Testing the ABOx-SC method: Dating known-age charcoals associated with the Campanian Ignimbrite

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ABSTRACT

Over the past decade several studies have shown the improvements to radiocarbon chronologies that arise when Acid Base Oxidation-Stepped Combustion (ABOX-SC, Bird et al., 1999) pretreatment methods are applied to the dating of charcoal thought to be >30 ka BP. However, few studies have examined whether the use of ABOx-SC produces dates that are not only older, but accurate on known-age charcoal samples that could not be decontaminated using the routine Acid–Base–Acid (ABA) pretreatment protocol. In this study we date 9 charcoal fragments found below the Campanian Ignimbrite (CI) tephra layer, dated by 40Ar/39Ar to 39,230 ± 45 years (De Vivo et al., 2001; Rolandi et al., 2003), from three Palaeolithic sites. When treated with the ABOx-SC pretreatment protocol, the radiocarbon dates provide an accurate terminus post quem for the CI. In contrast, the ABA protocol consistently underestimates the age of the tephra. These results serve as a warning against the use of consistency as an indicator for reliability, demonstrate that the routine ABA method is not sufficient to decontaminate charcoal samples from sites of Palaeolithic age, and show that ABOx-SC produces not only older, but accurate age estimates.

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1. Introduction

1.1. Background

Over the last decade it has become increasingly apparent that the routine pretreatment protocol used to clean charcoal (Acid–Base–Acid, ABA) prior to radiocarbon dating does not always remove sufficient contamination to produce reliable dates for material beyond c. 30 ka BP. There are now numerous examples in the literature. For example, at the Grotta di Fumane in Italy, ages of charcoal fragments from single hearth features span nearly 10 ka (Peresani et al., 2008). In Australia a so-called “radiocarbon barrier” has been identified where charcoal dates appeared to reach a limit at around 40 ka BP while alternative OSL chronologies continue to increase in age (Roberts et al., 1994; Chappell et al., 1996). In contrast, there has been a perception within the archaeological community that charcoal produces reliable dates, where stratigraphic integrity can be maintained, because it is relatively inert and not susceptible to contamination. As a result, charcoal dates have often been favoured over those on bone (Joris et al., 2003).

However, charcoal can be lost from the burial environment through photo (Skjemstad et al., 1996) or chemical (Haumaier and Zech, 1995; Cohen-Ofri et al., 2006, 2007; Rebollo et al., 2008; Braadbaart et al., 2009; Ascough et al., 2011) oxidation processes that may be microbiologically mediated (Bird et al., 2002, 2008; Ascough et al., 2010a). Moreover, charcoal can readily adsorb a range of chemical contaminants, especially from the depositional environment (Zackrisson et al., 1996; Cornelissen et al., 2005). Humic acids, for example, can be water-soluble and move easily through the sediment column. Degraded, partially oxidised charcoal is comparatively rich in carboxylate groups and is therefore hydrophilic (Cohen-Ofri et al., 2007), and likely to adsorb carboxylate rich humic substances (Rebollo et al., 2008) which may be of a different 14C age than charcoal from the same sedimentary horizon.

In these cases, the age of Pleistocene samples in particular are likely to be severely underestimated, since the addition of just 1% modern contamination to a sample of >60 ka BP will produce an age of ~37 ka BP. These observations, coupled with the intense...
archaeological interest in the biological and technological transformations that occurred between 30 and 50 ka BP across the world, have stimulated the development of new pretreatment protocols (Higham, 2011).

The ABA pretreatment consists of a series of weak acid and base washes designed to remove carbonates and humic acids respectively. ABOx-SC, developed by Bird and Grocke (1997) and Bird et al. (1999), combines this concept with others taken from the field of Black Carbon research. It aims to select the charcoal fraction most resistant to oxidation and so least susceptible to alteration and contamination in the burial environment, a component known as Oxidation Resistant Elemental Carbon (OREC). Following concentrated acid and base washes, acidified potassium dichromate is used to oxidise the charcoal before any remaining labile components are removed during a low temperature combustion step.

The effect of ABOx-SC is significant. Dates on charcoal pretreated with ABA and ABOx-SC do not always differ beyond 30 ka BP. Where they do, the latter is usually older, and the difference may be up to several thousand years (Bird et al., 1999; Turney et al., 2001a, b; Santos et al., 2003; Higham et al., 2006, 2009; Douka et al., 2010; but see Rebollo et al., 2011). As the effect of young contamination is greater than ancient contamination, dates produced by the ABOx-SC technique are regarded as more reliable (Jöris and Street, 2008).

Unfortunately, comparisons with independent chronologies are rare, and it is difficult to assess whether the older ages produced by the new method are accurate. Moreover, OREC is defined operationally as the residue remaining after ABOx-SC treatment (Bird and Grocke, 1997), and it is not yet fully understood how OREC relates to the original charcoal. Until such an understanding is obtained, it is imperative that the accuracy of the technique is established with known-age samples.

