Securing timelines in the ancient Mediterranean using multiproxy annual tree-ring data

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Calendar-dated tree-ring sequences offer an unparalleled resource for high-resolution paleoenvironmental reconstruction. Where such records exist for a few limited geographic regions over the last 8,000 to 12,000 years, they have proved invaluable for creating precise and accurate timelines for past human and environmental interactions. To expand such records across new geographic territory or extend data for certain regions further backward in time, new applications must be developed to secure “floating” (not yet absolutely dated) tree-ring sequences, which cannot be assigned single-calendar year dates by standard dendrochronological techniques. This study develops two approaches to this problem for a critical floating tree-ring chronology from the East Mediterranean Bronze–Iron Age. The chronology is more closely fixed in time using annually resolved patterns of ¹⁴C, modulated by cosmic radiation, between 1700 and 1480 BC. This placement is then tested using an anticorrelation between calendar-dated tree-ring growth responses to climatically effective volcanism in North American bristlecone pine and the Mediterranean trees. Examination of the newly dated Mediterranean tree-ring sequence between 1630 and 1500 BC using X-ray fluorescence revealed an unusual calcium anomaly around 1560 BC. While requiring further replication and analysis, this anomaly merits exploration as a potential marker for the eruption of Thera.

Significance

This study demonstrates how different lines of evidence from tree rings in widely spread growth locations can combine to fix an approximately dated tree-ring record from the East Mediterranean Bronze–Iron Age to an exact calendar-dated range. This tree-ring record is of high importance for regional chronology and spans the time period in which the major volcanic eruption of Thera (Santorini) occurred. Exact dating of this eruption is important because it provides a prominent marker horizon through which ancient timelines of the East Mediterranean, Egypt, and the Levant can be synchronized. Chemical analysis of the dated tree-ring sequence identifies a chemical change in their growth environment around 1560 BC, which while requiring further substantiation, may be evidence of the Thera eruption.

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PNAS Latest Articles | 1 of 6
In an earlier attempt to trace the Thera eruption, Pearson et al. (24) conducted elemental analysis on a wide growth-ring anomaly from one of the tree-ring site chronologies overlapping with the Gordion record (Porsuk in southern central Turkey) (Fig. 1). In that study, we found significant changes in elemental chemistry associated with a wide growth-ring anomaly, which was then dated to c. 1650 BC; at the time, this was within the possible radiocarbon range suggested for the Thera eruption (25), although at odds with certain lines of archaeological evidence (26, 27). The elemental response was consistent with what might be expected from a volcanic event but as noted at the time, also consistent with what might be expected following a forest fire. The date for this elemental change and growth response is now outside the possible range for the Thera eruption [although it may originate from some other unidentified eruption; for example, the Yali-Nisyros volcano (28)]. The revised radiocarbon ranges for Thera-relevant materials suggested by Pearson et al. (29) (Fig. 2) indicate that the majority of the 16th century BC should now be searched for evidence of the eruption.

In this study, a combination of two approaches is used for improving and securing the date range for the floating tree-ring series from Gordion. First, we compare a sequence of annual $^{14}$C measurements from single rings of the Gordion series with a contemporary time series of annual $^{14}$C from absolute, calendar-dated bristlecone pine (29) and Irish oaks (30) across the period 1700 to 1500 BC.

Similar applications (31–32) have relied on detecting the presence of significant rapid excursions in the annual $^{14}$C measurements from single rings of the Gordion series with a contemporary time series of annual $^{14}$C from annual, calendar-dated bristlecone pine (29) and Irish oaks (30) across the period 1700 to 1500 BC. In the case of the AD 774/775 marker event, the potential is clear, but for time periods where no such dramatic markers are present, like 1700 to 1500 BC, a different strategy has to be applied. Here, we make use of less pronounced and consequently, less secure $^{14}$C time markers (36, 37) for a proposed annual $^{14}$C pattern-matching approach.

