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Problems with radiocarbon dating the Middle to Upper Palaeolithic transition in Italy

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ABSTRACT

Radiocarbon dating of material from Late Pleistocene archaeological sites is challenging. Small amounts of modern ^{14}C-labelled contamination will significantly affect the reliability of dates from the period, producing erroneous results. Recent developments in sample pre-treatment chemistry have shown that problems in reliable age determination during this period are surmountable. In this paper we provide an example of one such case, from the Middle to Upper Palaeolithic transitional site of the Grotta di Fumane, in northern Italy. We AMS dated two fractions of the same charcoal samples derived from a series of superimposed Mousterian, Aurignacian and Gravettian levels excavated at the site. One fraction was treated using the routine acid–base–acid (ABA) method, the other with the more rigorous acid–base-oxidation/stepped combustion (ABOx–SC) method. The latter method produced consistently older, and almost certainly more reliable, results. The eruption of the known-age Campanian Ignimbrite from the Phlegrean Fields near present-day Naples at 39.3 ka yr BP seals Ulluzzian and Proto Aurignacian levels in the south of Italy. Equivalent cultural levels are present at Fumane and the results obtained with the ABOx–SC methods are consistent with the ages inferred for sites in the south of Italy based on the presence of the Campanian Ignimbrite. New results from a sample found beneath the Campanian Ignimbrite at the Russian site of Kostenki, obtained using both the ABA and ABOx–SC, methods are also presented. They support the conclusion reached at Fumane by demonstrating that, in many cases, the ABOX–SC treatment effectively removes contamination where the ABA treatment does not. The results of the work offer a sobering examination of the problems inherent in the current radiocarbon database relating to the period, and highlight the dangers of an uncritical use of the corpus of ^{14}C results obtained over the last few decades. Based on our results, we predict that more than 70% of the 53 previously available determinations from Fumane are erroneously young. A way forward is suggested, using these improved chemical preparation methods, applying analytical methods to characterise the material dated, and testing existing site chronologies to establish which previous determinations are liable to be inaccurate.

1. Introduction

Radiocarbon dates provide the framework for understanding the chronology of the European Middle and Upper Palaeolithic transition. Unfortunately, the method is plagued with problems in its proper application through this period because the low amount of residual radiocarbon (<3%, equivalent to ~30,000 BP[1]) may be significantly influenced by the trace presence of contaminating carbon of a more recent age. The application of radiocarbon dating over almost 60 years has created a blurred vision of chronology over the latter part of the Late Pleistocene period in Europe, and this has, in turn, provided fertile ground for the strong debates that characterise the discipline (eg. D'Errico et al., 1998; Mellars, 1999; Zilhão and D'Errico, 1999). Several thousand radiocarbon determinations are available on various databases[2]. However, deciphering quite which of them are reliable and which not, is an often

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[1] In this paper, all ages 'BP' or 'ka BP' are conventional radiocarbon ages BP. Calendar/calibrated ages are given with the term 'cal BP' or in the case of Ar/Ar ages 'ka yr BP').

[2] For example the Radiocarbon Palaeolithic Database Europe (http://geo.kuleuven.be/geography/projects/14c-palaeolithic/download/) which contains over 4300 radiocarbon dates for the Palaeolithic, and the Stage 3 database, developed at the University of Cambridge (http://www.esc.cam.ac.uk/oistage3/Details/Homepage.html).

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impossible task, because the key information we require in order to diagnose this, such as a pre-treatment method description and basic analytical data, is almost always unavailable. Recent developments have signalled that an improvement in the situation is near. A new interim calibration curve reaching ~55,000 BP is due to be released soon through the INTCAL group and more refined pre-treatment methods are being applied which, along with improved instrumentation, are facilitating increased levels of accuracy. However, much more work remains to be done. In this paper we point to the crucial requirements of sample preparation and chemistry in deriving reliable radiocarbon dates and provide a case study from the Italian Palaeolithic that illustrates the pitfalls and problems apparent.

2. The chronology of the Italian Palaeolithic during Marine Isotope Stage (MIS) 3

Several authors (Mussi, 2001; Giaccio et al., 2006; Peresani, 2006; Bietti and Negrino, 2007; Milliken, 2007) have recently reviewed the Italian Middle to Upper Palaeolithic sequence, a period which saw the disappearance of Mousterian and Uluzzian techno-complexes, considered as an expression of the last Neanderthals, and the appearance of the Aurignacian (or the Proto Aurignacian, in its earliest manifestation[3]) which is largely accepted as a proxy for the spread of anatomically modern humans in western Eurasia. One major area of uncertainty they highlight is the radiocarbon dating of sites from the period. The first problem is the genuine scarcity of radiocarbon dates. The reports cite four radiocarbon determinations from the Uluzzian levels of Italy, from two sites. These range from about 29 ka BP to about 34 ka BP. Similarly, there are only six dates in total from Mousterian contexts. The majority of measurements are derived from Aurignacian contexts, and comprise a suite of about 30 dates ranging over 29–39 ka BP. Standard errors are uniformly wide. It is impossible to consider the temporal nature of the various Middle to Upper Palaeolithic industries, their relationship to one another, and the question of the route by which the Proto Aurignacian entered Italy. Italian colleagues have long considered whether southern transitional sites pre-date those in the north, but the chronometric evidence falls far short of what is required to confirm or falsify those models. The second problem, of course, is identifying which of these dates is reliable, and which not.

In the south of Italy the chronometric framework of the transitional phase has received a considerable boost due to the recent dating work relating to the deposition of the Campanian Ignimbrite (hereafter CI). The CI probably erupted from the Phlegrean Fields, near Naples, Italy (see Giaccio et al., 2008 for discussion on location) and its distributed tephra products fell over a substantial part of the Italian Peninsula as well western Russia and Greece (Fedele et al., 2002). The CI has been dated using laser $^{40}Ar/^{39}Ar$ techniques at 39,280 ± 110 yr BP (De Vivo et al., 2001), and Pyle et al. (2006) have suggested that an age of 39.3 ka yr BP be adopted as the age of the Y5/CI (the Y5 is the name given to the same tephra in marine core archives). Giaccio et al. (2006) and Fedele et al. (2008) adopt an age of 40,012 yr BP through comparison against the GISP2 ice core chronology, but we favour the more conservative $^{40}Ar/^{39}Ar$ age for the time being because of uncertainties in the precise age derivations within the ice core chronology and the possibility for the acid spike being from another volcanic eruption (Blockley et al., 2008).

The 39.3 ka yr BP age derived for the CI, therefore, represents a key isochronic layer of relevance to archaeological sites within the tephra distribution and dating to this approximate period. Giaccio et al. (2006) have usefully summarised the relevant points as they relate to the Palaeolithic. In Italy the CI seals final Middle Palaeolithic (Mousterian), Uluzzian and Proto Aurignacian levels at Castelcivita, Uluzzo Cave, Uluzzo C Cave, Bernardini Cave and Cavallo[4] (see Fig. 1 for locations) (see also Giaccio et al., 2008), whilst in Russia, a level of the site of Kostenki ("Cultural layer in volcanic ash") was discovered in 2002 sealed by CI tephra. These archaeological levels must, therefore, be older than the age of the tephra. Of course, in some cases there may be problems with the ascription of age to a specific tephra due to site-based reasons, for instance, re-working of tephra deposits, erosion and re-deposition. In the majority of cases, and with such a large and significant eruption, these possibilities can probably be set to one side. This enables us to view in a new light the previously determined radiocarbon chronologies. The picture that emerges does not inspire confidence. If the CI age is correct, then radiocarbon dates from Uluzzian and Proto Aurignacian levels ought to be yielding results of ~34,000–34,600 BP. Instead, they range as young as 27,400 BP (at Kostenki in Russia). In the vast majority of cases, the dates are markedly too young, but their variation is manifestly wide.