Turney et al. (2001a) and Bird et al. (2003) compared ABOx-SC dates to chronologies produced by OSL and ESR, but neither demonstrated that the ABA method was unable to remove contamination. Douka et al. (2010) demonstrated that charcoal pretreated with the ABOx-SC method produced an accurate age in comparison to the Campanian Ignimbrite (CI) layer at the site, whereas ABA did not. However, only a single charcoal fragment was dated. As a result, the reliability of the protocol is currently only established by the larger number of studies which have demonstrated that ABOx-SC produces dates that are stratigraphically consistent (Turney et al., 2001a; Bird et al., 2003; Higham et al., 2006, 2009). Whilst reassuring, these studies cannot identify systematic offsets.

This paper assesses the accuracy of the ABOx-SC method as used at the Oxford Radiocarbon Accelerator Unit (ORAU), first by dating charcoal standards to assess the laboratory pretreatment blank, and second by dating charcoal closely associated with the CI tephra.

1.2. The Campanian Ignimbrite (CI)

With visible deposits stretching from the Mediterranean to Russia, the CI and its related ash deposit (V-5 in marine deposits) is thought to have resulted from one of the largest explosive volcanic events of the Late Quaternary (Fedele et al., 2008). The precise location of the vent is not known, but it is thought to have been located in the Phlegraean Fields, in the vicinity of Naples, Italy (Barberi et al., 1991). Close to its source, the tephra has a distinctive two-phase structure with pyroclastic flow units situated above a pumice layer (Giaccio et al., 2008). In more distal areas the diagnostic major and trace element composition of the glass shards in the ash have been used for correlation to proximal deposits (Pyle et al., 2006; Giaccio et al., 2008).

The tephra is found at the start of Heinrich event 4 (H4) (Watts et al., 1996; Paterne et al., 1999; Ton-That et al., 2001; Margari et al., 2009) and at the end of, or shortly after, the Laschamp event (Ton-That et al., 2001; Giaccio et al., 2006). The Laschamp geomagnetic excursion is dated to 40,650 ± 425 b1950 by 40Ar/39Ar on lava flows (Singer et al., 2009) and the maxima of the 10Be peak in NGRIP occurs at 41,200 ± 800 b1950 GICC05, although it spans around 1000 years and most of GI10 (Svensson et al., 2006). The stadial between GI8 and 9 in which H4 occurs is dated between 38,170 ± 725 b1950 and 39,810 ± 790 b1950 GICC05 in the NGRIP record (Wolfli et al., 2010; Andersen et al., 2006).

It is unlikely that this event occurred simultaneously in all regions across the Northern Hemisphere, and to be sure should be taken until synchronicity is established. However, the age of the event in NGRIP is in agreement with its occurrence in the Hulu speleothem (Wang et al., 2001). Furthermore, ice rafted debris associated with H4 found in the Alboran Sea in the western Mediterranean basin coincides with the start of a decline in arboreal pollen related with terrestrial stadial conditions (Sánchez Goñi et al., 2002; Sepulchre et al., 2007). Given its close geographic and latitudinal proximity, it is possible that stadial conditions in southern Italy occurred at a similar time.

This stratigraphic correlation is in excellent agreement with an age of 39,230 ± 55 years (De Vivo et al., 2001), equivalent to 39,180 ± 55 b1950, produced from an average of 36 40Ar/39Ar measurements on sanidine crystals from twelve proximal deposits of the CI. Although it is possible that xenocrysts were present in some samples, with the exception of two samples excluded from the average, no evidence for them was observed by De Vivo et al. (2001). Earlier 40Ar/39Ar measurements by Ton-That et al. (2001) on a distal marine core and Watts et al. (1996) on a lacustrine deposit suffer from large error ranges, and in the case of the latter, incomplete publication. As a result, the average provided by De Vivo et al. (2001) is favoured by most researchers as the most reliable age estimate of the CI eruption (e.g. Pyle et al., 2006). Eight further proximal samples of the ignimbrite were 40Ar/39Ar dated by Rolandi et al. (2003) and were in agreement with the estimate of De Vivo et al. (2001). When incorporated into the weighted average the date remains unchanged and the error decreases to just 45 years at 1 sigma.

Fedele et al. (2008) suggest that a sulphate peak in the GISP2 core at 40,012 b1950 GISP2 may have been caused by the eruption. However, in their preliminary study of tephra within NGRIP, Davies et al. (2010) found that tephra shards were rarely found in the same location as spikes in sulphate concentration, and the CI was not identified. Until identified, this age must therefore be treated with some caution.

Here, the weighted average of dates from De Vivo et al. (2001) and Rolandi et al. (2003) will be used, providing an age estimation of 39,180 ± 45 b1950. The CI and its tephra is thus an excellent chronos stratigraphic marker with which to test the accuracy of the ABOx-SC method. Indeed, Giaccio et al. (2006), Blockley et al. (2008), Higham et al. (2009) and Douka et al. (2010) have all employed it to demonstrate that radiocarbon dates beyond 30 ka BP are often underestimates of their true age.
2. Materials

Two sets of charcoal have been dated as part of this study (Table 1). A modern sample of Buddleia charcoal from Oxfordshire, collected and charred in 2002 has been used to assess whether fossil carbon is added in the laboratory, whilst an ancient standard from Maninjau, Indonesia, has been used to assess whether young carbon is added (Brock et al., 2010).

