PRELIMINARY RADIOCARBON ANALYSES OF CONTEMPORANEOUS AND ARCHAEOLOGICAL WOOD FROM THE ANSANTO VALLEY (SOUTHERN ITALY)

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ABSTRACT. The Ansanto Valley (southern Italy) is characterized by hydrothermal phenomena, with volcanic gas emissions arising from some vents. In the 1st millennium BC, a sanctuary dedicated to the goddess Mephitis was built but later destroyed by landslides in the valley. During archaeological excavations in the 1950s, many items were found including wooden artifacts, preserved thanks to the imbibition and subsequent mineralization of the wood tissues due to the gas emissions. Radiocarbon dating of these objects is underway at CIRCE (Centre for Isotopic Research on Cultural and Environmental Heritage), in Caserta, Italy. Unfortunately, 2 main problems arise in dating these materials. The first is possible fossil dilution caused by the CO_2 emitted from the nearby volcanic vents, which could affect the trees of the valley and also the archaeological materials. In order to determine the magnitude of the fossil dilution in the area, ^{14}C measurements were performed on contemporaneous wood cored from 2 oak trees growing near the vents. ^{14}C values measured in these samples confirmed the presence of a strong fossil dilution in the Ansanto Valley. The second problem is the restoration that the objects underwent during the last century (mostly by using modern organic substances). To investigate suitable pretreatment procedures for removing the restoration materials from the archaeological findings, contemporaneous wood was also analyzed. The wood of trees from the Ansanto Valley and from a distant village (unaffected by the Ansanto fossil dilution) were submitted to the same restoration process applied to the archaeological artifacts, followed by an "artificial weathering" process. Some archaeological materials were also tested for the removal of restoration materials. We subjected the artificially aged trees and the archaeological samples to different chemical processes. Here, we present the results of these processes. Almost all methods turned out to be suitable for the contemporaneous wood, while the results for the archaeological samples remain uncertain. For this reason, more tests are needed, concerning the "artificial weathering," the restoration, and the chemical procedure for removing the consolidation materials.

INTRODUCTION

During archaeological excavations in the 1950s in the Ansanto Valley (southern Italy), many wooden materials were found in the sanctuary of the goddess Mephitis, preserved due to the imbibition and subsequent wood mineralization process. With these objects, other artifacts were found in the same archaeological context, dated based on archaeological considerations between the 6th and 4th centuries BC (Onorato 1960; Bottini et al. 1976; Rainini 1996, 2003, 2008). In order to have a more precise and accurate dating, we decided to radiocarbon date an aliquot of these wooden findings by accelerator mass spectrometry (AMS at the CIRCE (Centre for Isotopic Research on Cultural and Environmental Heritage) laboratory) in Caserta, Italy (Terrasi et al. 2008).

^{14}C dating of such materials is complicated by 2 factors: 1) the atmospheric characteristics of the site and 2) the restoration process applied to findings in the late 1950s. About the first point, the Ansanto Valley is an area characterized by secondary volcanism phenomena, with the emission of gases (mainly CO_2, H_2S, and N_2) from some vents (Ortolani and Pagliuca 2008). The CO_2 arising from the vents is depleted in ^{14}C due to its geological origin, and it causes depletion of the ^{14}C concentration in the local atmosphere. The depleted CO_2 alters the ^{14}C concentration in trees grown near the emit-

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ting source, yielding an older ^{14}C age than its true age, as demonstrated in various studies on volcanic emissions (Sulerzhitzky 1970; Bruns et al. 1980; Saupé et al. 1980; Pasquier-Cardin et al. 1999; Marzaioli et al. 2005; Yoshikawa et al. 2005) and pollution monitoring research (Kuc and Zimnoch 1998; Levin et al. 1989; Quarta et al. 2007; Rakowski et al. 2008; Capano et al. 2010).

The second complicating factor is the restoration of the artifacts, carried out using organic materials (e.g. glue and tannic acid), often contaminating the wood. These chemicals can alter the ^{14}C dating values towards younger results due to their modern components. It is thus important to apply the correct chemical procedure to remove these contaminants before ^{14}C measurement. Because of the historical and artistic value of the archaeological findings, just a small amount is available to sample for the analyses. For this reason, contemporaneous wood samples were analyzed, before the archaeological samples, to check the potential of restoration removal using different chemical procedures. The contemporaneous woods were reduced to conditions similar to the archaeological ones via interaction with the Ansanto gases, "artificial weathering," and restoration. Therefore, in order to determine the consistency of the fossil dilution phenomenon in the Ansanto Valley and the effectiveness of chemical pretreatments to remove the restoration materials applied to the archaeological artifacts, we designed a series of experiments using contemporaneous wood.

Some chemical differences could remain between the archaeological wood and the aged and restored contemporaneous wood, altering the chemical bonds between the wood and the restoration materials. In order to check the selected chemical procedures (already successfully tested on contemporaneous samples) on the archaeological wood, we performed tests also on a few archaeological wooden materials from the Ansanto Valley. The results of this preliminary phase of site characterization and methodology testing are presented in this paper.

