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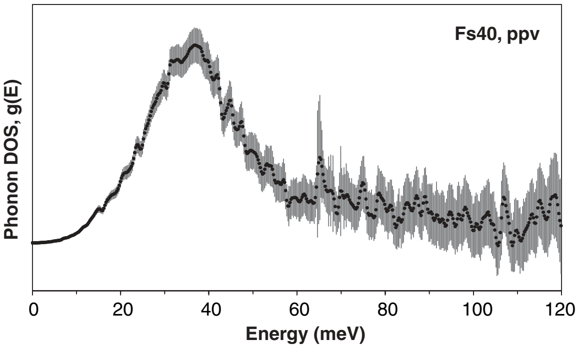

Fig. 3. NRIXS spectra showing the phonon DOS for ppv phase of Fs40 at 130 GPa after temperature quench from 2000 K.

(Fig. 2). We found that ρ = 6.08 g/cm^3, K = 792 GPa, and V_Φ = 11.43 km/sec at 130 GPa.

For the NRIXS experiment (*14*), we used a panoramic diamond-anvil cell to synthesize the Fs40 ppv sample at 130 GPa and 2000 K. After confirming the formation of ppv by x-ray diffraction at beamline 16-IDB, we carried out the NRIXS experiment at ambient temperature at beamline 3-ID of the APS. NRIXS spectra were collected in situ and converted to give the partial (Fe-related) DOS (*15*) (Fig. 3). The Debye sound velocity (V_D) was found to be 5.51 ± 0.03 km/sec from a fit to the low energy (long wavelength) portion of the DOS to a parabolic function (*16*). Using Eqs. 2 and 3 and our V_Φ and V_D values, we determined V_P = 12.72 ± 0.12 km/s, V_S = 4.86 ± 0.03 km/s, and ν = 0.41 ± 0.01 for Fs40 ppv at 130 GPa and 300 K. These parameters are close to those in the ULVZ at high temperature (Table 1).

Based on a first-order approximation of $\partial V/\partial T$ = –0.0003 km/s-K (*17*), temperature correction to the CMB conditions will reduce the velocities and increase the Poisson's ratio of Fs40 ppv beyond the ULVZ values (Table 1). Lower $FeSiO_3$ content than 40% or additional solid phases such as magnesiowüstite will bring the values into agreement with those observed in ULVZ. The present results indicate that the addition of Fe is sufficient for explaining seismic features of ULVZ, thus providing an alternative explanation to partial melting.

At the CMB, the silicate is in contact with the liquid Fe alloy. A 10- to 100-m-thick, reaction veneer of the Fe-rich ppv silicate could form at the interface through static, diffusive process alone. However, the CMB can hardly be regarded as static. We can expect turbulence, shear-induced dilation (*18*), and infiltration to promote local reactions to the kilometer levels. The Fe-rich ppv would be too heavy to rise in the mantle and would pile up beneath upwelling areas to form seismically observable ULVZ patches that could correlate with active hot spots and upwelling areas (*19*–*21*). With such a cumulative mechanism, we could also expect relics of ULVZ that do not correlate with the present day upwelling [for examples, see (*4*, *22*)] but reveal geodynamic patterns in Earth's history.

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Chronology for the Aegean Late Bronze Age 1700–1400 B.C.

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Radiocarbon (carbon-14) data from the Aegean Bronze Age 1700–1400 B.C. show that the Santorini (Thera) eruption must have occurred in the late 17th century B.C. By using carbon-14 dates from the surrounding region, cultural phases, and Bayesian statistical analysis, we established a chronology for the initial Aegean Late Bronze Age cultural phases (Late Minoan IA, IB, and II). This chronology contrasts with conventional archaeological dates and cultural synthesis: stretching out the Late Minoan IA, IB, and II phases by ~100 years and requiring reassessment of standard interpretations of associations between the Egyptian and Near Eastern historical dates and phases and those in the Aegean and Cyprus in the mid–second millennium B.C.