The second group of samples consists of archaeological charcoal found beneath and within the CI tephra in the open-air lacustrine setting of Serino, Italy, the cave site of Castelcivita, Italy, and the open-air loess sequence in Kostenki 14, Russia (Fig. 1). All samples were treated with both the ABA and ABOx-SC pretreatment protocols.

2.1. Group 1: standards for measuring the laboratory background

Between August 2009 and July 2010, the Buddleia standard charcoal was dated 47 times using the ABA protocol at the ORAU. The amount of charcoal surviving pretreatment (the pretreatment yield) ranged from 15 to 210 mg (% yield 85 ± 9; δ¹³C − 28 ± 1‰, δ¹⁴C 73 ± 6). During the same period, the charcoal was treated twice with the ABOx-SC protocol (δ¹³C − 29 ± 1‰, δ¹⁴C 88‰).

The Maninjau charcoal was sampled from charred trees, found in their growth position, within a tephra layer in the Maninjau caldera, Sumatra (Alloway et al., 2004). Glass shards within the flow deposit have been dated using Fission Track to 50 kya (fl). During the same period, the charcoal was treated twice with the ABOx-SC protocol (δ¹³C − 73 ± 6). A further 13 had been treated with the ABOx-SC protocol, whose pretreatment yields ranged from 12 to 100 mg (% yield 57 ± 13; δ¹³C − 24 ± 1‰, δ¹⁴C 91 ± 6).

2.2. Group 2: archaeological charcoal found beneath and within the CI tephra

2.2.1. Serino

Serino (40.866N 14.873E, Italy) is an open-air site 50 km east of the Phlegrean Fields, within the immediate dispersion area of both the CI flow deposits and ash fall (Fig. 1). Here, a single short-term Proto-Aurignacian occupation level in silty sediments was found beneath nearly 3 m of tephra whose two-phase structure is diagnostic of the CI (Accorsi et al., 1979; Giaccio et al., 2008). The occupation level has been associated with a single conventional radiocarbon measurement on charcoal at 31,200 ± 650 BP (F-108) (Fig. 2) (Azzi and Gulisano, 1979; Accorsi et al., 1979). We obtained five samples for dating, but did not survive the ABOx-SC treatment. These were found within a single hearth feature and therefore provide an excellent test for consistency (Fig. 3A).

2.2.2. Castelcivita

Castelcivita (40.495N 1515.237E, Italy) is a cave in central Campania containing a sequence of Mousterian, Ulluzzian and Proto-Aurignacian levels in clastic sediments. These are found at the base of a debris cone that is sealed by a volcanic deposit (Gambassini, 1997) with the distinctive two-phase structure of the CI (Glacio et al., 2008). Charcoal has not been dated at this site and the current radiocarbon chronology on layers immediately below...

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Table 1

A list of charcoal fragments dated in the study, with published age estimates. >39,230 ± 45 years refers to samples found beneath the CI.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Context</th>
<th>Species</th>
<th>Existing age estimate</th>
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</thead>
<tbody>
<tr>
<td>Suite 1: Laboratory standards</td>
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<tr>
<td>Owen Buddleia</td>
<td>N/A</td>
<td>N/A</td>
<td>Buddleia</td>
<td>2002 AD</td>
</tr>
<tr>
<td>Maninjau</td>
<td>N/A</td>
<td>N/A</td>
<td>—</td>
<td>Fission Track: 50,000 ± 3,000 years Radiocarbon, no pretreatment OxA-V-2190-49 53,400 ± 1,400 BP a Radiocarbon, ABA: Wk-13370 51,100 ± 3,200 BP b Wk-5370 &gt; 40,000 BP c NZA-8196 &gt; 47,000 BP d Radiocarbon, ABOx-SC: ANUA-13404/14112 52,300 ± 2,000 BP e</td>
</tr>
</tbody>
</table>

| Suite 2: Charcoal found beneath the CI |
| P25106 | Serino | H15, spit 7, 8, 9 | Pinus sylvestris/Pinus mugo Turra – Latewood | >39,230 ± 55 years |
| P25107 | Serino | H15, spit 7, 8, 9 | Pinus sylvestris/Pinus mugo Turra – Latewood | >39,230 ± 55 years |
| P25108 | Serino | H15, spit 7, 8, 9 | Pinus sylvestris/Pinus mugo Turra – Latewood | >39,230 ± 55 years |
| P27629 | Serino | H15, spit 7, 8, 9 | Pinus sylvestris/Pinus mugo Turra – Latewood | >39,230 ± 55 years |
| P27470 | Castelcivita | RSA, spit11, square H14 | c.f. Hex aquilorum | >39,230 ± 55 years |
| P25113 | Kostenki 14 | Cultural level IVa | Picea | GrA-22777 33,280 ± 650/−600 BP a |
| P25114 | Kostenki 14 | Cultural level IVa | Picea | Gra-31084 34,200 ± 300/−270 BP b |
| P25115 | Kostenki 14 | Cultural level IVa | Picea | GrA-13293 32,180 ± 450/−420 BP c |

a Ascough et al. (2009).
b Alloway et al. (2004).
c Anikovich et al. (2007).
the CI tephra is based on a series of burnt bones, which under-estimate the age of the tephra (Fig. 2) (Gambassini, 1997).