Giaccio et al. (2006) and Pyle et al. (2006) have suggested that the reason for these variable ages may be due to larger changes in the historic levels of ^{14}C concentration in the Earth's atmosphere than previously attested. There is a demonstrable ^{14}C production increase between ~40–42 ka cal BP associated with the Laschamp Geomagnetic Excursion, associated with peaks in ^{10}Be and ^{36}Cl in lake and marine sediments in both hemispheres (see Robinson et al., 1995; Yiou et al., 1997; Marco et al., 1998; Laj et al., 2000; Lal and Charles, 2007). Giaccio et al. (2006) presented evidence from a marine core sequence in the Tyrrhenian Sea (core CT85-5) which they suggest shows a much more significant increase in the radiocarbon concentration in the atmosphere at ~40,000 BP which may be related to the Laschamp event. The core contained a sediment sequence including the CI tephra. The dates of foraminifera within it ranged from 35,000 BP at the base of the CI volcano-clastic turbidite (CI_{VT}), to 20–25,000 BP within and at the top of the CI_{VT} with a return to dates of 32–33,000 BP a few centimetres above (Giaccio et al., 2006). If real, this evidence implies ^{14}C fluctuations of a far greater magnitude than previously thought over a brief time period. The substantial natures of this production increase led Giaccio et al. (2006) to claim that it must affect the radiocarbon dating of Middle to Upper Palaeolithic sequences in western Eurasia, and make a reliable radiocarbon-based chronology for the period impossible to achieve. The authors state, "*the radiocarbon chronology itself is thus entirely incapable of providing the requisite*

[3] We have already used, and we use again in this paper, the term Proto Aurignacian, with some reservations with respect to the site of Fumane. This term was introduced by Laplace (1966) to define those Aurignacian industries bearing a chrono-stratigraphic position earlier than the "typical Aurignacian" or the "Aurignacian I", as it has been defined in south-western France (see Bon et al., 2002). When one examines the lithic industries from the entire Aurignacian sequence of Fumane there is no clear differentiation visible in the organization of production and tool typology, even if some variations can be recognized in the composition of the lithic corpus, due to a decrease in the number of bladelets from units A to units D (Bartolomei et al., 1992, p. 165–167). The appearance of a few split-base osseous organic points in units A1 and D3 has, thus, no correspondence with modifications in lithic industry. It must be acknowledged, of course, that the "Proto Aurignacian" industry here might well persist (in accordance with the AMS–ABOx dates of unit D3bα) for about 1500 radiocarbon years (see below). Typically, the Aurignacian is associated with anatomically modern humans in this region, whilst Mousterian and Uluzzian industries are associated with Neanderthals.

[4] Paglicci is no longer included in this list, since new data now indicate that the tephra there is more likely to be the Codola ash, dated to ~33 ka BP (Giaccio et al., 2008) and higher in the sequence than the CI would be expected to be.

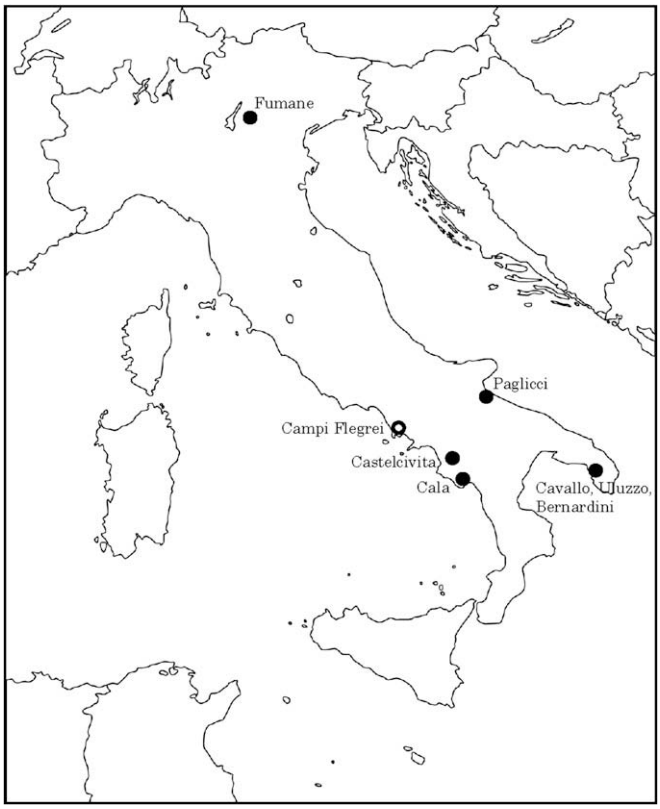


Fig. 1. Location of the site of Grotta di Fumane, and other sites in Italy mentioned in the text.

time dimensions for not only the appearance of the Upper Palaeolithic, regardless its definition (sic), and/or the supposed influx of anatomically "modern" humans, but also, and more importantly, the actual timing and dynamics of the Late Pleistocene biocultural shift".

Are there alternative explanations for the distributions we see in the Italian chronology? Giaccio et al. (2006) and Pyle et al. (2006) make no mention of possible contamination or radiocarbon error in their discussion of the ^{14}C ages obtained. Radiocarbon dating of material aged >25–30 ka BP can be problematic because of several principal influences. Perhaps the most significant is contamination of carbonaceous material by exogenous carbon, the extent to which it has become chemically associated or cross-linked and the success of radiocarbon pre-treatment chemistry in removing it. This is the subject of this paper. A further influence is the laboratory background and the ability of the radiocarbon facility to ensure stability in its quantification and confidence in the subtraction of background contributions to the measured ^{14}C activity. Reproducibility and stable backgrounds enable increased confidence to be generated in radiocarbon dating close to the limit of the technique (~55 ka BP). Radiocarbon measurements within two standard deviations of the values obtained for standards that are known to be beyond the radiocarbon limit (so-called 'background' materials) are reported as "greater than" ages. In an elegant paper written more than a decade ago, Chappell et al. (1996) showed that as ages creep closer to the limit of the technique (at around 40 ka BP at the time of their publication), they tend to cleave to an asymptote, resulting in ages that are more likely to underestimate the true age. Great difficulties often arise in obtaining reliable, finite ages for material of this antiquity and distinguishing them from those cleaving asymptotically to the measurement limit. In the case of dates from Castelcivita, one of the sites listed, contamination may be a significant influence, since the measurements are all on burnt bone. This is a notoriously unreliable sample type that often produces aberrant results because the fraction dated is poorly defined chemically. It is assumed to be predominantly the remains of pyrolised collagen that is often further degraded and low in carbon within which other contaminants may be present (Higham et al., 2006b). Analysis of carbon content and stable isotopes is one way of checking on the reliability of the resulting dates, but is fraught with problems due to lack of sensitivity. These determinations, therefore, ought really to be considered at best minimum ages only. Other dates listed in Giaccio et al. (2006) include some bone determinations from Temnata and the Kostenki–Borschevo complex of sites (see also Sinitsyn and Hoffecker, 2006). Recent work (Bronk Ramsey et al., 2004; Higham et al., 2006a,b; Jacobi et al., 2006) has shown that the application of ultrafiltration techniques to samples of Pleistocene-aged bone can offer improved contaminant removal and this often results in older determinations for samples of bone previously dated using less rigorous treatment methods. This does not necessarily mean the dates included by Giaccio et al. (2006) are unreliable or inaccurate – they may well not be, but problems have been shown in other contexts of Palaeolithic age in Europe and the presence of similar contamination within bone from these sites must be entertained seriously. Our work has focussed on evaluating the possibility of sample contamination being an influence, as we describe below.