The second millennium B.C. saw several major civilizations develop in the Aegean (Greece, Crete, and Anatolia) and on Cyprus, which became integrated into the trading and cultural worlds of the ancient Near East and Egypt. The analysis of these civilizations and their relationships depends upon an accurate chronology that establishes linkages and developmental frameworks. Chronologies for Aegean and east Mediterranean cultures during the second millennium B.C. have usually been derived from comparisons of artifact and style associations with those in the Near East, which can be related to the approximate historical chronologies of Egypt or Mesopotamia (*1*, *2*). Where there were extensive cultural exchanges, this approach seems sound, particularly during the Amarna period in the mid–14th century B.C. and again, but a little less clearly, during the Middle Kingdom period in the 19th to 18th centuries B.C. (*2*). But chronologies for other periods, including the initial Late Bronze Age, are ambiguous. This time marked the acme of New Palace civilization on Crete, the Shaft Grave period on mainland Greece, and the development of major new coastal polities on Cyprus.

Existing carbon-14 (^{14}C) dates for materials linked to the earlier Late Bronze Age cultural phases on Crete (Late Minoan IA, IB, and II, which are abbreviated as LMIA, LMIB, and LMII, respectively) or the associated Aegean region generally indicate ages older than expected. One critical tie point is the age of the Santorini eruption, which distributed tephra widely across the region. This event is placed in the mature or late LMIA phase and has conventionally been dated ~1525–1500 B.C. (*1–6*), but for 30 years ^{14}C dates have yielded earlier ages around 100 years older, leading to controversy (*7–15*).

We identify four key areas as central to resolving the current debate: (i) provision of robust, consistent, high-quality ^{14}C data by more than one laboratory; (ii) calibration of the ^{14}C evidence with the latest high-precision data sets, but also tests to show that outcomes are robust enough not to be sensitive to small changes in the calibration curve; (iii) consideration of whether volcanic CO$_2$ emissions may have affected ^{14}C ages obtained from Santorini; and (iv) appropriate, holistic analysis integrating ^{14}C data, archaeological information, and the ^{14}C calibration curve.

Here, we report a ^{14}C chronology for the Aegean at the beginning of the Late Bronze Age and for the wider region in the mid–second millennium B.C. (*16*). We focused on short-lived samples, which should offer ages contemporary with their use, obtained sets of ages from the successive stratigraphic phases from LMIA through LMII, and used multiple-set simultaneous calibration [using Bayesian modeling (*17*, *18*)] to resolve single-case dating ambiguities caused by the irregular shape of the ^{14}C calibration curve. Such a time-series comparison to the ^{14}C calibration curve also controls against any significant contamination (e.g., by volcanic CO$_2$), because affected data should not offer a good fit.

We sampled sites in the southern Aegean region (fig. S1), including Santorini, from the LMIA, LMIB, and LMII phases to obtain 100 ^{14}C dates (table S1) and selected for contexts where a minimum of two dates could be obtained (to try to obtain some control on reproducibility and outliers). We also included 27 previously published high-quality dates from the same or very similar samples (*19–21*) (table S1). Dates were analyzed by using the IntCal04 ^{14}C calibration curve (*22*). We studied the robustness of the conclusions by varying the data sets, the stratigraphic model, and the calibration curve itself [with use of IntCal98 (*23*)].