We attempted to date four charcoal samples. Unfortunately, all but one failed to yield enough material to produce a date using the ABA protocol. The only sample to be dated was from the uppermost Uluzzian deposit (level RSA), from the upper part of spit 11 which contained evidence of hearths (Fig. 3B) (Gambassini, 1997).

2.2.3. Kostenki 14 (Markina gora)

Kostenki 14 (51.39N 39.04E, Russia) is one of a large number of open-air sites on the terraces of the River Don, containing Gravettian, Aurignacian and earlier Upper Palaeolithic industries (Sinitsyn, 2003; Haesaerts et al., 2004; Sinitsyn and Hofacker, 2006). In Kostenki 14, a discontinuous tephra layer of 2 –>25 cm occurs in loamy deposits between the upper and lower humic beds (Fig. 3C). Both humic beds and the tephra level itself contain archaeological remains. Much of the variability in the tephra’s thickness is due to slope processes and periglacial phenomena such as cryoturbation, and evidence of redeposition has been observed by one of us (P.H.) recently in the field. This, however, must have occurred shortly after the initial tephra fall due to the angle of the deposition slope. The small size of the glass shards implies that they occurred shortly after the initial tephra fall due to the angle of the deposition slope. The small size of the glass shards implies that they occurred shortly after the initial tephra fall due to the angle of the deposition slope.

The current radiocarbon chronology of the cultural layer IVa and the tephra layer at Kostenki 14 is based on both AMS and conventional measurements of charcoal. Several, although not all, dates on charcoal are again underestimated of the predicted age (Fig. 2) (Haesaerts et al., 2004; Anikovich et al., 2007). One pertinent exception is an ABOx-SC measurement of a charcoal fragment (Sinitsyn, 2004). The Laschamp event is event within a fossil soil (FS in Fig. 3c) below cultural level IVa and the tephra deposit (Gernik and Pyle et al., 2006). On the basis of the major and trace element composition of the shards, Pyle et al. (2006) suggest that the tephra originates from the Campanian Region and can be correlated with the CI, as was first suggested by Melekestsev et al. (1984). The Laschamp event is event within a fossil soil (FS in Fig. 3c) below cultural level IVa and the tephra deposit (Gernik and Guskova, 2002), providing an additional stratigraphic marker. OSL dates exist, but their large errors mean that they are of little use in constraining the age of the tephra.

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3. Methods

The ABA and ABOx-SC protocols as used in Oxford are fully described in Brock et al. (2010). Briefly, the ABA protocol consists of treatment in 1 M HCl at 80 °C for 20 min, or until reaction is complete. The sample is then immersed in 0.2 M NaOH at 80 °C for 20 min, during which time the alkali is replaced until the solution remains colourless, before a final rinse in 1 M HCl at 80 °C for 1 h. The sample is rinsed three times with ultrapure water after each treatment and the charcoal is freeze-dried when the pretreatment is complete.

The ABOx-SC protocol involves treatment at room temperature in 6 M HCl for 1 h, followed by 2 M NaOH for 30 min, during which the sample is replaced until it remains colourless. The charcoal is subsequently oxidised in H2SO4/K2Cr2O7 (2 M/0.1 M) at 60 °C in a sealed tube for 20 h. As with the ABA protocol, the charcoal is washed three times with ultrapure water between each treatment. After freeze-drying, the charcoal is loaded into a quartz tube separated from CuO wire by quartz wool (both previously baked at 850 °C for 8 h), and heated under vacuum to 630 °C for 2 h.

The residue from both treatments is combusted in a CHN elemental analyser (Carlo-Erba NA, 2000) coupled to a gas source isotope ratio mass spectrometer (Sercon 20/20), enabling online measurement of carbon elemental ratios and stable isotopes (Brock et al., 2010). CO2 gas was collected and reduced with H2 over an Fe powder catalyst to produce graphite (Dee and Kronenberg, 2000) prior to measurement by AMS (Brock et al., 2004).

To enable comparison to the 40Ar/39Ar age, radiocarbon dates have been calibrated against the IntCal09 curve (Reimer et al., 2009). Calibration and Bayesian modelling has been undertaken in OxCal version 4.1 (Bronk Ramsey, 2009a). All models have assigned each date a prior probability of 5% of being an outlier within the General l-type Outlier Model (Bronk Ramsey, 2009b).