3. Charcoal dating

Charcoal is usually assumed to be a reliable material for dating, if the archaeological context is secure and inbuilt age issues can be set to one side. Routine treatment of such material in radiocarbon laboratories usually comprises an acid–base–acid (ABA) sequence. This pre-treatment method is designed to remove carbonates and humic complexes using acidic and basic solutions respectively (the latter most commonly using NaOH), with any atmospheric carbon dioxide adsorbed during the base wash removed by a final acidification. Evidence suggests that in many cases, this is sufficient to remove contaminants to an acceptable degree. Chappell et al. (1996) showed that for material approaching the radiocarbon limit, however, it is wise to be more cautious and critical of radiocarbon results obtained using these methods. Recent developments in sample pre-treatment chemistry assume importance. In investigating the so-called 'radiocarbon barrier' in Australian prehistory, Bird and Gröcke (1997) and Bird et al. (1999) developed a pre-treatment protocol for radiocarbon dating charcoals that comprised an additional oxidation step (an acid and base treatment, followed by a wet oxidation pre-treatment in an acid–dichromate solution (termed ABOx) and subsequent stepped combustions (SC) to remove any remaining labile components prior to graphitisation. The chemically resistant carbon (termed 'oxidation-resistant elemental carbon', or OREC) remaining after these treatments was argued to represent a significant improvement in the removal of organic contaminants from the charcoal/black carbon destined for AMS dating. Further improvements were achieved by the combustion of treated OREC on a double-vacuum line to reduce memory effects and the influence of trace contamination from atmospheric CO_2. Bird et al. (1999, 2003) suggested that the total methodological blank for the ABOx–SC method was 0.1 ± 0.02 pMC, which is equivalent to *c.* 55 ka BP. The effect of applying this methodology in key archaeological contexts has been notable. In Australia, it has resulted in an increase in the dateable age range, beyond around 40 ka BP, to finite ages up to 55 ka BP (Turney et al., 2001). Similar results have been reported from Border Cave in South Africa (Bird et al., 2003) and Pedra Furada, in Brazil (Santos et al., 2003).

The Oxford Radiocarbon Accelerator Unit (ORAU) has undertaken work on tropical sequences dating into the Pleistocene in Malaysia at the site of Niah Great Cave (Higham et al., 2008). There, ABA and ABOx–SC pre-treatments were applied to single pieces of charcoal to examine whether there was any substantial difference between them and the age of an untreated control sample, which was dated untreated. In some cases there were 4–5000 year differences between the dated samples, with the ABOx–SC dates always the older. In some instances, however, the ABOx–SC pre-treatments did not yield any significant difference when compared with the untreated samples or those treated with the ABA method. For samples less than 25–30 ka BP in age, ABOx–SC treatments produced little or no variation compared with the ABA method. Samples older than this, however, did show large differences with treatment, suggesting the ABA method was not sufficiently rigorous in decontaminating the charcoals. Work in progress is applying these techniques to archaeological sites around the rim of the Mediterranean (Brock and Higham, in press). Other ORAU ABOx–SC results for the Grotte Chauvet are reported in Cuzange et al. (2007).

4. The site of Grotta di Fumane

In recent work we have been re-evaluating the radiocarbon *corpus* from a key site in northern Italy, the Grotta di Fumane. The site lies at 350 m above sea level at the southern fringe of the Venetian Pre-Alps (Fig. 1) and is part of a complex karst system made up of several cavities which together form a sedimentary succession over 10 m thick (Fig. 2). It has produced a dated sequence for the Middle to Upper Palaeolithic which spans the period from MIS 5–MIS2 (Peresani et al., 2008). This has been divided into four main units, labelled as S, BR, A and D on the basis of lithology, pedological features and density of cultural evidence (Bartolomei et al., 1992). Excavations since 1988 have been undertaken both beyond the present-day drip-line and in the cave entrance, an area with Middle and Upper Palaeolithic levels. Well-preserved Mousterian and Aurignacian living-floors have been revealed in an excellent state of preservation.

Sediments dating from the final Mousterian to the Aurignacian are mostly formed by frost-shattered scree with a variable content of sand and aeolian dust, the former being prevalent in the western zone, the latter increasing progressively from the entrance to the outside. Lithic and faunal material, hearths and other internally stratified structures with micro-stratigraphy inside the cave entrance are frequently found, particularly in units A11, A10, A9, A6, A5 (Mousterian) and A2, A1 (Aurignacian; Broglio et al., 2006). By contrast, only isolated combustion structures and lithic workshops have been preserved in units A4, A3 (Uluzzian), D3 and D1 (Aurignacian; Broglio et al., 2006). Establishing contemporaneity between these various structures and the accumulation of other human residues is difficult, particularly in those units which have been subjected to intense anthropization or to low sedimentation rate (Broglio et al., in preparation). The most striking cases are in the Proto Aurignacian unit A2, where large hearth-like combustion structures (for example structure 14) appear to have been re-used after potential periods of abandonment.

Humans occupied the cave in different climatic and environmental conditions, from moist-temperate periods at the base of the late Mousterian sequence (units A11 and A10), with alternating cooling in the overlying levels (units A9–A3) and a shift to cooler and drier conditions at the top of the sequence (units A2–D3). A certain variability has been recognized in the spectrum of hunted ungulates (Fiore et al., 2004). Mousterian levels record a striking variability in lithic technology (Peresani, 1998), due to the progressive appearance in the latest phases of innovations and some implements comparable to lithic sets of the Uluzzian