Second, this is tested using an anticorrelation between tree growth response to the same volcanic forcing events in both the Mediterranean juniper trees and calendar-dated North American bristlecone pine. This test uses a well-established temporal association between high-elevation bristlecone pine frost rings and large-scale volcanic eruptions. It has been clearly demonstrated that latwood frost rings in bristlecone pine occur the year of or the year following a volcanic event (38, 39), and this causal connection has been strongly confirmed across the last 2,500 years (35). Beyond this period, bristlecone tree-ring chronologies are accurately dated to the calendar year over the past 5,000+ years (40, 41), and therefore, the record of precisely dated bristlecone response to volcanism covers the period across which the juniper sequence lies according to both conventional radiocarbon wiggle matching (18) and the annual $^{14}$C pattern-matching approach used in this study.

In western Turkey, the years of or following many of the same major volcanic eruptions that affected bristlecone growth in the more recent period are marked by wide growth rings in Austrian pine (Pinus nigra) (16) (Fig. 1). This indicates that an increase in May–June precipitation caused more favorable growth in this region as part of a chain of climatic disturbances associated with Northern Hemisphere cooling following major mid- or northern latitude volcanic eruptions. Assuming that similar climatic forcing prevailed during the Bronze Age and knowing that pine and juniper tree-ring chronologies from this region show strong interspecies correlation, we hypothesized that wide rings in the floating juniper sequence should correlate with calendar-dated frost events in bristlecone pine and that, if so, this could provide a means to test the annual $^{14}$C-matching approach and to refine to a fixed tree-ring date based on synchronization with the calendar-dated bristlecone record (in a similar approach...
Fig. 2. A shows annual $^{14}$C ages (radiocarbon years B.P.) from two calendar-dated tree-ring series [North American bristlecone pine (29) and Irish oak (30)] and the Mediterranean Gordion juniper series (positioned so the end ring of the whole sequence, which extends beyond the analyzed period, is at 745 BC) relative to the IntCal13 calibration curve. Data marked AA and ETH were collected at the University of Arizona and Eidgenössische Technische Hochschule Zurich radiocarbon laboratories, respectively. We note that these closely agreeing annual data seem to indicate that uncalibrated radiocarbon dates from pre-Thera contexts in the range from 3350 to 3310 $^{14}$C years B.P. could calibrate anywhere between c. 1620 and 1540 BC. An improved recalibration of such samples will be possible following the release of the IntCal20 curve, which will combine carefully screened annual data for this period from multiple laboratories using a different statistical method than was used for IntCal13. For this reason, we do not attempt to more closely compare curve shape between the annual data and the IntCal13 curve in this study. B shows the annual $^{14}$C ages in A converted to $\Delta^{14}$C (21) to emphasize patterns used to synchronize the floating chronology. Visual matching of the small-scale data feature shown for all growth locations at c. 1528 BC (arrow) further confirms the $\chi^2$ result. The feature at c. 1548 BC is present only in the juniper data but if replicated in this material, could indicate a localized disturbance in the carbon cycle.

Finally, we report the chemical study of this newly secured tree-ring sequence with the objective of seeing if any chemical indicator could be found that might help to further constrain the dating possibilities for the Thera eruption.

**Results**

Annual $^{14}$C measurements were made on 186 consecutive years (relative years 834 to 1019) of the 1,028-year Gordion juniper sequence [which starts with relative year 737 (18)]. These measurements (SI Appendix, Table S1) were then wiggle matched to IntCal13 using OxCal 4.3 (SI Appendix, Fig. S1) (45) to provide an end date for the entire calibrated tree-ring chronology within an 8-year range: 758 to 751 BC at 95.4% confidence level. This was in good agreement with previous wiggle matching of 128 decadal or 11-year blocks spaced over 987 years of the same juniper sequence, which placed the end of the tree-ring sequence at 751 BC +6/–8 at a 95.4% confidence level (18). A $\chi^2$ test for the Mediterranean $^{14}$C time series vs. the weighted mean of the annually resolved combined oak and pine data (29, 30) placed
the last ring of the Mediterranean sequence at a more precise date of 745 ± 4 BC (95.4% confidence level); this is statistically slightly younger (10 ± 6 years) than when the same data are wiggle matched to IntCal13. We consider the position using the annual \(^{14}\)C data as significantly more reliable as it is a result of comparing fine structure that is not available in IntCal13, which is primarily based on decadal data. Using the fine structure yields dating results free from the regional or laboratory offsets that may be combined in the coarser-resolution calibration data. The reasonably close agreement of the results via the different methods does, however, demonstrate that, for wiggle matches spanning multiple decades, the improved curve shape offered by the annual \(^{14}\)C data may have a relatively small effect on the final calibrated date range.