The IntCal09 curve is preliminary in nature, and is based on marine records beyond 26 ka cal BP (Reimer et al., 2009). Around the time of the CI, data from the Cariaco basin dominates (Reimer et al., 2009). Marine records are buffered from short-term fluctuations in 14C concentration, but strongly reflect changes in oceanic upwelling. In some speleothem (Beck et al., 2001) and planktonic marine records (Voelker et al., 2000; Hajdas et al., 2011), not included in the IntCal09 curve, fluctuations in 14C levels equivalent to more than 10 ka years are observed around 40 ka b1950. Whilst laboratory contamination caused the age reversal seen in Beck et al. (2001) (Hoffmann et al., 2010), no such explanation has been found to explain the fluctuations in the marine records. These have led to concern that young radiocarbon dates found below the CI are caused by uncertainties in the calibration curve (Conard and Bolus, 2003; Fedele et al., 2003, 2008; Giaccio et al., 2006).

Two factors have been used to explain these reversals: a change in the production rate of 14C caused by the Laschamp geomagnetic excursion and corresponding weakening of the earth’s magnetic field (Beck et al., 2001; Hajdas et al., 2011), and a decrease in the strength of the North Atlantic Deep Water formation during North Atlantic cold events altering the marine reservoir effect (Beck et al., 2001; Kromer et al., 2004; Singarayer et al., 2008; Hajdas et al., 2011). Neither, however, could have caused fluctuations as large as those observed by Voelker et al. (2000) and Hajdas et al. (2011).
Moreover, Hoffmann et al. (2010) found no evidence for an offset between the $^{14}$C content of speleothems from the Bahamas and foraminifera from the Cariaco basin (Hughen et al., 2006) around the time of H4. Until several independent atmospheric $^{14}$C records are available, caution must be exercised when using IntCal09. However, the large fluctuations seen in some marine records remain unexplained and are unlikely to affect all records.

(Hajdas et al., 2011).
4. Results

4.1. Group 1: laboratory background

The ABA protocol does not add old carbon contamination (Fig. 4a, Table 1). When calibrated, the weighted average of the 47 measurements of the modern Buddleia charcoal is in agreement with a date of 2002 AD (Hua and Barbetti, 2004). The average laboratory uncertainty (0.0031 ± 0.0002 \(^{14}C\)) is of a similar magnitude to the variation in measurements (0.004 \(^{14}C\)), indicating that the laboratory errors are not underestimated (Table 1). Too few ABOx-SC dates are available for statistical analysis, but visual inspection of Fig. 4a suggests that they are in agreement with dates after the ABA protocol.

In contrast, small amounts of young contamination are present in the Maninjau charcoal after both ABA and ABOx-SC pretreatment protocols. The average of both sets of data is younger than the date on the untreated charcoal and the data is significantly more scattered than predicted by the laboratory uncertainty (Table 1). Too few ABOx-SC dates are available for statistical analysis, but visual inspection of Fig. 4a suggests that they are in agreement with dates after the ABA protocol.

Often a constant amount of modern carbon is added to each sample during pretreatment (Kirner et al., 1995; Schleicher et al., 1998). As a result, smaller samples will appear younger than larger samples, and a linear relationship between the inverse carbon content of a sample and its \(^{14}C\) is expected. Few small Maninjau samples exist to test whether this relationship may be appropriate. However, it is worth noting that the youngest sample, highlighted in Fig. 4b, is also one of the smallest, and it remains feasible that future work may demonstrate a sample-size dependency. In the absence of further information, this youngest sample is identified as an outlier (more than two times the inter quartile range from the median of the ABA results) and has been excluded from the analysis. Therefore a correction unrelated to sample size has been calculated.

The age of the Maninjau charcoal is not precisely known, and so only a tentative pretreatment background correction can be produced. Assuming that the untreated charcoal reflects the true age of the sample, the amount of modern carbon contamination required to produce each date has been calculated, expressed as a percentage of the total amount of carbon within each sample, and averaged. A correction of 0.14 ± 0.07% and 0.11 ± 0.06% modern carbon for the ABA and ABOx-SC protocols respectively (Table 1) will be applied tentatively for samples containing more than 10 mg carbon after pretreatment. The main impact of this correction will be to increase the error of the dates. The correction is tentative, and is not applied to any dates ascribed an OxA-number.