STUDY AREAS

The Ansanto Valley (40°58′N, 15°08′E, ~720 m asl) is located in the municipality of Rocca San Felice, near Avellino, in the Campania region of southern Italy (Figure 1). In the 1st millennium BC, a sanctuary dedicated to the goddess Mephitis existed in the area, between the top of the woody hill and the volcanic lake, near the Ansanto stream (Figure 1). The *templum* was first identified at the end of the 18th century by Vincenzo Maria Santoli, a priest interested in the history of his village, Rocca San Felice (Gambino 1991). Archaeological excavation began in the 1950s and 1960s with Oscar G Onorato and in the 1970s with Ivan Rainini (Bottini et al. 1976). Recent archaeological interpretation indicates a distinction between the sanctuary, frequented by people, and the sacred goddess area (part of a forest), which was forbidden to humans (Rainini 2008).

Volcanic lakes are the main feature of the valley: under the rock layer (comprising a clayey and marly ground) gas exhalations (mainly CO_2) arise from a fault and, interacting with the groundwater table, give rise to secondary volcanic phenomena, like fumaroles (Augusti 1961; Ortolani and Pagliuca 2008). Many landslides have also occurred in the valley. They are the product of deforestation and the erosion of the rocks caused by the acidic ground (Ortolani and Pagliuca 2008). Due to the landslides, the structures discovered during the archaeological excavations are not visible today. Some of the samples studied in this work (described below) were collected in the municipality of Pietrastornina (near Avellino) in the Natural Regional Park of Partenio (40°59′22″N, 14°43′49″E, ~570 m asl; Figure 1). This village is ~30 km from the Ansanto Valley. The area is characterized by calcareous soils, with pyroclastic deposits from the eruptions of Vesuvius.

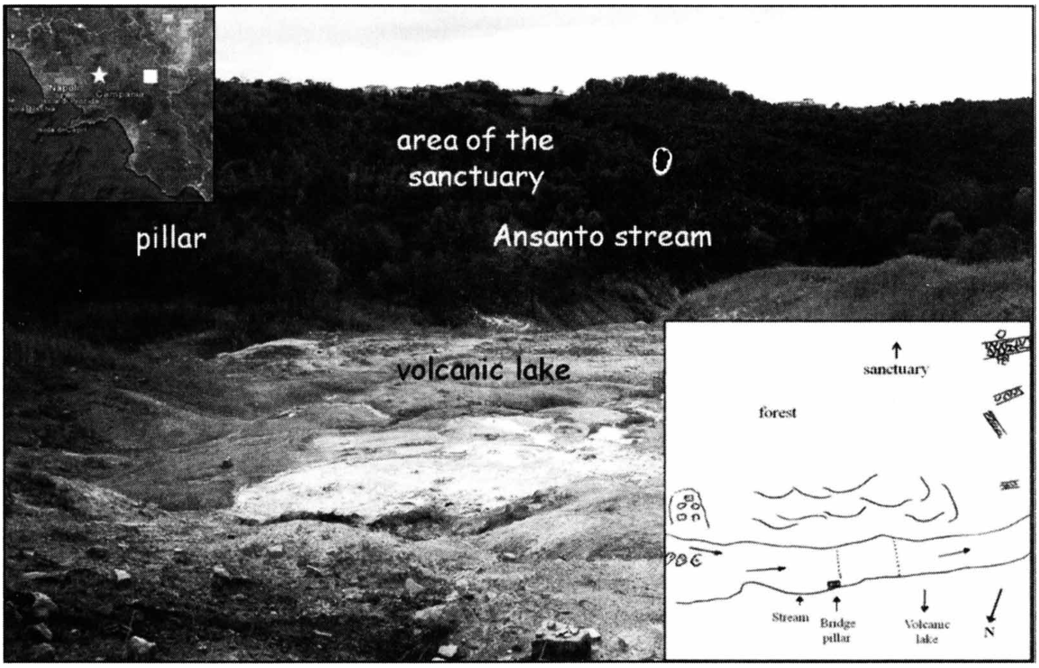

Figure 1 Photo of the Ansanto Valley (by Giovanni Iannone, modified) and plan (lower right) of the archaeological features (modified from Gambino 1991). Top left: map of the Campania region (southern Italy), showing the locations of Pietrastornina (star) and the Ansanto Valley (square).

MATERIALS AND METHODS

Fossil Dilution Investigation

In order to determine the presence of fossil dilution in the Ansanto Valley, in February 2011 two living deciduous oaks were sampled in the valley; we refer to them as Q_Ansanto1 and Q_Ansanto2 (Table 1). One core of 5 mm diameter was taken from each tree at breast height with a Pressler increment corer, before the beginning of the growing period. The trees are ~30 m from the nearest vent. We chose oak trees because of the presence of deciduous oak among the identified archaeological findings. We isolated the rings corresponding to the years 2010, 2005, 2000, 1998, and 1997 from both trees and sliced them into small pieces, without homogenizing them. We pretreated the samples with the standard AAA method applied at CIRCE (Passariello et al. 2007): a 3% HCl solution attack of 1 hr; followed by a bath in a 3% concentration of NaOH solution for 1 hr; and a final wash in a 3% concentration of HCl solution for 1 hr. Between the different steps, the solution was sequentially rinsed with deionized water until reaching neutral pH.

