The reliability of late radiocarbon dates from the Paleolithic of southern China

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We have concerns over the reliability of the radiocarbon data used to support a later arrival of *Homo sapiens* in southern China (1). The pretreatment chemistry methods used to derive their accelerator mass spectrometry dates are not reported, they fail to define the nature of the dated material, and the limited analytical data fall almost completely outside accepted parameters, raising doubts over accuracy.

Sun et al. (1) state that they followed the collagen extraction methods outlined in ref. 2, but there are two different protocols described in that paper. We assume they refer to the basic collagen method rather than ultrafiltration. We note that this includes neither a base wash to mobilize humics nor molecular ultrafiltration to remove smaller potentially contaminating molecules. There is a good possibility of unremoved contamination in cases where humates are present. Second, they apply a method called "TOC" ("total organic carbon") but, again, without a method statement. We assume this is the approach used in ref. 3, essentially an acid–base–acid pretreatment with gelatinization. Such pretreatment techniques have been shown, over the last two decades, to yield significantly underestimated radiocarbon ages for Paleolithic-aged material, a problem that becomes more acute with lower collagen-yielding bones (4–6).

Reasonably preserved bone collagen should yield C:N atomic ratios of 2.9 to 3.5, and % C and % N values that range between ~40% and 45% and between 11% and 16%, respectively (7, 8). The data in table S3 of ref. 1 fall outside these parameters. While the actual collagen yields are not reported other than in selected samples, these were very low, and below the suggested cutoff of 1%; % N values are uniformly below 1% and most less than 0.01%. The % C values are also extremely low. C:N ratios give a series of values all outside of the maximum acceptance range, and often over 40 to 50. This shows that the collagen or the proportion of collagen in the TOC is virtually zero, and the date is being obtained on what might be predominantly exogenous (sediment-derived?) carbon. Previous efforts in Oxford to extract collagen from animal bones from Fuyan Cave all failed to produce collagen.

Analysis of duplicate bone dates on the same specimen treated with either collagen or the TOC method confirms the extent of the problems. Of the 16 dates, 75% give statistically different results, raising further doubts about reliability.

The charcoal dating is equally problematic. The material (single specks of charcoal; e.g., figure S2 in ref. 1) picked from sections cannot be linked securely to human occupation and may well derive from natural events. As important, however, is the absence of advanced oxidation-based pretreatment protocols suitable for old charcoal (9).

We hold that the radiocarbon data are essentially unreliable, and the results should be considered minimum ages. More work, following higher standards, is required to resolve the issue of chronology of these sites. Until then, these data ought to be set to one side along with conclusions about the late appearance of *Homo sapiens* in southern China.

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