<table>
<thead>
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<th>Table 2</th>
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<tr>
<td>Summary statistics for the modern and ancient charcoal standards dated at ORAU between August 2008 and July 2010. % modern contamination refers to the % modern contamination required to produce the measured age, assuming that the actual age of the Maninjau charcoal is equivalent to the date on the untreated material (OxA-V-2190-49, Table 1). The weighted sample standard deviation of the modern Buddleia dates is of a similar magnitude to the average laboratory uncertainty. In contrast, the weighted sample standard deviations of both ABA and ABOx-SC pretreated aliquots of the Maninjau charcoal are more than the average laboratory uncertainty, suggesting that the error term is underestimated for ancient samples.</td>
</tr>
<tr>
<td>Standard</td>
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<td>Modern Buddleia</td>
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<td>Maninjau</td>
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Fig. 3. Composite stratigraphy of A) Serino (modified from Accorsi et al., 1979) B) Castelcivita (modified from Gambassini, 1997 and Giaccio et al., 2008) and C) Kostenki 14 with the location of the samples dated and CI ash indicated. Not to scale.
Fig. 4. Radiocarbon dates of A) Modern Buddleia and b) Maninjau charcoal standards pretreated with the ABA (grey circles) and ABOx-SC (open squares) protocols. The dashed lines in figure a represent the weighted average of the ABA measurements, and in figure b the untreated radiocarbon date (OxA-V-2190–49, Table 1). No old carbon is added to the Modern Buddleia, but young carbon is added by the ABA and ABOx-SC pretreatments to the Maninjau sample. If a constant amount of young carbon is added, a linear relationship between the inverse yield and F/C yield is observed (Fig. 4B). This is not the case here. The circled date is an outlier, defined as more than twice the inter quartile range from the median of the ABA results. All errors are shown at one sigma.

Two samples (P25107 and P27629) contained less than 50% C after both ABA and ABOx-SC pretreatment and the ABOx-SC fraction was substantially more depleted in carbon. FT-IR analysis indicated that the ABOx-SC residue of P25107 contained significant quantities of silica. In contrast, all other charcoal fragments contained more than 50% C after treatment, with ABOx-SC producing a residue richer in carbon than the ABA protocol. Despite concerns over the two low-carbon charcoal fragments, the results are consistent (Table 3).

When the dates uncorrected for pretreatment-derived carbon are considered, the ABOx-SC and ABA dates are statistically different for all samples except P25107, whose ABOx-SC date is imprecise (Table 3). In each case, the ABOx-SC date is older than the ABA date. When the OxA-dates are calibrated and compared to the age of the CI, none of the ten ABA dates are younger at 95.4% probability (Fig. 5A). In contrast, seven of the ABOx-SC products predate the CI at 95.4%, and the remaining three overlap in age. Furthermore the ABOx product of P25113 is identical to the Groeningen measurement (\(\chi^2, df = 1, T = 0.8, 5\% = 3.8\)), and both are significantly younger than the ORAU ABOx-SC measurement (Table 1). Of the two Groeningen dates on charcoal sample P25114, GrN-22277 is significantly younger than the product of the ABOx-SC pretreatment (\(\chi^2, df = 1, T = 4.6, 5\% = 3.8\)). In contrast, GrA31084 is indistinguishable from the ABOx-SC product (\(\chi^2, df = 1, T = 2.4, 5\% = 3.8\)) (Table 1).

When tentatively corrected for pretreatment-derived contamination, the error on the measurements increases. However, the difference between the ABA and ABOx-SC dates is still visible. Only three ABA – ABOx-SC pairs pass a \(\chi^2\)-test (P25107, 25108 and 27560, all from Serino). All other pairs are significantly different at 95.4% probability, with the ABOx-SC sample always older than the ABA sample. The larger error ranges mean that none of the calibrated corrected ABA dates overlap with the age of the CI.