The samples were oven-dried at 80 °C and later oxidized to CO_2 by combustion in precleaned quartz tubes with copper oxide. The reaction took place in a muffle furnace at 920 °C for 6.5 hr. Reduction of the CO_2 to graphite was performed using Fe as catalyst and Zn and TiH_2 as reagents in a muffle furnace at 560 °C for 8 hr (Marzaioli et al. 2008). The graphite was pressed into aluminum cathodes that were then placed in the 40-position wheel of the accelerator ion source for ^{14}C AMS measurement at CIRCE (Terrasi et al. 2008). Several replicated standards (primary standard NIST OXII and control standards IAEA C3 and C5) and blanks (Alfa Aesar graphite) were simultaneously processed with the same combustion and graphitization procedures as the unknown samples. NIST OXII was used for normalization and ^{13}C fractionation correction, Alfa Aesar graphite for the back-

Table 1 List and description of the samples analyzed with the indication of the kind of investigation and the pretreatments performed on each sample.

Sample	Investigation	Description	Pretreatment
Q_Pietra	Restoration removal tests	Wood of a deciduous oak from Pietrastornina; rings corresponding to years 2002–2007 were analyzed. The wood was cut into small pieces, subjected to the Ansanto Valley gas interaction, restored, and artificially aged. The chemical pretreatment was performed without homogenizing the sample.	Methanol bath followed by AAA with NaOH at 17% and HCl at 3% concentration
Q_Ansanto1	CO_2 fossil dilution in Ansanto Valley	Core of a deciduous oak growing ~30 m from the volcanic lake in the Ansanto Valley. Rings corresponding to years 2010, 2005, 2000, 1998, and 1997 analyzed.	AAA with the reagents at 3% concentration
	Restoration removal tests	Core of a deciduous oak growing ~30 m from the volcanic lake in the Ansanto Valley. Rings corresponding to years 2001–2004 and 2006–2009 were cut into small pieces, subjected to the Ansanto Valley gas interaction, restored, and artificially aged all together. Chemical pretreatment performed without homogenizing the sample.	1. No pretreatment 2. AAA with reagents at 3% 3. AAA with NaOH 10%, HCl 3% 4. AAA with NaOH 17%, HCl 3% 5. Methanol bath 6. Ethanol and toluene with a following bath in ethanol 7. Step 5 followed by step 2 8. Step 5 followed by step 3 9. Step 5 followed by step 4 10. Step 6 followed by step 2 11. Step 6 followed by step 3 12. Step 6 followed by step 4
Q_Ansanto2	CO_2 fossil dilution in Ansanto Valley	A core of deciduous oak growing ~30 m from the volcanic lake in the Ansanto Valley. Rings corresponding to years 2010, 2005, 2000, 1998, and 1997 analyzed.	AAA with the reagents at 3% concentration
"Cervione" glue	Restoration removal tests	Organic glue made with animal bones, the same kind used for restoration of the archaeological materials.	No pretreatment
X3304	Restoration removal tests	Archaeological wooden carving n. 3304 representing a human body. Not uniformly restored, using the glue to fix spare parts.	1. No pretreatment 2. AAA with the reagents at 3% 3. Methanol bath, followed by AAA with NaOH at 17% and HCl at 3%
X3305	Restoration removal tests	Archaeological wooden carving n. 3305 representing a human face. Not uniformly restored, using the glue to fix spare parts.	1. No pretreatment 2. AAA with the reagents at 3% (repeated twice) 3. Methanol bath, followed by AAA with NaOH at 17% and HCl at 3%
PR.X3305	Restoration removal tests	Loose fragments of archaeological wooden artifacts. The wood appeared similar to carving X3305; we thus assumed that the fragments belong to X3305. Each pretreatment was performed on a different fragment. The 3 fragments analyzed were visibly contaminated by glue.	1. No pretreatment 2. AAA with the reagents at 3% 3. Methanol bath, followed by AAA with NaOH at 17% and HCl at 3%

ground correction, and IAEA C3 and C5 for evaluation of overall accuracy and precision (Terrasi et al. 2008).

$F^{14}C$ values (Stuiver and Polach 1977) of the samples were compared with those obtained from the "clean air" signal (a mean of Northern Hemisphere zone 1, Hua and Barbetti 2004; Jungfraujoch data, Levin et al. 2008; and data from the NOAA ESRL/GMD, Niwot Ridge Forest, Colorado, USA). The percentage of fossil dilution was then calculated by applying an isotopic mass balance (Quarta et al. 2007), following the equation:

$$X_{ff} = \frac{F^{14}C_{atm} - F^{14}C_{sample}}{F^{14}C_{atm}} \times 100\,\%$$

where X_{ff} represents the percentage of fossil CO_2 of the total CO_2, $F^{14}C_{atm}$ the atmospheric $F^{14}C$ value, and $F^{14}C_{sample}$ the $F^{14}C$ of the unknown samples. The 5 fossil dilution % values of each tree were later averaged in order to have a rough estimation of the dilution of the trees.

Restoration Removal Tests

The aim of our tests is optimization of the procedure for removing restoration materials from the wooden archaeological artifacts of the Ansanto Valley. Since we could sample only small amounts from the archaeological materials, we performed most of the tests on contemporaneous woods (Table 1): the wood from a tree grown in Pietrastornina; the wood of a contemporaneous tree grown in the Ansanto Valley; a piece of the Cervione glue; and some archaeological woods from the Ansanto Valley.

The Pietrastornina tree ("Q_Pietra" in Table 1) is a cross-section from a deciduous oak, cut in the spring of 2008. It shows the beginning of earlywood formation before the bark. A piece measuring 2 × 3 × 13 mm and weighing ~80 mg was sliced from the section, isolating the rings corresponding to the years 2002 to 2007.