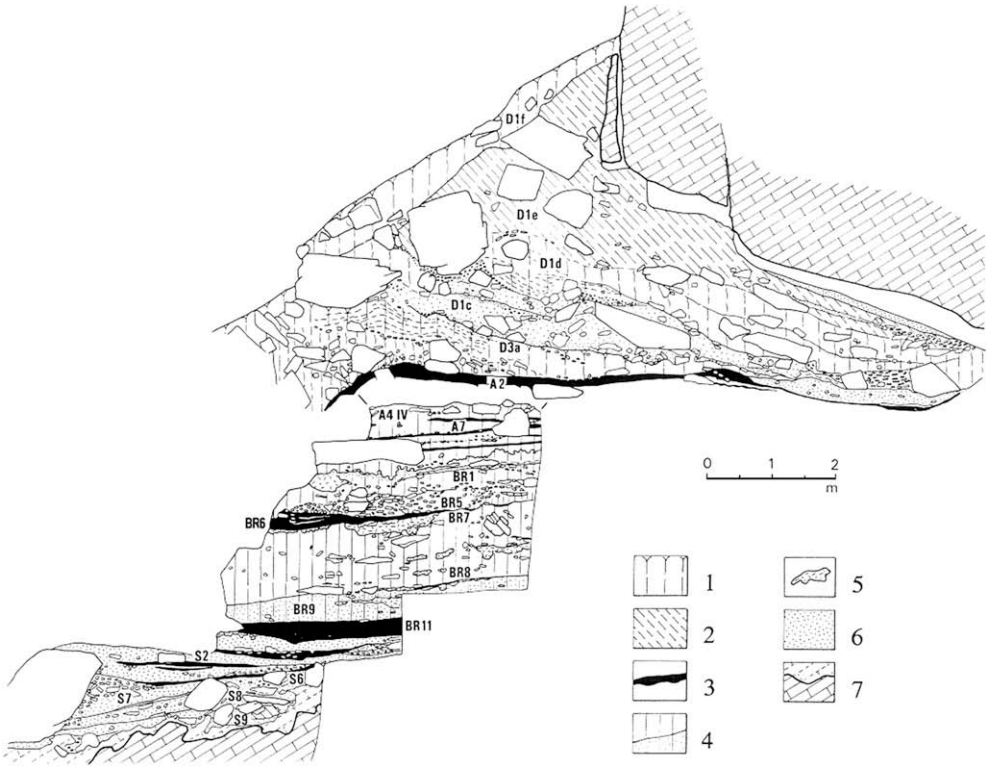


Fig. 2. Stratigraphic sequence at the Grotta di Fumane. Levels A2, D3 and D1c are the Proto Aurignacian level, D1d is Gravettian, whilst below these, A4 and A3 are Uluzzian levels, A5–S9 are Mousterian levels. Key: 1: denotes rendzina, upper soil; 2 – slope deposits with boulders; 3 – living floors, with high concentrations of organic matter or charcoal; 4 – loess and sandy loess; 5 – $CaCO_3$ cemented layers; 5 – sandy deposits; 6 – unweathered and weathered bedrock.

(Peresani, 2008). Complex dwelling structures, lithic, bone technology and pierced molluscan shells mark the abrupt appearance of the Proto Aurignacian at the site (Broglio and Gurioli, 2004; Broglio et al., 2006).

The ORAU has been involved in the dating of several samples from this sequence over the past ten years. The radiocarbon ages that have been obtained are listed in Table 1. Several other laboratories have also provided AMS and conventional radiocarbon determinations (see Cremaschi et al., 2005; Giaccio et al., 2006; Peresani et al., 2008). Due to the fine stratigraphic resolution, the presence of well-preserved hearths and other structures in the Aurignacian, Uluzzian and Mousterian layers, Fumane is one of the key European sites for investigating the timing of bio-cultural innovations during the Middle to Upper Palaeolithic transition. Unfortunately, unlike sites further to the south of the Italian Peninsula, Fumane has, so far, yielded no evidence of the CI tephra.

5. Materials and methods

The Fumane radiocarbon sequence was re-examined to determine whether some of the ages previously obtained were reliable or not. Several charcoal samples were dated using both ABOx–SC and ABA techniques, and the results were compared with previous measurements from throughout the sequence. Consistent results between ABOx–SC and ABA determinations would suggest strongly that the original chronometric sequence was reproducible, though extremely variable in radiocarbon age. This result would thereby add support to the suggestions of authors such as Conard and Bolus (2003) and Giaccio et al. (2006) that large variations in radiocarbon production conspire to render the method unreliable between 30 and 40 ka BP. Statistically significant differences, with ABOx–SC determinations being older, would imply potential contamination remaining in the initial series shown in Table 1.

We obtained charcoal archived in the ORAU remaining from previously dated Mousterian and Aurignacian contexts at Fumane and collected additional samples from the University of Ferrara. The majority of the samples are from macro-unit A taken at variable positions from the surface. OxA-6463 was collected from a 4 m^2 area across the present-day drip-line, where level A5 is differentiated from the underlying level A6. We also obtained material from a hearth found in layer D3bα outside the present-day cave and from layer D1d, the Gravettian level at the site.

The previous ORAU radiocarbon determinations in Table 1 were all ABA-treated. The standard ABA method at ORAU comprises treatment with 1 M HCl for 20 min, followed by 0.2 M NaOH for 20 min, and finally 1 M HCl for a further 60 min. All treatments are carried out at 80 °C, and the sample is washed 3 times with ultrapure (MilliQ™) water between each step, or until no more humics are leached.

The ABOx–SC method involves treating each sample with 6 M HCl for 1 h, followed by 1 M NaOH for 30 min. The samples were washed 3 times with ultrapure water after each treatment or until no more humics were leached, and then treated with 0.1 $K_2Cr_2O_7$ in 2 M H_2SO_4 for 20 h at 60 °C. The samples were then combusted in an evacuated tube at 630 °C for 2 h in the presence of pre-combusted copper oxide wire, prior to combustion and graphitisation as standard.

Charcoal was given both a new ABA treatment if previously undated, or if the OxA- number was older than OxA-10000.

The results are given in Table 2. Pre-treatment yields for the ABOx–SC determinations are low, as expected, due to the rigorous nature of the oxidation step and the preceeding stronger acid and alkali washes. Higher % carbon (%C) yields on combustion prior to graphitisation for the majority of the ABOx–SC samples are as expected, with one exception (OxA-X-2275-45).

6. Results

We can compare our new results with the series listed in Cremaschi et al. (2005), Giaccio et al. (2006: 363, Table 4) and Peresani et al. (2008)(see Table 1 above). The results for Level A2 in Table 3, (OxA-11360, an ABA determination, for example, may be compared with OxA-17570, an ABOx–SC determination; and OxA-11347 (ABA) with OxA-17569 (ABOx–SC)) show clearly that routine ABA pre-treatment was not sufficient to remove contamination from charcoal excavated within this context. The substantially older results obtained using ABOx–SC pre-treatment methods suggest that these ages are more reliable than the ABA-treated samples and probably comprise less contaminating carbon. The ABOx results suggest that this Proto Aurignacian level must date to ~35,000 BP, rather than be younger. By stratigraphic logic, this means that all other determinations within and below this level that have younger radiocarbon ages are almost certainly erroneous if the assumption of reliable stratigraphic succession holds. There are 21 determinations from five laboratories from level A2, ranging from ~18,000 to 40,000 BP, of which 16 determinations are now seen to be too young for their context. Three of the four determinations from level A3 are also too young, by 6000–8000 years. Of course archaeological sites are not static, and they are subject to bioturbation, mixing of sediments, cryoturbation, incipient pedogenesis and the like, and this can introduce variation and error in interpretations of site stratigraphic sequences. Until such processes can be identified, however, we suggest that the most parsimonious explanation for the variation in radiocarbon age is due to contamination, unremoved by previous techniques but removed by ABOx–SC, since the pre-treatment chemistries were undertaken on the same shards of charcoal.