5. Discussion

To understand how these different pretreatment techniques would affect our interpretation of the age of the CI in the absence of any other information, it is possible to model the dates within OxCal (Bronk Ramsey, 2009a). All charcoal fragments were found below or within the CI, and should therefore predate it. In addition, charcoal fragments found close to the tephra were sampled in preference to those found deeper within the stratigraphy. Therefore,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Method</th>
<th>OxA Date (BP)</th>
<th>(\chi^2) test T (df = 1, 5% 3.8)</th>
<th>95% calibrated range (cal BP)</th>
<th>Yield (mg)</th>
<th>Yield (%)</th>
<th>%C</th>
<th>(\delta^{13}C)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25106</td>
<td>Serino</td>
<td>ABA</td>
<td>21315</td>
<td>32,960 ± 200</td>
<td>25.7</td>
<td>38,490–36,860</td>
<td>18.04</td>
<td>42.3</td>
<td>67.3</td>
<td>-24.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ABOx-SC</td>
<td>21869</td>
<td>34,830 ± 330</td>
<td>40,830–38,940</td>
<td>6.82</td>
<td>18.2</td>
<td>78.2</td>
<td>-23.6</td>
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<td>P25107</td>
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<td>ABA</td>
<td>22060</td>
<td>33,100 ± 450</td>
<td>1.1</td>
<td>38,810–36,710</td>
<td>4.32</td>
<td>11.6</td>
<td>45.3</td>
<td>-25.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ABOx-SC</td>
<td>22061</td>
<td>34,300 ± 1100</td>
<td>41,600–36,850</td>
<td>10.92</td>
<td>11.6</td>
<td>37.5</td>
<td>-25.3</td>
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<tr>
<td>P25108</td>
<td>Serino</td>
<td>ABA</td>
<td>21316</td>
<td>33,630 ± 230</td>
<td>5.6</td>
<td>39,020–37,530</td>
<td>20.78</td>
<td>46.5</td>
<td>61.2</td>
<td>-25.5</td>
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<tr>
<td></td>
<td></td>
<td>ABOx-SC</td>
<td>21870</td>
<td>34,530 ± 310</td>
<td>40,470–38,770</td>
<td>11.68</td>
<td>25.4</td>
<td>74.3</td>
<td>-25.5</td>
<td></td>
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<tr>
<td>P27560</td>
<td>Serino</td>
<td>ABA</td>
<td>23066</td>
<td>33,650 ± 320</td>
<td>5.4</td>
<td>39,320–37,340</td>
<td>20.39</td>
<td>42.4</td>
<td>60.8</td>
<td>-25.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ABOx-SC</td>
<td>22626</td>
<td>34,760 ± 360</td>
<td>40,800–38,870</td>
<td>20.80</td>
<td>76</td>
<td>25.2</td>
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<td></td>
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<tr>
<td>P27629</td>
<td>Serino</td>
<td>ABA</td>
<td>22663</td>
<td>32,700 ± 340</td>
<td>9.5</td>
<td>38,450–36,600</td>
<td>8.2</td>
<td>16.5</td>
<td>50.6</td>
<td>-25.9</td>
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<tr>
<td></td>
<td></td>
<td>ABOx-SC</td>
<td>22583</td>
<td>34,400 ± 450</td>
<td>40,740–38,540</td>
<td>8.6</td>
<td>12.1</td>
<td>33.3</td>
<td>-26.3</td>
<td>Low % C</td>
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<tr>
<td>P27470</td>
<td>Castelcivita</td>
<td>ABA</td>
<td>22660</td>
<td>33,350 ± 310</td>
<td>34.1</td>
<td>38,860–37,070</td>
<td>9.16</td>
<td>9.16</td>
<td>63.7</td>
<td>-24.8</td>
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<td>36,120 ± 360</td>
<td>41,910–40,570</td>
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<td>14.2</td>
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<td>P22352</td>
<td>Kostenki 14</td>
<td>ABA</td>
<td>19787</td>
<td>33,220 ± 200</td>
<td>36.2</td>
<td>38,680–37,160</td>
<td>8.54</td>
<td>23.1</td>
<td>52.8</td>
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<td></td>
<td>ABOx-SC</td>
<td>19021</td>
<td>35,080 ± 240</td>
<td>40,840–39,210</td>
<td>3.16</td>
<td>N/A</td>
<td>68.6</td>
<td>-24.1</td>
<td>Douka et al. (2010)</td>
</tr>
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<td>Kostenki 14</td>
<td>ABA</td>
<td>21317</td>
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<td>26.0</td>
<td>38,490–36,850</td>
<td>15.08</td>
<td>33.6</td>
<td>59.9</td>
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<td></td>
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<td>21871</td>
<td>34,900 ± 340</td>
<td>40,920–38,990</td>
<td>6.01</td>
<td>8.2</td>
<td>73.3</td>
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<td>21318</td>
<td>32,610 ± 210</td>
<td>16.7</td>
<td>37,970–36,560</td>
<td>11.08</td>
<td>33</td>
<td>60.5</td>
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<td></td>
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<td>21872</td>
<td>34,240 ± 360</td>
<td>40,410–38,510</td>
<td>8.3</td>
<td>15.5</td>
<td>72.5</td>
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<td>P25115</td>
<td>Kostenki 14</td>
<td>ABA</td>
<td>21319</td>
<td>32,660 ± 200</td>
<td>47.8</td>
<td>38,040–36,590</td>
<td>13.4</td>
<td>32.9</td>
<td>61.9</td>
<td>-23.4</td>
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<td></td>
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<td>ABOx-SC</td>
<td>21873</td>
<td>35,270 ± 350</td>
<td>41,270–39,370</td>
<td>8.19</td>
<td>14.8</td>
<td>78</td>
<td>-23.2</td>
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</tbody>
</table>
when the dates are placed within a Phase with a Tau_Boundary at the base, the upper boundary will provide a terminus post quem for the CI. When all the ABOx-SC dates are placed within a Phase, this age is estimated at 40,200 ± 38,740 cal BP at 95% probability and is consistent with the 40Ar/39Ar estimate. Dates of the ORAU ABA products predict an age of just 37,900 ± 36,650 cal BP, underestimating the age of the tephra by as much as two millennia (Fig. 5B).

Fig. 5C and D represent the results with the pretreatment blank subtracted. Despite the larger error ranges of the dates, an age difference still exists when the dates are modelled as phases in OxCal. The corrected ABOx-SC dates now predict that the CI dates to 41,110–39,710 cal BP, whilst the corrected ABA dates suggest it dates to 38,870–37,460 cal BP. Although nine of the dates of the ABA products overlap with the age of the CI, when treated as a group they still underestimate the age of the tephra.