We know that the archaeological wood is different in terms of chemical and physical characteristics with respect to the modern wood (Obataya 2007). Natural weathering produces a deterioration of the wood, mainly due to solar irradiation, relative humidity, temperature, and atmospheric gases (Anderson et al. 1991; Sudiyani et al. 1999). To try to reproduce some of the characteristics of the archaeological wood on the modern wood, we exposed the Q_Pietra sample to an "artificial weathering" of 11 days, corresponding to a period of ~110 days of natural aging; in fact, the correspondence between the artificial and natural aging may vary from 5 to 20 times, depending on the selected conditions of exposure (Arnold et al. 1991). This period is clearly very short compared to the centuries of the archaeological findings, but even in that short duration some processes can begin during the applied "artificial aging". Because we cannot know the kind of degradation that the woods have undergone since the time they were buried to their discovery, we applied aging procedures commonly suggested in the literature (Anderson et al. 1991; Arnold et al. 1991; Podgorsky et al. 1994; Curling and Murphy 1999; Sudiyani et al. 1999). A Fitotron chamber was used for our test process. The Q_Pietra sample was placed inside the chamber at 40 °C, subjected to ultraviolet light (365 nm wavelength), which reproduces the damaging rays of sunlight (Feist and Hon 1984; Brennan and Fedor 1987; Anderson et al. 1991; Arnold et al. 1991; Sudiyani et al. 1999). The relative humidity was changed during the day between 20% and 90% and the sample was also placed for 2 hr daily in a water bath to simulate varying wet conditions.

In addition to the solar rays, moisture, and temperature, strong and continuous exhalation of atmospheric gases can damage wood. It is possible that some chemical interactions occur between the salts (generated in the Ansanto Valley especially by the H_2S gas and absorbed by the wood) and the consolidation materials of the restoration. We thus decided to simulate a similar interaction between gases from the Ansanto Valley and the Q_Pietra sample. The sample was sliced into small pieces and sealed in a glass vacuum-tight canister (previously evacuated in the laboratory) near the volcanic lake. The canister was later closed to expose the sample to the same gas atmosphere as the

Ansanto Valley for 2 weeks. The sample was later consolidated following the same procedure used on the archaeological objects by Augusti (1959, 1961), but limited to just the first step (see below).

After the sample was exposed to the gases from the Ansanto Valley and consolidated, it was then "artificially aged" again due to the possible change of chemical bonds between the restoration materials and the wood caused by aging. Q_Pietra was left in the Fitotron chamber for 9 days at 40 °C, with a variable relative humidity between 20% and 90%, and subjected to ultraviolet light (365 nm). We omitted the step with the bath in water due to the lack of rain inside the museum.

In order to remove the consolidation materials from the Q_Pietra sample before ^{14}C analysis, we submitted it to a chemical pretreatment. After preservation of most of the material for future chemical analyses, Q_Pietra was reduced to a small piece; for this reason, we chose to employ only the most effective chemical treatment. This sample was pretreated with methanol followed by the AAA procedure, with HCl at 3% and NaOH at 17%. We presume that this method is best among those employed because of the kind and concentration of reagents: the consolidating materials used in restoration are generally removed with organic solvents and we know that Augusti (1959, 1961) used the tannin to make the glue solution insoluble. Because methanol can dissociate the tannin molecules (Hagerman 2002), we used methanol and the AAA method, increasing the concentration of the alkali solution, which removes fats, resins, and tannins.

The second contemporaneous tree comes from the Ansanto Valley. It is the same tree employed in the fossil dilution study, Q_Ansanto1, described above (Table 1). For tests on the restoration material removal, we isolated the rings corresponding to the years 2009, 2008, 2007, 2006, 2004, 2003, 2002, and 2001. Because we did not know about the presence of the fossil dilution at ~30 m from the emitting source and its possible effects on the archaeological wood, we decided to simulate an interaction state between the gases from the Ansanto Valley and the sampled wood. The wood of Q_Ansanto1 was sliced into small pieces and sealed in a glass vacuum-tight canister (previously evacuated) near the volcanic lake and left inside for 2 weeks. Later, it was consolidated and "artificially aged," like the Q_Pietra sample.

In order to remove the organic consolidation materials (mainly glue and tannins), the Q_Ansanto1 sample was pretreated using different chemical procedures on different parts of the sample. The method normally employed at CIRCE for dating of wood samples is the AAA pretreatment with a concentration of all the solutions of 3% (Passariello et al. 2007). Thus, we started with this method on 1 piece and repeated it 3 times on the other pieces, increasing the concentration of the alkali solution to 10% and 17%. We chose to test several alkali concentrations in order to verify if a higher base concentration is more effective or not. Each solution was left for 1 hr on a heating plate at ~80 °C; between the acid and alkali attacks, the solution was rinsed with deionized water until neutral pH. Finally, the samples were oven-dried at 60 °C overnight. Other pretreatments were performed using an organic solvent extraction or adding this step before the AAA procedure, in order to evaluate eventual improvements in the organic contamination removal. We used ethanol and toluene solution (1:1) followed by only an ethanol bath or a methanol bath (Table 1). All these extractions were carried out in an ultrasonic bath (to enhance the extraction efficiency) under the hood. The duration of these procedures were 3 hr for the ethanol and toluene extraction, 3 hr for the ethanol, and 5 hr for the methanol (the solutions were refilled every 30 min).