To establish data quality, we divided 17 of our Aegean Late Bronze Age samples, either identical tree-ring fractions or groups of same species seeds from the identical prehistoric storage container, between the Oxford and Vienna laboratories. In addition, one prehistoric wood-charcoal sample and one more recent known-age tree-ring sample were divided between Oxford and Heidelberg and between Vienna and Heidelberg, respectively. The Oxford-Vienna data, 23 measurements from Oxford (where six samples were in fact measured twice, independently, on two different accelerators) and 17 measurements from Vienna, corresponded well, with a mean difference of only 11.7 ^{14}C years (Fig. 1). Just 2 of the 17 pairs offered divergent outcomes at the 95% confidence level using a χ^2 test [sample key 7, where $T = 5.6 > 3.8$, and sample key 15, where $T = 22.5 > 3.8$ (*16*)]; the sample key 15 case offered the only clear disagreement between the laboratories: This sample is an irrelevant early *terminus post quem* date, so its inclusion or exclusion makes no difference to our analyses below. The Oxford-Heidelberg pair returned almost identical data. The five Vienna measurements on the same tree-ring decade show a tight scatter of results with the mean close to the Heidelberg high-precision estimate, and all the constituent data include the known dendro-age within their 1σ (68.2% confidence) calibrated calendar age ranges (fig. S6). These comparisons support the accuracy of our Aegean ^{14}C measurements.

Our measurements include 13 different short-lived samples (groups of seeds) from four larger seed samples recovered in situ from prehistoric storage containers found in the volcanic destruction level (VDL) on Santorini (samples shown as 16 to 19 in Fig. 1 from Akrotiri, Thera). An issue sometimes raised with regard to ^{14}C measurements from the final VDL on Santorini is whether volcanic CO$_2$ might be affecting the samples and producing ages that are too old (*15*). Such volcanic effects, when observed (*24*, *25*), are typically only relevant either close to a vent or in low-lying areas or sinks. It is possible that some of the samples found at Akrotiri on Thera could have been so affected, although none from secure VDL contexts exhibit the large old-age offsets typical of such contaminated samples. However, it would seem unlikely that all the VDL samples from different pots and different crops were consistently affected. Our data, and other published Santorini VDL data available as the result of measurements on full seeds, groups of seeds, or a short-lived twig (*19–21*), n = 28, show a consistent age of 3344.9 ± 7.5 ^{14}C years before the present [^{14}C yr B.P. from A.D. 1950 (*23*)], which equates to 1683–1611 B.C. at 2σ confidence with the use of IntCal04 (*22*) (Fig. 2B). Samples from Miletos (western Turkey) and Trianda (Rhodes) yield ages compatible with those from LMIA on Santorini (Fig. 2A and table S1). As a further test, we modeled the Santorini VDL age range excluding all data from Santorini, avoiding any possible volcanic effect. This placed the VDL at 1668–1585 B.C.