Positioned relative to an end date of 745 ± 4 BC (Fig. 2), the visual correlation of the annual data around the increased production event of c. 1528 BC (Fig. 2B, arrow) is clearly evident. The Gordian data more closely agree with the annual oak and pine data than with IntCal13 and show the same offset from the curve as shown by the other annual data between 1650 and 1540 BC (Fig. 2A). They are also valuable in providing an annually based record of \(^{14}\)C fluctuation from the Mediterranean region in this time period relevant for the Thera eruption. While no large-scale localized offsets in \(^{14}\)C are evident, for the years where contemporary oak (30), pine (29), and juniper measurements from the same laboratory can be directly compared (1680 to 1580 BC) (Fig. 2), the Mediterranean juniper is offset from the Irish oak by +9.0 ± 3.5 \(^{14}\)C years, whereas they are only +3.4 ± 2 \(^{14}\)C years different from the North American pine. While this slight difference is within the stated measurement errors, it is possible that the closer agreement between the pine and juniper may reflect a shared, more southerly latitude than the Irish oak (see also ref. 30). These data agree with the findings of ref. 46, however, that there is no major regional offset in the period. We also note that the data in Fig. 2A indicate that, around the period of lower solar activity (higher \(\Delta^{14}\)C; c. 1600 BC) and during the period of more rapid \(^{14}\)C production (c. 1540 to 1528 BC), there is no significant difference between the multiregional annual \(^{14}\)C data, which might be related to the growth season. We do, however, note the possibility of a localized excursion in \(^{14}\)C around 1548 BC. This requires further investigation as, if it is not an analytical outlier, it could represent an influx of “old carbon” into the environment, potentially consistent with a volcanic eruption such as Thera.

The validity of the dated position produced by \(\chi^2\) analysis (745 ± 4 BC at a 95.4% confidence level) (\(\chi^2\) Appendix, Fig. S2) and supported by annual \(^{14}\)C pattern matching around the 1528 BC \(^{14}\)C excursion was then independently tested using the previously described correlation between years of known eruptions, calendar-dated bristlecone pine frost-ring years, and wide tree rings in Mediterranean sequences. We hypothesized that, if our temporal placement of the juniper chronology was correct at 745 ± 4 BC, then it should show wide rings in the year of or following a bristlecone pine frost ring. On this basis, superposed epoch analysis (SEA) was used to test the significance of the effects of a mean tree-ring response to the proxy record of volcanic forcing across the full Bronze–Iron Age juniper chronology (17) in the adjusted position suggested by this study. In this position, the SEA analysis showed significantly \((P < 0.05)\) wider rings than would be expected by chance in the Mediterranean chronology in the year following a bristlecone frost ring (Fig. 3). This nonrandom association provides strong corroborative evidence for the annual \(^{14}\)C position to, in fact, be correct to the year. Within the 4 years on either side of the 745 BC dating placement (error ±4), no other positions provide this strong association. This provides additional support that the position of the Gordian chronology determined by the \(\chi^2\) analysis is indeed correct to within 1 year and allows us to derive an exact calendar-dated position for the tree-ring series.

Having arrived at a secure date range for the tree-ring series, we made multiple scans using a desktop ATLAS Micro-X-ray Fluorescence unit across the transverse surface of a subsample of GOR-76. The scans covered the period from c. 1630 to 1500 BC. These revealed a single major disturbance of the element calcium (Ca) around 1560 BC (Fig. 4 and SI Appendix, Fig. S3). The exact onset of the change may be as early as 1562/1 BC, and the effect appears to last until around 1557 BC. Other analytical techniques will be used to refine this temporal association. Ca is an essential element in wood that is needed to support fundamental biological functions, including cell membrane stability and stress response. Declines in tree-ring Ca have previously been associated with drought (47); however, in this case, the growth rings that feature the depletion are not unusually narrow (as would indicate drought). A forest fire response is also a possible explanation, and this can manifest as either an increase of Ca as it becomes more available for uptake after burning (47) or as a depletion where areas of the sample are scarred (48), but again, the tree-ring growth pattern does not indicate a growth release or scar typical of fire impact.