The Cervione glue (Table 1), a glue made from animal bones, was also analyzed. This glue is similar to the one used by Augusti in the consolidation process of the archaeological materials, but it is not exactly the same, so probable differences cannot be excluded. We dated the glue in order to know the age of the contaminant introduced in the wood samples (Q_Pietra and Q_Ansanto1). No chemical pretreatment was performed on this sample.

The archaeological materials come from the sanctuary of the goddess Mephitis in the Ansanto Valley. They include wooden carvings, a wooden *patera* (a wide, flat plate used in ritual contexts), and some pieces of a wooden throne (Bottini et al. 1976), preserved in the Museo Irpino of Avellino. All wooden materials were found in the Ansanto streambed: they are believed to have been thrown there by the ancient population as offerings to the goddess or brought to the stream by the landslides (Rainini 2008). Mineralization of the wood tissues occurred in the stream water. When the objects were discovered, they were strongly impregnated with water and greatly altered in structural and chemical composition, caused by the mineralization process (Augusti 1961).

In the late 1950s, these objects were restored by Selim Augusti, the head of the chemical laboratory of Capodimonte Museum in Naples (Augusti 1959, 1961). The restoration occurred in 2 steps: 1) consolidation of the wood in a bath of organic glue and sodium fluoride (NaF) and in a successive bath of tannic acid, used to make the glue solution insoluble; 2) blanks in the wood, appearing after the first step, were refilled with a wood pulp obtained by mixing a powder of tannin and glue with a powder of wood, either pieces of the archaeological wood or of a similar wood (Augusti 1961).

We analyzed 2 carvings (3304 and 3305), referred to as X3304 and X3305 (Table 1), where X is the first letter of *xoanon*, the Greek name of the archaic wooden carvings. There is evidence indicating the absence of the second step of the restoration in these 2 carvings. Moreover, the deep degradation in the wood of these *xoana* and their preservation in the museum basement (contrary to most other carvings displayed in the museum) suggest a nonuniform restoration process, in which the glue was used only to fix the spare parts. X3305 represents a human face, divided into 2 parts with some wood missing on the back. X3304 represents a human body, where only the torso and 1 leg are present. The fragmentary state of these *xoana* allowed us to take fragments of ~1 g each, sampled from the back of the carvings with a surgical blade. In the box where these carvings were preserved, there were also other carvings, some throne pieces, and some loose fragments. We took some of these fragments, assuming that they belong to X3305, because the wood looked the same (same color and same state of conservation). We refer to them in the text as PR.X3305 ("PR" for "presumed"). Three of these fragments were visibly contaminated by glue; we chose them for our tests.

The archaeological samples were pretreated with the standard AAA procedure (HCl at 3% concentration and NaOH at 3%); with the AAA procedure (HCl at 3% concentration and NaOH at 17%) preceded by a methanol bath; and we also analyzed the samples without any chemical pretreatment (Table 1). In this case, we decided to test the classic AAA procedure of CIRCE for wooden materials and a stronger pretreatment, with methanol extraction and a higher alkali concentration, in order to check if a strong pretreatment is necessary for the archaeological samples. The combustion and graphitization processes and the ^{14}C measurement are described above. ^{14}C ages of the archaeological findings were calibrated with the OxCal program v 4.17 (Bronk Ramsey 2009), using the IntCal09 calibration curve (Reimer et al. 2009).

RESULTS AND DISCUSSION

Fossil Dilution Investigation

^{14}C dating of the 2 oak trees sampled in the Ansanto Valley shows the presence of a strong fossil dilution (Table 2). Comparing the $F^{14}C$ values of these trees with the "clean air" $F^{14}C$ allows us to evaluate how much our values are depleted in ^{14}C content with respect to the values of trees not subjected to local emission of fossil CO_2 (Figure 2).

Table 2 $F^{14}C$ values and ^{14}C age of 2 trees (Q_Ansanto1 and Q_Ansanto2) sampled in the Ansanto Valley. A strong % fossil dilution is noted due to CO_2 emission from the volcanic lake.

Lab code	Sample name[a]	Chemical pretreatment	^{14}C age (BP)	$F^{14}C$	% fossil dilution
DSH2617	Q_Ansanto1_2010	AAA	2006 ± 23	0.780 ± 0.002	25 ± 0.21
DSH2618	Q_Ansanto1_2005	AAA	2372 ± 26	0.740 ± 0.002	31 ± 0.22
DSH2619	Q_Ansanto1_2000	AAA	2015 ± 22	0.780 ± 0.002	29 ± 0.19
DSH2621	Q_Ansanto1_1998	AAA	1547 ± 21	0.820 ± 0.002	26 ± 0.19
DSH2622	Q_Ansanto1_1997	AAA	1715 ± 22	0.810 ± 0.002	27 ± 0.20
DSH2623	Q_Ansanto2_2010	AAA	1616 ± 23	0.820 ± 0.002	22 ± 0.22
DSH2624	Q_Ansanto2_2005	AAA	1218 ± 22	0.860 ± 0.002	19 ± 0.21
DSH2625	Q_Ansanto2_2000	AAA	690 ± 78	0.920 ± 0.009	16 ± 0.81
DSH2626	Q_Ansanto2_1998	AAA	786 ± 46	0.910 ± 0.005	18 ± 0.47
DSH2627	Q_Ansanto2_1997	AAA	813 ± 30	0.900 ± 0.003	19 ± 0.31

[a]Tree name and calendar year of the ring analyzed.