Units A3 and A4 (Uluzzian), and A5 and A6 (Late Mousterian), are below A2 and, therefore, must also contain radiocarbon ages that are clearly too young in the light of the new results, again by stratigraphic superposition. Dates of 33,000 BP from level A4II are younger than they ought to be given the new ages obtained using ABOx–SC from Level A2 that seals it. Only LTL-1795A (37,828 ± 430 BP) appears within sequence from A3. This date is of key importance for the Uluzzian sequence and may record the first appearance of this technocomplex in the Peninsula.

Our ABOx–SC results from A5 suggest it dates to 40.1–41.6 ka BP (a previous measurement, OxA-6463 at 33,700 ± 600 BP, for example, has a new ABOx–SC date (OxA-17980) which is 6000 years older) and therefore any determinations younger than this in the same context, and below it, would appear aberrant. OxA-8022 (38,800 ± 750 BP) and OxA-8023 (38,250 ± 700 BP) from context A5 + A6 do not appear to fit in sequence chronologically and the new ABOx–SC determination (OxA-17566) from the same sample of charcoal, is statistically older than both of them. Two additional ABA-treated dates (derived again from the same charcoal) were dated as a check on the first pair of results. Whilst as a group the four ABA-treated samples are statistically indistinguishable from one another, they do not agree as a group when the ABOx–SC result is included (even though the ABOx–SC result appears older, however, it is indistinguishable statistically from the two more recently treated ABA samples (($t' = 4.97$; $df = 2$ ($\chi^2 = 5.99$) suggesting contamination is not proportionally as large as in other cases) (Table 2).

None of the 7 determinations from A6, with the exception of the 'greater than' ages (R-2758 and 2759) can be considered reliable. Because of the results obtained from A5 and A5 + A6, it is highly likely that every date from levels below these of <40,000 BP is likely to be erroneously young. Of the 13 dates below this level, 8 are demonstrably too young, almost certainly influenced by unremoved contaminants. One is a 'greater than' age and the remainder, we suspect, might be apparent ages as well. Further work is

Table 1
The radiocarbon dataset of the Gravettian (D1d), Aurignacian (D3–A2), Uluzzian (A3–A4) and final Mousterian (A5–A11) sequence of Fumane Cave obtained prior to this paper. Further dates from layers D1d, D3bα, A2, A5 and A5 + A6 are reported in Table 2. Str. = combustion structure. R-2510, R-2518, R-2527, R-2757, R-2758, R-2759, R-2784, Ly-9920 have been obtained with conventional techniques. For further details see Cremaschi et al., 2005; Broglio et al., 2006; Broglio et al., in preparation; Peresani et al., 2008. As noted in Peresani et al. (2008), the two OxA- results from A5 + A6 are duplicate measurements on the same charcoal.

Layer	Material	Lab. number	Conventional radiocarbon age BP
D1e	Terrestrial shell	R-2784	26,890 ± 530
D1d	Charcoal	OxA-11348	31,490 ± 250
D1d base	Charcoal	LTL374A	29,828 ± 390
D1d base	Charcoal	UtC-2050	30,700 ± 400
D3b	Charcoal	UtC-1775	31,700 ± 1200/−1100
D3b	Charcoal	UtC-2045	32,300 ± 400
D3bα str. 15 – lev. A	Charcoal	OxA-8050	30,320 ± 320
D3bα, str. 15, sq. 57	Charcoal	OxA-8051	32,020 ± 340
D6	Charcoal	UtC-2046	32,300 ± 500
D6	Marine shell	OS-5872	37,100 ± 240
D3 + D6	Bone collagen	R-2510	23,157 ± 319
A1	Charcoal	UtC-2049	31,900 ± 500
A2	Charcoal	UtC-2047	32,100 ± 500
A2	Charcoal	UtC-2048	36,500 ± 600
A2	Charcoal	OxA-8054	33,160 ± 400
A2	Marine shell	OS-5999	32,000 ± 90
A2	Marine shell	OS-5871	32,700 ± 140
A2	Charcoal	OxA-11360	31,830 ± 260
A2 sq. 97d	Charcoal	OxA-11347	30,650 ± 260
A2 IIext	Bone collagen	R-2518	18,836 ± 258
A2 int	Bone collagen	R-2527	27,485 ± 691
A2R	Charcoal	LTL-375A	34,312 ± 347
A2 – str. 9	Charcoal	UtC-2044	31,600 ± 400
A2 – str. 10	Charcoal	UtC-2051	32,800 ± 400
A2 – str. 10	Charcoal	UtC-1774	40,000 + 4000/−3000
A2 – str. 16	Charcoal	Ly-9920	31,300 ± 395
A2 – str. 19	Charcoal	Ly-1286 OxA	32,415 ± 1045
A2 – str. 19	Bone collagen	Gr-16231	33,140 ± 460
A2 – str. 14 top	Charcoal	OxA-6566	31,900 ± 1100
A2 – str. 14 top	Charcoal	OxA-8052	34,120 ± 460
A2 – str. 14 lev. A	Charcoal	UtC-2688	36,800 + 1200/−1400
A2 – str. 14 lev. B	Charcoal	UtC-2689	35,400 + 1100/−1300
A2 – str. 14 lev. B2	Charcoal	UtC-2690	34,200 + 900/−1100
A2 – str. 14 base	Charcoal	OxA-6465	31,620 ± 500
A2 – str. 14 base	Charcoal	OxA-8053	33,640 ± 440
A3 – str. I	Charcoal	LTL-1830A	29,602 ± 240
A3 – str. II	Charcoal	LTL-1831A	29,233 ± 350
A3 – str. IV	Charcoal	LTL-1796A	29,361 ± 320
A3 – str. IV	Charcoal	LTL-1795A	37,828 ± 430
A4II	Charcoal	OxA-8021	33,300 ± 400
A4II	Charcoal	OxA-6462	33,150 ± 600
A4II	Charcoal	LTL566A	33,700 ± 350
A5 + A6	Charcoal	OxA-8022	38,800 ± 750
A5 + A6	Charcoal	OxA-8023	38,250 ± 700
A6	Charcoal	OxA-11331	34,400 ± 800
A6	Charcoal	OxA-6464	34,950 ± 700
A6	Charcoal	LTL-569A	35,450 ± 1180
A6	Charcoal	LTL-568A	37,300 ± 450
A6	Charcoal	R-2758	>29,000
A6	Charcoal	R-2759	>35,000
A6base – str. I	Charcoal	LTL-570A	37,750 ± 400
A5 + A6	Charcoal	OxA-8022	38,800 ± 750
A5 + A6	Charcoal	OxA-8023	38,250 ± 700
A8	Charcoal	LTL-571A	36,650 ± 350
A9I	Charcoal	LTL-573A	36,450 ± 400
A9	Charcoal	LTL-574A	38,550 ± 540
A9	Charcoal	OxA-11346	39,950 ± 550
A9	Charcoal	LTL-572A	40,150 ± 550
A9	Charcoal	LTL-376A	42,750 ± 700
A9	Charcoal	R-2757	>31,400
A10	Charcoal	LTL-377A	41,350 ± 750
A10I	Charcoal	LTL-575A	37,100 ± 450
A11	Charcoal	LTL-577A	36,850 ± 350
A11	Charcoal	LTL-378A	42,000 ± 750
A11a	Charcoal	LTL-578A	39,850 ± 500
A11base	Charcoal	LTL-579A	38,100 ± 600

Table 2
Radiocarbon ages of charcoal from the Grotta di Fumane. From each context, only one charcoal fragment has been dated. In column 2, all determinations are repeat measurements from the same context and are on identical samples of charcoal. Samples with OxA-8000s numbers were analysed in 1998 at the ORAU. All others were AMS dated in 2008. $\delta^{13}C$ values are expressed in ‰ wrt to VPDB with a measurement precision of ±0.2–0.3‰. %C is the carbon content of the pre-treated charcoal after combustion. Treatment denotes the pre-treatment method, ABA for acid–base–acid and ABOx for acid–base-oxidation/stepped combustion: see text for details. One of the results is given an OxA-X- prefix, because this sample produced a much lower than expected combustion yield (only 24.4%). This is sometimes associated with problematic samples that are particularly degraded or fragile charcoal composition. In the sequence, however, it does not appear aberrant (see Fig. 3 for the model results).

