to Jull et al. Subtracting from this value the fraction of modern carbon before FSM experiment ....P_{2195BP}, we arrive at a maximum expected change of only 0.0077, on the order of their quoted precision error, 0.0067, for the net change in Fm ^{14}C in the Table 1 of the paper by Jull et al to which we are responding.

Thus, as seen from the above, the heating (FSM) experiment of Jull et al. did not contain the requisite number of carbon atoms in the surrounding atmosphere to override the precision limitations of their experiment so as to observe any significant isotopic exchange, unlike the experimental conditions clearly described by us.

Furthermore the physical/chemical conditions for our Fire Simulation experiment were recommended to our group by two quite different, and independent fire-fighting specialists. As we have demonstrated, these conditions can promote significant, though possibly temporary alterations to a linen sample's radiocarbon content. By contrast, the pressure conditions used by the Arizona laboratory are unrealistic relative to any such fire. Therefore the results they obtained in their effort to 'reproduce' our findings may well be misleading with regard to the issues on the Shroud carbon dating that our group raised in close cooperation with the Turin Shroud Center, Colorado Springs, Colorado. Needing special emphasis is that in order to reproduce modern chemistry findings the recommendations that the authors of those findings set down should be followed as closely as possible. In our case those recommendations included atmosphere composition, incubation time, also water and silver cations concentration. Yet our Arizona opponents inexplicably ignored these.

With regard to the Arizona laboratory's criticisms, it should also be pointed out that they included in their calculations the common correction for external fractionation of C-isotopes (i.e. redistribution of isotopes between green plant-like flax and the environment), but not for internal biofractionation of C-isotopes (i.e. re-distribution of C-isotopes between different classes of

biomolecules within the flax stems). According to our findings, the latter type of biofractionation is really critical for radiocarbon dating since the cellulose fraction (5-7% of the dry weight of the flax), contains not less than 60-65% of all C14 atoms of the whole plant homogenate. This means that the manufacture of the linen (in essence, just isolation and purification of cellulose) leads to the textile being enriched with C14 (also C13), as compared with a total flax stem homogenate.

We have never insisted that our findings can prove the Shroud to be two thousand years old. Nor do we claim to have proved any precise age for the cloth. Rather, we have developed a general approach to re-evaluating the Shroud radiocarbon dating in the light of both the Fire Simulation Model experiment and internal biofractionation corrections. But we do believe that our findings show the Shroud's true calendar age to be much older than the dating announced in 1988. Certainly the subject demands further research.

Finally, we would like to make clear our agreement with those critics who argue that our findings are inadequate to account for the very significant, almost 20x increase in the linen cellulose's radiocarbon content as noted in our FSM experiments. We acknowledge that although the FSM-induced cellulose carboxylation is a fact, it cannot be the only, or even necessarily the main factor responsible for the marked shift in C14. The carboxylation process and the already-mentioned necessary correction for internal C-isotopes biofractionation go part way to explain it, but not all the way. We believe that further careful research into the possible isotopic kinetic effects promoted by high temperatures in the presence of the fire-specific CO2/CO-concentration in a surrounding atmosphere could lead to a much better understanding of how the marked changes in the linen cellulose's isotopic composition cattle about.

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[The above has been substantially edited, and allowance runs be made for the Editor's unfamiliarity with some of the scientific detail. Dr. Kouznetsov has recently been visiting the U.S.A. to present his findings to American scientists. He writes of this trip: 'My lectures were delivered and actively discussed at the following institutions during the period starting with September 16 through October 20, 1995: the University of California at Los Angeles, the University of North Texas at Denton, Texas: the US Air Force Academy at Colorado Springs, Colorado; St. Louis University and Washington University (both at St. Louis. Missouri); Duke University at Durham, North Carolina, and the US Textile Research Institute at Princeton, New Jersey. The Duke University presentation comprised a five hour seminar at which the speakers were (besides myself), my colleague Dr. Andrei Ivanov; and Dr. John Jackson (now back in his position as Professor of Physics at the USAF Academy, Colorado Springs. Those who attended included Dr. Alan Whanger; Dr. Thomas D'Muhala; Dr. August D'Accetta; Dr. Witold Brostow [head of the Dept of Chemistry University of North 'Texas at Denton, Texas]; Fr. Kim Dreisbach; and staff members and students from Duke University, chiefly from the departments of Chemistry, Physics and Materials Sciences. During the trip we signed an agreement for further cooperation in archaeological chemistry research between our laboratory and the Turin Shroud Center of Colorado at Colorado Springs; also the Department of Chemistry at North Denton, Texas.']