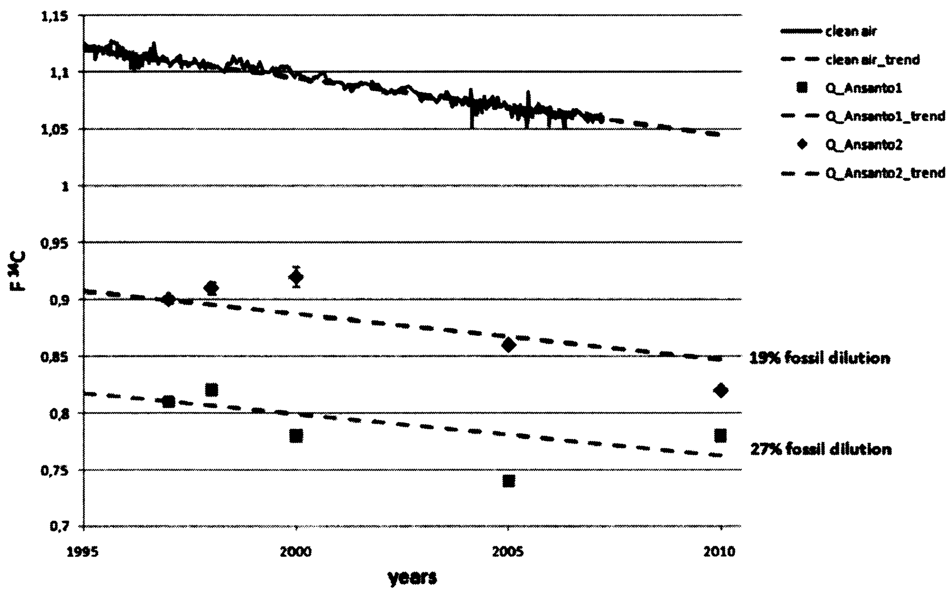

Figure 2 $F^{14}C$ values of Q_Ansanto1 and Q_Ansanto2 are compared with $F^{14}C$ of "clean air." The black dotted line is a linear interpolation of the "clean air" values. The same line is scaled by an arbitrary factor for the 2 trees, while the percentage of fossil dilution indicated is the mean of the fossil dilution % of the 5 points for each tree.

The calculated average dilution for Q_Ansanto1 and Q_Ansanto2 is 27% and 19%, respectively (Figure 2). However, the dilution appears to be variable for a range of years and different trees, probably due to their distance from the emitting source, the wind direction, and the intensity of the diluted CO_2 fumes.

The recent presence of fossil dilution in the Ansanto Valley suggests its presence also in ancient times, with Latin sources describing a pestiferous land (e.g. Cicero and Vergilius). We can thus assume the influence of fossil CO_2 also in trees grown in the 1st millennium BC, with similar variability found in the contemporaneous trees. For this reason, it will probably be difficult to date the archaeological wood affected by such fossil dilution.

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During preparation of the Q_Pietra sample, a sample studied for restoration removal tests, we reproduced an interaction of the sample with the volcanic lake gases for 2 weeks. The ^{14}C dating result of this sample shows no fossil dilution. This implies that the exposition of dead wood to fossil CO_2 atmosphere does not alter the accuracy of ^{14}C dating (Figure 3). We therefore expect to find no fossil dilution in the archaeological woods if they were cut from trees grown far from the volcanic lake influence and only after they were thrown in the stream near the lake.

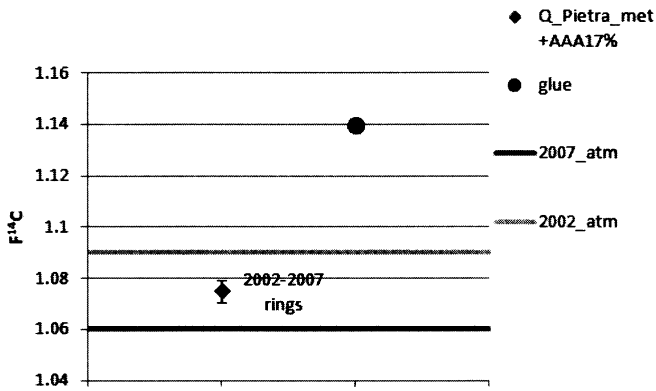

Figure 3 $F^{14}C$ of pretreated Q_Pietra and that of the glue employed for its consolidation. The dark and light gray lines indicate the bomb spike value corresponding to the years 2007 and 2002 of atmospheric ^{14}C concentration.

Restoration Removal Tests

Regarding the chemical test for removing the consolidation materials, the contaminated Q_Pietra sample shows a correct date after being subjected to treatment using methanol and AAA with the base at 17% concentration (Table 1): its date is between the bomb peak dates of 2002 and 2007, corresponding to the tree rings analyzed (Figure 3). The "Cervione" glue showed a ^{14}C content of 1.14 ± 0.004 $F^{14}C$, corresponding to a modern contamination (Figure 3). If the consolidation materials were not removed by our pretreatment, we expected to find for the Q_Pietra sample a ^{14}C date older than the age of its rings, in the range between its age and the glue age.