Context	ABA radiocarbon age (BP)	% C	$\delta^{13}C$ (‰)	ABOx–SC radiocarbon age (BP)	% C	$\delta^{13}C$ (‰)
Gravettian						
Lyr D1d	31,490 ± 250 (OxA-11348)	55.4	−23.4	31,590 ± 160 (OxA-17571)	78.6	−22.3
Aurignacian						
Lyr D3bα, str. 15, sq. 57	32020 ± 340 (OxA-8051)	62.2	−24.8	33,890 ± 220 (OxA-17981)	68.7	−24.8
	32,600 ± 190 (OxA-18200)	47.6	−24.5			
Proto Aurignacian						
Lyr A2, sq. 97d	30,650 ± 260 (OxA-11347)	58.5	−25.2	35,640 ± 220 (OxA-17569)	80.6	−22.5
Lyr A2/struc.18	33,380 ± 210 (OxA-19525)	64.4	−24.7	35,850 ± 310 (OxA-19584)	40.5	−23.8
Lyr A2/struc.16/lev. B[a]	32,120 ± 240 (OxA-19413)	44.2	−24.5	34,180 ± 270 (OxA-19414)	48.6	−24.7
Lyr A2/struc.17[a]	32,530 ± 240 (OxA-19411)	60.7	−25.6	34,940 ± 280 (OxA-19412)	61.8	−24.2
Lyr A2, sq. 107i	31,830 ± 260 (OxA-11360)	44.3	−23.3	35,180 ± 220 (OxA-17570)	74.5	−21.7
Mousterian						
Lyr A5, sqs. 85,86,95,96	33,700 ± 600 (OxA-6463)	62.3	−22.1	40,150 ± 350 (OxA-17980)	74.4	−21.1
	36,860 ± 700 (OxA-18199)	60.7	−21.2			
Lyr A5 sq. 88i,3789/struc.III	34,500 ± 270 (OxA-19410)	58.8	−24.6	41650 ± 650 (OxA-X-2275-45)	24.4	−23.0
Lyr A5 + A6, sq.90	38,800 ± 750 (OxA-8022)	42.1	−23.8	40,460 ± 360 (OxA-17566)	62.1	−24.4
	38,250 ± 700 (OxA-8023)	66.3	−24.2			
	39,500 ± 330 (OxA-17567)	60.4	−24.2			
	39,490 ± 350 (OxA-17568)	57.8	−24.5			

[a] See Broglio (2005: 25) for an illustration of these contexts.

required. Taken together, of the 53 radiocarbon determinations available from level A2 to A11, at least 39 are aberrant (72% of the total), with almost all too young for their stratigraphic position.