The consistency with which the ABA pretreatment underestimates the age of the CI is concerning; no outliers were identified when the ABA dates were modelled in Fig. 5B and D. The consistency of a group of radiocarbon dates is often used to assess the reliability of a dataset. For example, Pettitt et al. (2003) developed a rigorous and comprehensive set of criteria for the evaluation of radiocarbon dates beyond two half lives. For the highest degree of certainty, they recommend that five consistent dates should be...
obtained from a single context. Likewise, in their “chronometric hygiene” criteria Spriggs and Anderson (1993) argue that confidence in the age of an archaeological culture may be increased where dates from multiple deposits are in agreement.

Without ABOx-SC, the ABA dates obtained in this study would have strongly suggested that the $^{40}$Ar/$^{39}$Ar age for the CI was incorrect. This would have implications for the timing of the arid phase associated with H4 in south eastern Europe and the arrival of modern humans in Italy (Fedele et al., 2008). Alternatively, the dates could have lead to increased doubt over the reliability of the IntCal09 calibration curve during H4 and around the time of the Laschamp geomagnetic excursion. Such doubts would lend support to explanations like the “Middle Palaeolithic Dating Anomaly” proposed by Conard and Bolus (2003) to explain inconsistent dates from Palaeolithic horizons from Germany. They may also have implications for models of ocean circulation.

The reason for the consistency of the ABA dates and their offset from the ABOx-SC results we have obtained is unclear. Such a constant offset between two the protocols is not always observed (Higham et al., 2009). It is possible that it is just coincidence that these charcoals, from three very different depositional environments, contained unremoved contamination of a similar amount and age.

An alternative hypothesis may relate to the amount of carbon that is added to different types of charcoal during pretreatment, although this also requires a high level of coincidence. Hatté et al. (2001) found that atmospheric carbon dissolved during the base rinse was added to wood during ABA pretreatment. They suggested that cellulose acted as an ion-exchange resin, and carbonate ions that became ionically bound to the electropositive groups of cellulose could not be displaced by the final hydrochloric acid wash. Instead, they found that the sulphate ions from sulphuric acid, with their higher ionic affinity, could displace the adsorbed carbonate ions. Not all studies have shown that carbon is added to samples during ABA pretreatment (Souton and Magana, 2010), possibly because Hatté et al. (2001) used a pretreatment designed to maximise the addition of carbonate ions during the base wash. However, the ABA pretreatment at ORAU does appear to add a small amount of carbon to the Maninjau charcoal. In contrast to Hatté et al. (2001) findings, although the scatter in dates appears to be reduced by the ABOx-SC protocol which employs a final sulphuric acid wash, the errors assigned by the laboratory still do not account for the observed scatter in dates.

The physical and chemical structure of charcoal is variable, and may affect the amount of carbonate that could be adsorbed. For instance, well preserved high temperature (>500 °C) charcoal is dominated by an organised phase consisting of domains of graphic sheets, whilst lower temperature and degraded charcoal contains more oxygen containing functional groups (Cohen-Ofrì et al., 2006, 2007; Ascough et al., 2010b). Structurally, porosity is also expected to differ between these groups (Bird et al., 2008; Ascough et al., 2010b). This study obtained a pretreatment back-ground correction from the well preserved, high temperature Maninjau charcoal standard. It is feasible that the pretreatment background of this sample is different to the degraded archaeological samples found below the CI tephra. Further work is clearly required to establish whether the ABA protocol adds differing quantities of carbon to charcoal fragments with different chemical and physical structures, and if necessary, how it may be removed.

6. Conclusions

This study confirms the emerging consensus that the discrepancy between radiocarbon age estimates and the $^{40}$Ar/$^{39}$Ar date for the CI is related to difficulties in removing contamination from charcoal (Blockley et al., 2008; Higham et al., 2009; Douka et al., 2010). This replaces earlier hypotheses that cited fluctuations in the calibration curve relating to the Laschamp magnetic excursion (Fedele et al., 2003, 2008; Giaccio et al., 2006). ABOx-SC does appear to effectively remove contamination from all the samples examined. The addition of a small (and in the case of the CI charcoals, unimportant) quantity of young contamination during laboratory pretreatment cannot be excluded. In this study, low-carbon contents (<5% C) and the inclusion of significant quantities of silicates did not affect the measured age. This is not always the case (e.g. Kebara Cave; Rebollo et al., 2011) and dates on such samples should be viewed with caution, particularly where the carbon content decreases significantly between the ABA and ABOx-SC protocols.

Our results show that the ABA protocol did not correctly predict the age of the CI even after correction for contamination added during pretreatment. Particularly disconcerting is the consistency with which the ABA dates underestimate the age of the tephra. It is unclear why this may be. It is possible that the ABA protocol did not effectively remove contamination from the archaeological charcoal. However, the possibility that significantly more carbon is added to degraded, as opposed to modern, charcoal during pretreatment should also be considered. The study serves as a warning against the use of consistency as a marker for reliability, where a pretreatment protocol has not been tested against known-age samples.

Acknowledgements

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