The Q_Ansanto1 sample provides a broader picture of the chemical pretreatments for the removal of consolidation materials. In fact, the greater amount of sample enables testing several chemical procedures. Looking at Figure 4 we are confident of the effectiveness of nearly all the chemical pretreatments employed in removing the consolidation material. The presence of a strong fossil dilution (Figure 2) prevents reading an annual ^{14}C value matching with the bomb spike curve. However, we can compare these values with the ^{14}C content of the Q_Ansanto1 sample not subjected to restoration contamination (years 2010, 2005, and 2000; Figure 2, Table 2). The values of the chemically pretreated consolidated wood fluctuate between 2238 ± 21 and 2450 ± 22 yr BP (Figure 4), while the nonconsolidated wood of the same period fluctuate between 2006 ± 23 and 2372 ± 27 yr BP (Figure 2). Figure 2 presents an oscillation of the fossil-diluted rings of Q_Ansanto1. Analysis of groups of rings from the same sample for the restoration removal test, without homogenization of the wood, explains the imperfect correspondence between the 2 sets of values (Figures 2 and 4). This is especially true when one notes that the 2 sets of data come from different years (Table 1, Figures 2 and 4). The only ineffective pretreatment is the method employing ethanol and toluene, followed by only ethanol. This sample gave a value (1807 ± 24 yr BP) younger than its real age

(Figure 2), near the value of the sample dated without any chemical treatment (Figure 4). This is caused by incomplete removal of the contaminant.

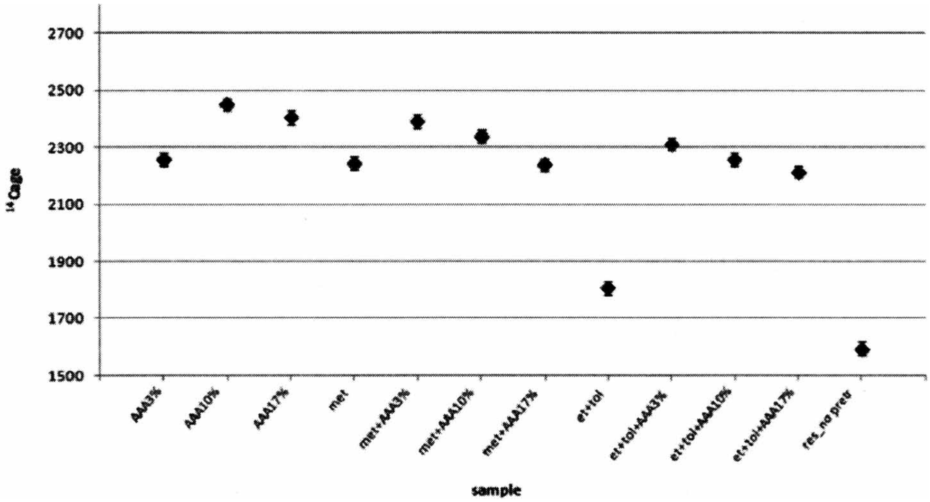

Figure 4 ^{14}C age of Q_Ansanto1 consolidated and after being pretreated several different ways in order to remove the consolidation materials: AAA3% = acid-alkali-acid with NaOH 3% and HCl acid 3%; AAA10% = acid-alkali-acid with NaOH 10% and HCl acid 3%; AAA17% = acid-alkali-acid with NaOH 17% and HCl acid 3%; met = methanol bath; et+tol = ethanol and toluene with a following bath in ethanol; res_no pretr = sample restored not pretreated chemically.

The ^{14}C dates of X3304 and X3305 are mostly coherent with the archaeological expectation (Onorato 1960; Bottini et al. 1976; Rainini 1996, 2003, 2008), as shown in Figure 5 (with archaeological age expected highlighted by the gray vertical band). No fossil signal seems to be present in the ^{14}C data; therefore, we can suppose that the wood used in these carvings is from an area far from the volcanic lake or from the sacred goddess forest.

In the "Materials and Methods" section, we assumed a different restoration methodology for X3304, X3305, and PR.X3305, with the use of the glue only to fix spare parts. The ^{14}C data support this hypothesis (see X3304 and X3305 in Figure 5). In fact, we found the same dates for these findings in the samples chemically pretreated and in those without pretreatment (with 1 exception described below). Therefore, in the samples not pretreated the glue was likely not present and thus could not rejuvenate the dates.

For the chemical procedures used on the X3304 and X3305 samples, the results are inconclusive regarding their effectiveness in restoration removal. ^{14}C measurement of X3305 pretreated by the AAA method with reagents at 3% concentration (Table 1) was repeated twice (Figure 5). These repeated samples are indicated as DSH2555 and DSH2612. The DSH2555 ^{14}C date is younger than the expected date (Figure 5). This could be due to contamination with the modern glue, not removed by that kind of chemical procedure. Therefore, we can be sure about the ineffectiveness of the method AAA with reagents at 3% concentration. Nevertheless, in order to test the uniformity of the restoration, we decided to repeat the measurement of X3305 pretreated with this procedure. The repetition (DSH2612) gave a ^{14}C value compatible with the archaeological expectation (Figure 5), indicating in this case absence of the glue.