Alternatively, Ca can be reduced in tree rings following foliar exposure to acid mist or other such precipitation (49, 50). Therefore, the finding of a Ca depletion is consistent with the impact of volcanically induced acid deposition [reported in lake sediments as a result of the Thera eruption (22)]. On its own, this Ca response in a single tree might not be worth reporting; however, the date around which it occurs makes it worthy of further discussion because 1560 BC also coincides with evidence for volcanic impact indicated in two other records. Subfossil pine trees from a calendar-dated record in Finnish Lapland indicate a possible eruption immediately preceding 1560 BC in the form of a negative departure in \(\delta^{13}\)C, which has been shown to correlate with periods of reduced visibility due to volcanic acid fog (51). The high-altitude bristlecone pine record also includes an indicator year at 1560 BC along with 4 other years in the 16th century BC when unusually narrow growth or frost-damaged cells are recorded. These dates (1597, 1560, 1546, 1544, and 1524 BC) are all indicative of major volcanic eruptions, the

![Fig. 3. SEA—departures of actual (larger than average growth rings) from 1,000 simulated events based on bristlecone pine frost rings from the full 1,979-year Bronze–Iron Age juniper chronology (17) and now placed in time relative to a 745 BC end date for the Gordian sequence (which is a subset of the full chronology). Departures represent 95% confidence limits. In the 745 BC position, a significant (\(P < 0.05\)) positive growth response in the Mediterranean trees shows the year after frost rings (eruptions).](image-url)
Fig. 4. A high-resolution XRF scan of the transverse section of GOR-76 featuring an unusual depletion of the element Ca. The mapped area was identified as the only significant elemental anomaly in the 16th century BC growth rings from this sample (a longer scan area is provided in SI Appendix, Fig. S3). This scan shows that a calcium depletion occurs from around 1562 to 1558 BC and is centered on an unusually wide, slightly pale in color growth ring at 1560 BC. A similar wide, pale ring occurs in 1550 BC but does not indicate the same degree of depletion.

Calcium XRF map

Sample image

Calcium intensity

Low

High

2mm

origins of which are not yet known. The coincidence of these two additional records around 1560 BC makes further investigation essential. The apparent increase in old carbon around 1558 BC also requires further exploration as, although the tree grew several 100 km from the eruption, this too could hypothetically connect with the Thera eruption, and all potential indicators should be explored. We note, however, that 1560 BC is more recent than indicated likely for the chemical change associated with the Thera eruption at Sofular cave (23) and older than is indicated likely for the event via certain lines of archaeological evidence (26, 52). Nevertheless, these findings clearly merit further careful investigation to define better the onset and duration of the response and to see if it can be replicated in other trees and expanded via the detection of other more clearly volcanogenic (or otherwise) elemental markers.

Conclusion

This study shows that, even in the absence of a large-scale interannual 14C excursion (such as at AD 774/775), comparing the fine structure in annually derived 14C time series via a range of approaches can offer a way to improve the dating precision and accuracy possible for floating tree-ring sequences previously dated by conventional radiocarbon wiggle matching to the IntCal calibration curve. First, critically, matching based on two annual 14C time series (one of which is calendar dated via dendrochronology) offers a dated position for the floating sequence, which is fixed. This differs from modeled dates via conventional radiocarbon wiggle matching, which may change with new iterations of the calibration curve. Second, χ2 testing of longer annually based time series can refine dating for floating tree-ring sequences to a precise year within a ±4-year range, and this can be visually tested and confirmed across small-scale 14C features (such as at 1528 BC). Third, as is the case in this study, additional proxy information can be used to refine the dating further. We found that other tree-ring associations strongly suggested that the dating indicated by the annual 14C-matching approach yielded a result that was in fact accurate to within 1 year. This combination of methods opens up opportunities to anchor floating tree-ring sequences in time outside the capacity of standard dendrochronological techniques, demonstrating potential to fill in a range of critical temporal and geographic gaps in the tree-ring record.