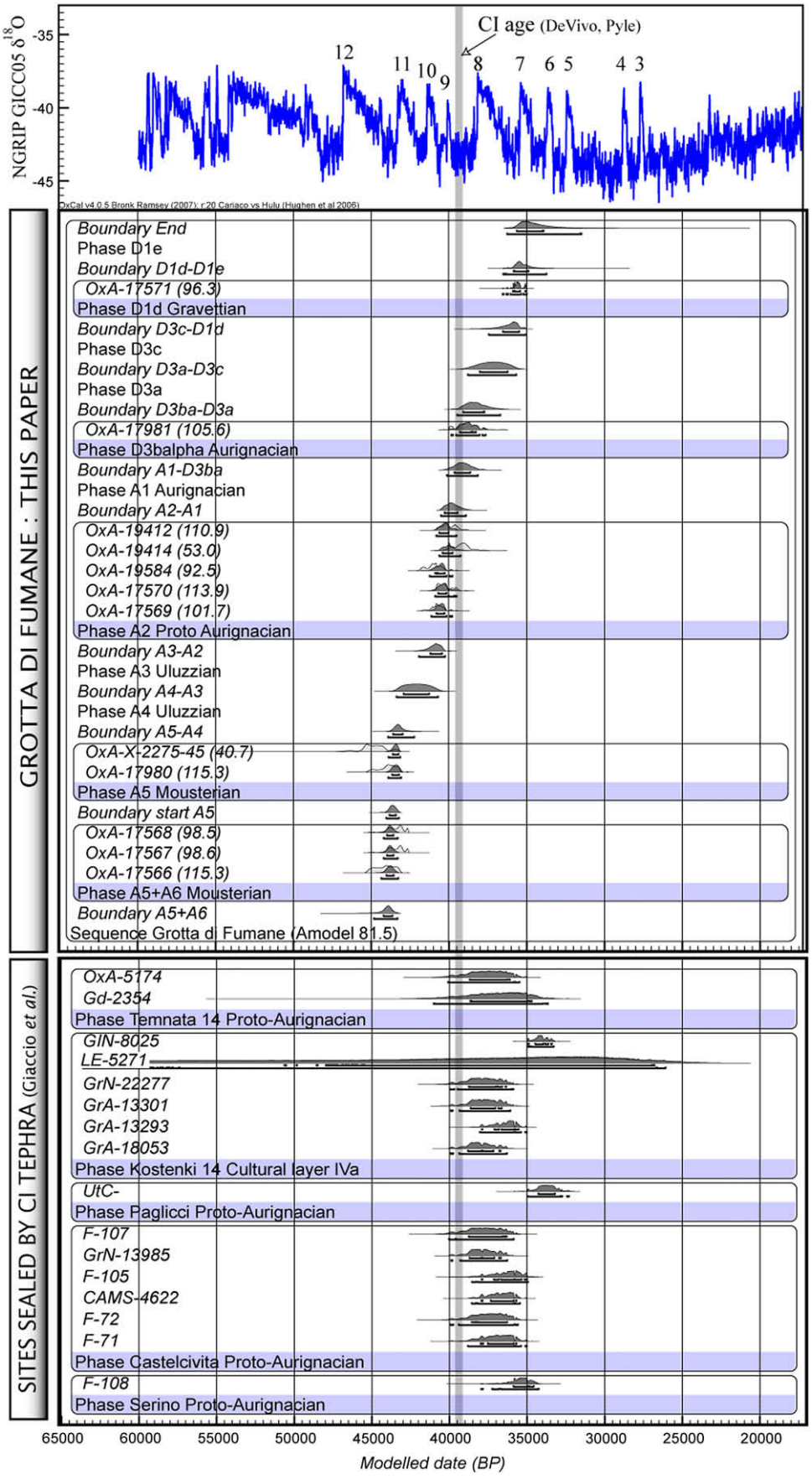
7. Discussion

A revised chronology for the Middle to Upper Palaeolithic sequence at Fumane is shown in Fig. 3 using a modelled Bayesian sequence generated with OxCal 4.0 (Bronk Ramsey, 2001). In the model we have compared (see discussion in van der Plicht et al., 2004) our ABOx–SC radiocarbon determinations against the Cariaco Basin ^{14}C record published by Hughen et al. (2006). This dataset has a greater number of radiocarbon analyses than the previously published data (Hughen et al., 2004), and an age model based on comparison with the Hulu Cave $\delta^{18}O$ speleothem record from China dated by U/Th methods (Wang et al., 2001). This approach allows us to compare our results against a climate proxy, in this case the GICC05 $\delta^{18}O$ ice core data of Svensson et al. (2006, 2008) and Andersen et al. (2006), as well as the Ar/Ar determination of De Vivo et al. (2001) for the deposition of the CI. Further work is required to determine the synchroneity of climatic changes recorded in Greenland and Mediterranean Europe. Therefore, this comparison may require modification and must be viewed cautiously. The modelled comparison results for Fumane are shown in Table 3. If it is assumed that the age of the Proto Aurignacian contexts in the Italian peninsula must be greater than the age of the CI eruption, then our results from Fumane compare very favourably with the age determined for the CI which is also plotted on Fig. 3, since the results all pre-date this age. The modeling shows that the Level A2 Proto Aurignacian dates to *after* 41,200–40,450 $BP_{CARIACO–HULU}$ (68.2% prob) (Table 3). Acknowledging the measurement uncertainties, this suggests that the Proto Aurignacian dates to GIS 10–9 on the GICC05 timescale (GIS10 starts at 41,460 ± 817 b2k (Svensson et al., 2008) (see Fig. 3)). The latest Mousterian occupation of A5 takes place prior to 43,580–42,980 $BP_{CARIACO–HULU}$, so the Uluzzian levels must lie between this and 41,200–40,450 $BP_{CARIACO–HULU}$.

In another model the A2 dates from the Utrecht laboratory that appear to fit within the sequence were included, as well as the A3 Uluzzian determination of LTL-1795A. The results show that the two models are sensitive to the inclusion of these other likelihoods for some of the model parameters, particularly for the boundary distribution between A3 and A2, as one might expect. With only the OxA dates included the boundary is 41,200–40,450 $BP_{CARIACO–HULU}$

Table 3
Modelled results for the data shown in Fig. 3, from the levels A5 + 6 to A2 at Fumane. These results are obtained from the Bayesian modeling via comparison with the Cariaco Basin ^{14}C record of Hughen et al. (2006) and the Hulu Cave $\delta^{18}O$–U/Th age model, as discussed in the text. Compared ages are rounded to the nearest 10.

Sequence Grotta di Fumane	Comparison age (Cariaco:Hulu) BP (68.2% prob.)		Comparison age (Cariaco:Hulu) BP (95.4% prob.)	
	From	To	From	To
Boundary A5 + A6	44,200	43,640	44,820	43,310
Phase A5 + A6 Mousterian				
OxA-17566	44,010	43,550	44,350	43,260
OxA-17567	43,980	43,580	44,190	43,290
OxA-17568	43,980	43,570	44,190	43,290
Boundary start A5	43,820	43,410	44,020	43,220
Phase A5 Mousterian				
OxA-17980	43,640	43,220	43,900	43,070
OxA-X-2275-45	43,600	43,250	43,880	43,130
Boundary A5-A4	43,580	42,980	43,910	42,240
Phase A4 Uluzzian				
Boundary A4-A3	42,910	41,280	43,370	40,704
Phase A3 Uluzzian				
Boundary A3-A2	41,200	40,450	41,930	40250
Phase A2 Proto Aurignacian				
OxA-17569	40,810	40,300	41,130	39,790
OxA-17570	40,690	40,160	40,880	39,510
OxA-19584	40,870	40,280	41,230	39,770
OxA-19414	40,410	39,770	40,610	39,250
OxA-19412	40,620	40,020	40,810	39,510
Boundary A2-A1	40,280	39,440	40,510	38,910


NGRIP GICC05 δ18O
-35
-40
-45
CI age (DeVivo, Pyle)
12
11
10
9
8
7
6 5
4 3
OxCal v4.0.5 Bronk Ramsey (2007): r:20 Cariaco vs Hulu (Hughen et al 2006)
GROTTA DI FUMANE : THIS PAPER
Boundary End
Phase D1e
Boundary D1d-D1e
OxA-17571 (96.3)
Phase D1d Gravettian
Boundary D3c-D1d
Phase D3c
Boundary D3a-D3c
Phase D3a
Boundary D3ba-D3a
OxA-17981 (105.6)
Phase D3balpha Aurignacian
Boundary A1-D3ba
Phase A1 Aurignacian
Boundary A2-A1
OxA-19412 (110.9)
OxA-19414 (53.0)
OxA-19584 (92.5)
OxA-17570 (113.9)
OxA-17569 (101.7)
Phase A2 Proto Aurignacian
Boundary A3-A2
Phase A3 Uluzzian
Boundary A4-A3
Phase A4 Uluzzian
Boundary A5-A4
OxA-X-2275-45 (40.7)
OxA-17980 (115.3)
Phase A5 Mousterian
Boundary start A5
OxA-17568 (98.5)
OxA-17567 (98.6)
OxA-17566 (115.3)
Phase A5+A6 Mousterian
Boundary A5+A6
Sequence Grotta di Fumane (Amodel 81.5)
SITES SEALED BY CI TEPHRA (Giaccio et al.)
OxA-5174
Gd-2354
Phase Temnata 14 Proto-Aurignacian
GIN-8025
LE-5271
GrN-22277
GrA-13301
GrA-13293
GrA-18053
Phase Kostenki 14 Cultural layer IVa
UtC-
Phase Paglicci Proto-Aurignacian
F-107
GrN-13985
F-105
CAMS-4622
F-72
F-71
Phase Castelcivita Proto-Aurignacian
F-108
Phase Serino Proto-Aurignacian
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
Modelled date (BP)

but with the other dates added this boundary shifts earlier to 42,000–40,900 $BP_{CARIACO-HULU}$ (at 68.2% prob.). The results overall suggest that these non-ABOx ages may be reliable because they fit statistically within the age model. Further dating work on bone and charcoal samples from throughout the sequence is currently being undertaken, and additional precision is expected to resolve the chronometric modeling more precisely. It is a significant improvement already, however, compared with the previous chronology.