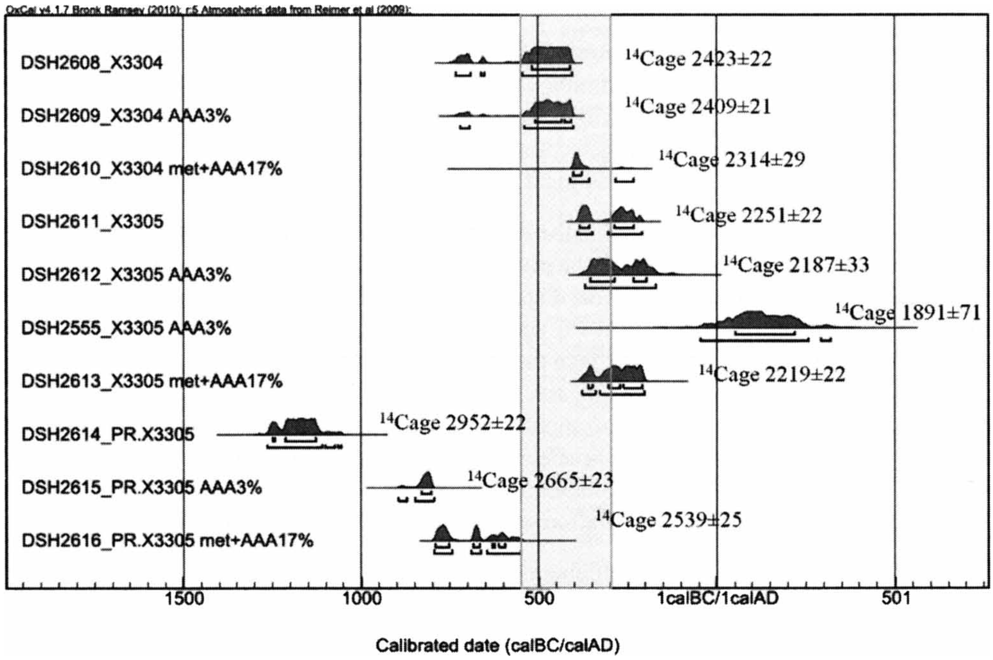

Figure 5 Calibration of the archaeological findings dated. "DSH" indicates laboratory code, "X" the *xoanon* number, and "PR" means "presumed." If the sample was pretreated, the kind of pretreatment used is indicated at the end of the name: AAA3% = acid-alkali-acid with concentration of base 3%; methanol+AAA17% = methanol bath followed by AAA attack with base 17% of concentration.

Provided that not all the pieces of X3304 and X3305 are impregnated with the restoration glue, we cannot be sure about the effectiveness in consolidation removal of the other pretreatment used (methanol followed by AAA with the NaOH at 17%) (Table 1). In fact, we cannot be sure about the presence of glue in the ^{14}C-dated pieces.

For the PR.X3305 samples, their ^{14}C dates are not coherent with archaeological expectations. They certainly do not belong to X3305, their previously supposed original material, nor with X3304. In fact, they are older than the ages obtained for the other carvings (only sample DSH2616 is partially contemporaneous with X3304; Figure 5). Because these 3 fragments were visibly contaminated by a piece of glue, we expected to find in the sample without chemical pretreatment an age younger than the archaeological dating, but instead it was 2952 ± 22 BP (1264–1056 cal BC, 2σ), at least 300 yr before X3304 and 500 yr before X3305 (Figure 5). Moreover, the other 2 pretreated samples should be older than the sample without pretreatment because of the assumed removal of glue by the chemical pretreatments applied. Their ^{14}C ages are younger, however (Figure 5). Those results suggest that the dated fragments belong to different findings (with a different age). We can also assume the presence of fossil dilution for these fragments of wood. As with the contamination introduced by the restoration glue, the fossil dilution should be strong enough for the age obtained (Figure 5). If the fossil dilution presence was real, these wood fragments could belong to trees grown in a different location compared to the trees whose wood was used for X3304 and X3305, a location in the vicinity of the volcanic lake of the Ansanto Valley.

CONCLUSION

Our study indicates the presence of strong fossil dilution in contemporaneous trees growing in the Ansanto Valley. The intensity of the dilution varies over the years. We can presume the presence of a fossil dilution also in the past, also with a variable intensity. For this reason, it would be difficult to date the archaeological findings affected also by contamination of modern restoration materials. In any case, we can draw some archaeological information from the ^{14}C data.

We propose in future work to core trees in the Ansanto Valley at an increasing distance from the volcanic lake and at different exposures to the prevailing winds, and evaluate their fossil dilution percentage. This work can inform us about the distance from the lake where the fossil CO_2 has negligible influence. Analyzing the archaeological ^{14}C ages (once we are sure to have removed all the contaminants), we can assume that dates older than the expected archaeological dates are affected by fossil dilution. If we know approximately where the fossil dilution disappears from the trees grown in the valley, we can have an approximate idea about the provenience of the archaeological wood used for the wooden artifacts (e.g. if the sample is affected by fossil dilution, the wood can derive from a tree grown near the volcanic lake and the goddess sacred forest). We can thus obtain useful information about land use in that period, also in relation with the worship of the goddess Mephitis.

As for the restoration removal tests, all chemical procedures on contemporaneous wood appeared effective, except for that using ethanol and toluene. Meanwhile, the chemical pretreatments tested on the archaeological materials did not show results as satisfactory as those on contemporaneous wood. The results can be explained by several factors. One is the Cervione glue that we used for the consolidation, similar to that used by Augusti. However, our glue has features different from the one employed by the restorer due to the years of production. This suggests that also a different composition can be expected. Moreover, also the time of aging is different: many centuries aging introduce chemical transformations in the wood that can interact in a different way with the consolidation materials. Therefore, it is important to repeat the experiment on contemporaneous wood samples not affected by fossil dilution, increasing the "artificial weathering" time, before and after the restoration, and to also test other reagents. In order to better address the influence of other contamination sources, we will test organic solvent extractions on standard samples (i.e. IAEA C3).

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