Anchoring the Gordion tree-ring series more securely in time is an important contribution to improving timelines in the ancient East Mediterranean and maximizing the potential of this record as a paleoenvironmental resource. The first step toward this is the identification of the calcium anomaly around 1560 BC, which while clearly requiring replication and much further substantiation, opens up potential that may now be pursued toward finding an exact date for Thera.

Materials and Methods

Subsamples of Juniperus excelsa wood from the East Mediterranean Bronze–Iron Age tree-ring chronology were taken from Log #7 from the base of the eastern outside wall of the Midas Mound Tumulus (also identified as “GOR-76”) and GOR-161 from Kizilarkaya Tumulus A from the University of Arizona Tree-Ring Archive. These were remeasured and checked against the Gordion master chronology. The security of the dendrochronological placement for these trees has been repeatedly reaffirmed, and various subsamples have been taken in previous studies on 10- to 11-year blocks (18), providing a laboratory intercomparison for data quality control. Relatively dated rings beginning with relative year 834 were dissected in a single continuous sequence using a binocular microscope and steel blade. In each case, the whole tree ring, both early and late wood, was dissected.

The wood samples were converted to holocellulose at the University of Arizona Accelerator Mass Spectrometry (AMS) Laboratory one sample at a time (29, 30). This involved standard 1 N HCl/NaOH/HCl extractions at 70 °C followed by a holocellulose extraction at the same temperature using a bleaching solution made from sodium chlorite, HCl, and water. The dissection method generated submillimeter-thick chips with large surface areas and short diffusion distances that facilitated the uptake of reagents and the extraction of contaminants to produce pure white holocellulose. Samples were combusted to CO2 and converted to graphite using standard procedures (53); then, they were measured using a National Electrostatics Corporation AMS system operated at a terminal voltage of 2.5 MV. The 14C/12C ratio of each sample was compared with National Institute of Standards and Technology standards SRM4990B and 4990C, and the resulting fractionation was corrected to a Δ13C value measured offline on a stable isotope mass spectrometer.

The χ2 matching was carried out using a weighted mean of oak and bristlecone pine data vs. the juniper sequence positioned as per radiocarbon dating (18) as a starting position. Data points outside 3σ were removed from the Gordion juniper sequence (n = 5). For the SEA, each year in a list of event dates, in this case years with prominent frost rings in upper tree-line bristlecone pine from three mountain ranges in western North America (54), was taken as a key or zero-window year. Chronology values for the key years and for windows of years, in this case 5 years before and 5 years after key years, were expressed as departures from the mean. The departures for all of the 11-year windows were superposed and averaged. A Monte Carlo simulation technique was used to assess statistical significance. One thousand simulations were performed by random sampling with replacement (55) to determine the probability associated with the average departures for the frost-ring (proxy volcano) dates. The SEA was conducted using the program EVENT version 6.02P (http://www.ltrr.arizona.edu/software.html).

The SEA used a set of 18 key years when frost rings occurred in multiple samples from 2656 to 668 BC, the current length of the full Bronze–Iron Age Mediterranean chronology (17).

The X-ray fluorescence (XRF) elemental mapping was collected using iXRF System’s Atlas Micro-XRF unit, with a primary excitation source of 50 kV/50 W/1 mA and a rhodium target. Multiple scans were made of sample GOR-76
at a range of resolutions and dwell times. The scans presented in this study used a 10-μm spot size and had a 20-μm point dwell under vacuum. The Atlas Micro-XRF uses X-rays to excite the surface of the sample, producing characteristic X-rays that are at measurable energies specific to the elements present. By moving the sample under the X-ray source in a precise, organized fashion, a qualitative elemental map is produced.

Dendrochronological cross-matching statistics for the Gordon tree-ring chronology and specific samples used in this study are published in ref. 18. Full data and metadata for oak and pine annual C\textsubscript{14} sequences used for comparison with the juniper data presented in SI Appendix, Table S1 are published in refs. 29 and 30. SI Appendix also contains further detail for wiggle matching (SI Appendix, Fig. S1) and χ\textsuperscript{2} analysis (SI Appendix, Fig. S2) plus additional XRF data and metadata (SI Appendix, Fig. S3).

Physical samples are archived at the Laboratory of Tree-Ring Research, University of Arizona.

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