As mentioned previously, Giaccio et al. (2006) have suggested that the often young and variable radiocarbon determinations obtained from Middle to Upper Palaeolithic sites in Italy might be caused by large fluctuations in radiocarbon production. Conard and Bolus (2003) invoked similar variations to explain the distribution of radiocarbon dates from sites in the Swabian Jura, such as Geißenklösterle and Höhle Fels. We are obtaining new dates from both German sites at present to test this proposition further. Pyle et al. (2006) have invoked production variations in ^{14}C to explain the variable ages at Kostenki in Russia where radiocarbon ages of 32,000 BP underlie the CI. Giaccio et al. (2006) found wide variations in radiocarbon ages obtained from a marine core in the Tyrrhenian Sea, which in their view appear to show large production pulses in ^{14}C at around the time of the CI deposition and the Laschamp Geomagnetic Excursion (~40–42 ka cal BP). Whilst there is a demonstrable ^{14}C production increase around the period of the Laschamp event it is questionable whether it is as large as that claimed by Giaccio et al. (2006) based on the evidence from this core. No such significant variations are documented through this period in the Cariaco Basin record of Hughen et al. (2006), for instance. Duplicating the data from the Tyrrhenian core is required to add strength to the production increase explanation. Equally, it would be interesting to consider re-dating some of the archaeological charcoal samples from the sites in the south of Italy, which contain the CI eruptives, as well as geological sites sealed by ash-fall and outlined in Giaccio et al. (2006). Our hunch is that the application of methods such as ABOx–SC might result in different and more consistent results. An AMS date we have recently obtained from Kostenki 14 (Markina Gora; "Cultural layer in volcanic ash") offers an interesting preliminary glimpse into this. A sample of charcoal obtained from a hearth and pre-treated using the ABOx–SC method yielded a result of 35,080 ± 240 BP (OxA-19021). This determination comes from a level dominated by archaeological lenses about 1 m in diameter that were separated from one another and sealed by pure volcanic glass (Sinitsyn, 2003). This volcanic glass has been identified as the CI tephra (Pyle et al., 2006). The level was previously dated at 32,420 ± 440 BP (GrA-18053) and below it in Cultural level IVa are three further determinations of about the same age (32.0–33.3 ka BP) (Hoffecker et al., 2008). The suspicion must be that these are simply charcoal samples not fully decontaminated. The new Kostenki result yields a comparison age of 40,840–39,990$_{CARIACO-HULU}$BP (at 77.5% prob.) and 39,700–39,310$_{CARIACO-HULU}$BP (at 17.9% prob.) (Fig. 4). This is entirely consistent with the age of the CI, as shown in Fig. 4, providing further evidence that suggests pre-treatment chemistry is the significant influence on the reliability of the current *corpus* of age determinations from the site, rather like Fumane. Further work at the site of Kostenki 14 is underway.

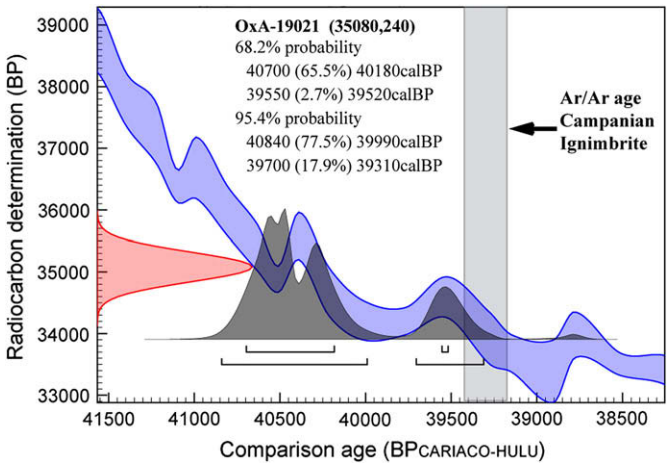


Fig. 4. Comparison age for the new ABOx–SC determination obtained from the site of Kostenki, Russia. The result is compared against the Cariaco Basin data of Hughen et al. (2006) (see caption for Fig. 3 and the text for details).

8. Conclusions

Our new ABOx–SC series shows that the previous chronology from the important site of the Grotta di Fumane is dominated by radiocarbon measurements that are erroneously young, but they also show that there are some samples of charcoal, mostly <30 ka BP, which appear to be less contaminated than others and which produce statistically identical results regardless of pre-treatment chemistry. This mirrors results from other sites in Malaysia, Europe and the Palaeolithic of the Mediterranean (Higham et al., 2008; Brock and Higham, in press). A revised chronology, based on the ABOx–SC series, discloses a significantly different chronology from the previous determinations. The results are consistent with the ages inferred for sites containing similar Middle to Upper Palaeolithic industries to the south of the Italian peninsula. These are now widely recognized as dating to before the deposition of the CI tephra at 39.3 ka yr BP. Taken together, the results suggest a greater consistency and contemporaneity in the ages of sites in both northern and southern Italy dating between 35 and 45 ka BP, but more careful dating work is required to add further confidence to this scenario.

Some workers have observed that charcoal samples generally provide older and less temporally varied radiocarbon ages compared with bone (eg. Jöris et al., 2003) and, therefore, may be preferred over the latter material. This study demonstrates that erroneous radiocarbon determinations of charcoal are perhaps more common than previously thought within this period of the European Palaeolithic. Wider application of ABOx–SC techniques for dating archaeological charcoals from this period, or, perhaps, the newer HyPy method (Ascough et al., in press), are clearly warranted if we are to build the types of chronometric frameworks that are required to understand more fully the Middle to Upper Palaeolithic transition and its spatio-temporal variation. Further methodological work is required, however. The ABOx–SC method is rigorous but very harsh and large amounts (typically >100 mg) of well-preserved charcoal are required for successful AMS dating.

Fig. 3. Bayesian model for the Fumane sequence produced using OxCal 4.0 (Bronk Ramsey, 2001). The radiocarbon ages are compared against the Cariaco Basin ^{14}C record of Hughen et al. (2006) consisting of a radiocarbon dated sediment core calendrically pinned using an age model derived from the Hulu Cave, China (Wang et al., 2001). The Fumane model is shown in the upper part of the figure and is based on the series of separate excavated phases which are divided by boundaries. Individual radiocarbon likelihoods are shown by the light shaded distributions, whilst the darker outlines represent posterior probability distributions. The Fumane radiocarbon dates include only those derived in this paper using ABOx–SC. The data from Fumane are compared with determinations in the lower section of the figure, which are those from the other sites summarised in Giaccio et al. (2006) that contain archaeological assemblages sealed by the CI tephra. Note that these ages are all later than the CI age, when they ought to be older since the samples dated were in contexts sealed beneath the tephra. The CI is given the Ar/Ar ash age of De Vivo et al. (2001), recommended by Pyle et al. (2006). The ages are compared with the GICC05 $\delta^{18}O$ record, with Greenland interstadials numbered where relevant (data from Andersen et al., 2006; Svensson et al., 2006, 2008).

Brock and Higham (in press) found failure rates were high in some cases because of the small amounts of charcoal available and its poor preservation state. Structural characterisation of the charcoal prior to dating is likely to be increasingly important to understand the most appropriate chemical treatments, but at present the variable influences of chemical preparation methods on the charcoal substrate and on the continuum of charred organic matter are not well-established. Some work has been, and is being undertaken (eg Alon et al., 2002; Cohen-Ofri et al., 2006; Bird et al., 2008; Ascough et al., in press; Rebollo et al., in press) on charcoal and environmental black carbon of different ages and from different locations, using analytical techniques designed to characterise more precisely the archaeological materials destined for radiocarbon dating. A combination of improved analytical chemistry and pre-treatment methods will further improve the routine radiocarbon dating of Palaeolithic charcoal.

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