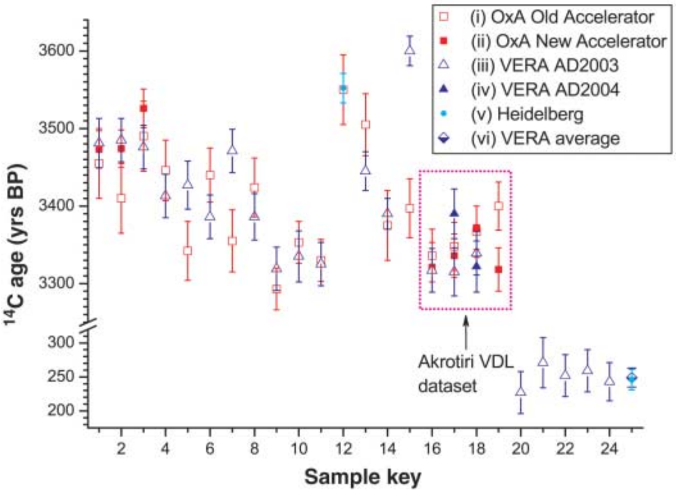

Fig. 1. Comparison of ^{14}C age estimates for fractions of identical Aegean samples between (i) Oxford Old Accelerator (samples measured from A.D. 2000–2002), (ii) Oxford New Accelerator (measured in A.D. 2003), (iii) VERA (measured in A.D. 2003), (iv) VERA (measured in 2004), and (v) Heidelberg. The weighted average of the five VERA measurements on a sample of known age wood are shown (vi) as compared to the Heidelberg measurement of the same sample. Sample key includes the following samples: 1, Trianda AE1024 rings 21 to 30; 2, Trianda AE1024 rings 11 to 20; 3, Trianda AE1024 rings 1 to 10; 4, Akrotiri M4N003 rings 6 to 8; 5, Akrotiri M4N003 rings 3 to 5; 6, Akrotiri M4N003 rings 7 and 8; 7, Akrotiri M4N003 rings 5 and 6; 8, Akrotiri M4N003 rings 3 and 4; 9, Akrotiri 65/N001/I2 ring 3; 10, Akrotiri 65/N001/I2 ring 2; 11, Akrotiri 65/N001/I2 ring 1; 12, Akrotiri M54/2/VII/60/SE>247; 13, Kommos K85A/62D/9:92; 14, Kommos K85A/66B/4:22+23; 15, Kommos K85A/62D/8:83; 16, Akrotiri M31/43 N047; 17, Akrotiri M2/76 N003; 18, Akrotiri M7/68A N004; 19, Akrotiri M10/23A N012; 20 to 24, Çatacık tree rings A.D. 1640 to 1649; and 25, weighted average VERA Laboratory data (samples 20 to 24) versus Heidelberg measurement of same sample. Samples 20 to 25 also offer a known-age test. All five VERA ^{14}C measurements included the correct calendar age range within their 1σ calibrated ranges (*17*, *22*), as does the VERA weighted average and the high-precision Heidelberg measurement. Error bars indicate 1σ ranges.

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(2σ) and 1659–1624 B.C. (1σ) (Table 1 and fig. S5), consistent with results including the Santorini data (Fig. 2 and Table 1).

We constructed Bayesian models for the analysis of the sets of LMIA to II age determinations. The models account for the stratigraphic order of the samples implying a definite chronological sequence and include variable parameters like boundary dates of phases. The analysis calculates how successfully the ^{14}C measurements conform to the prior knowledge of the chronological sequence and yields estimates for parameters and narrowed (constrained) dates for the ^{14}C samples (*16*). In model 1, we represent the archaeological data as simply reduced to the secure evidence, with the criteria being two or more data comprising each specific grouping or sample set (Fig. 2A). No interpretative development has occurred in this model. We considered other more refined models or variations (*16*), and the outcomes were similar in all cases (figs. S2 to S5 and table S3).

The sequence model (Fig. 2A) offers a coherent chronology from LMIA through LMII. This model includes two tree-ring samples where defined sequence (D_Sequence) analysis (so-called wiggle matching, WM, where the time differences of the elements within the sequence are exactly known) was possible; these samples help set *terminus post quem* (tpq) ranges for the late Middle Bronze Age and/or early LMIA phase, respectively, and for the specific Akrotiri VDL (*16*). The internal consistency of the Aegean archaeological sequence and our data over the three centuries compared to the Northern Hemisphere atmospheric ^{14}C record indicates that no unusual offset exists within the Aegean sequence.

All of the ages calculated for the transitions or the events or phases for the LMIA and LMIB phases using OxCal (*17*) and the new internationally recommended IntCal04 ^{14}C calibration data set (*22*), or the previous IntCal98 data set (*23*), are significantly earlier than many previous estimates (*1*–*7*, *11*, *12*, *14*, *15*) (Table 1 and Figs. 2A and 3). This study has obtained dates consistent with, but much more refined than, previous ^{14}C work for the LMIA to II phases and for the Santorini VDL (*7*–*9*, *13*, *26*–*28*) and has demonstrated intra- and interlaboratory comparability. The date for the major Minoan eruption of Santorini (the VDL) is placed in the later 17th century B.C. (Fig. 2B): within the 95.4% confidence range of 1660–1613 B.C. [with 1639–1616 B.C. the most likely subrange looking at the 1σ ranges of 1656–1651 B.C. (P = 0.113) and 1639–1616 B.C. (P = 0.569)] from the analyses using IntCal04 or 1661–1605 B.C. from IntCal98 (Table 1). This age, from short-lived samples stored at the time the town

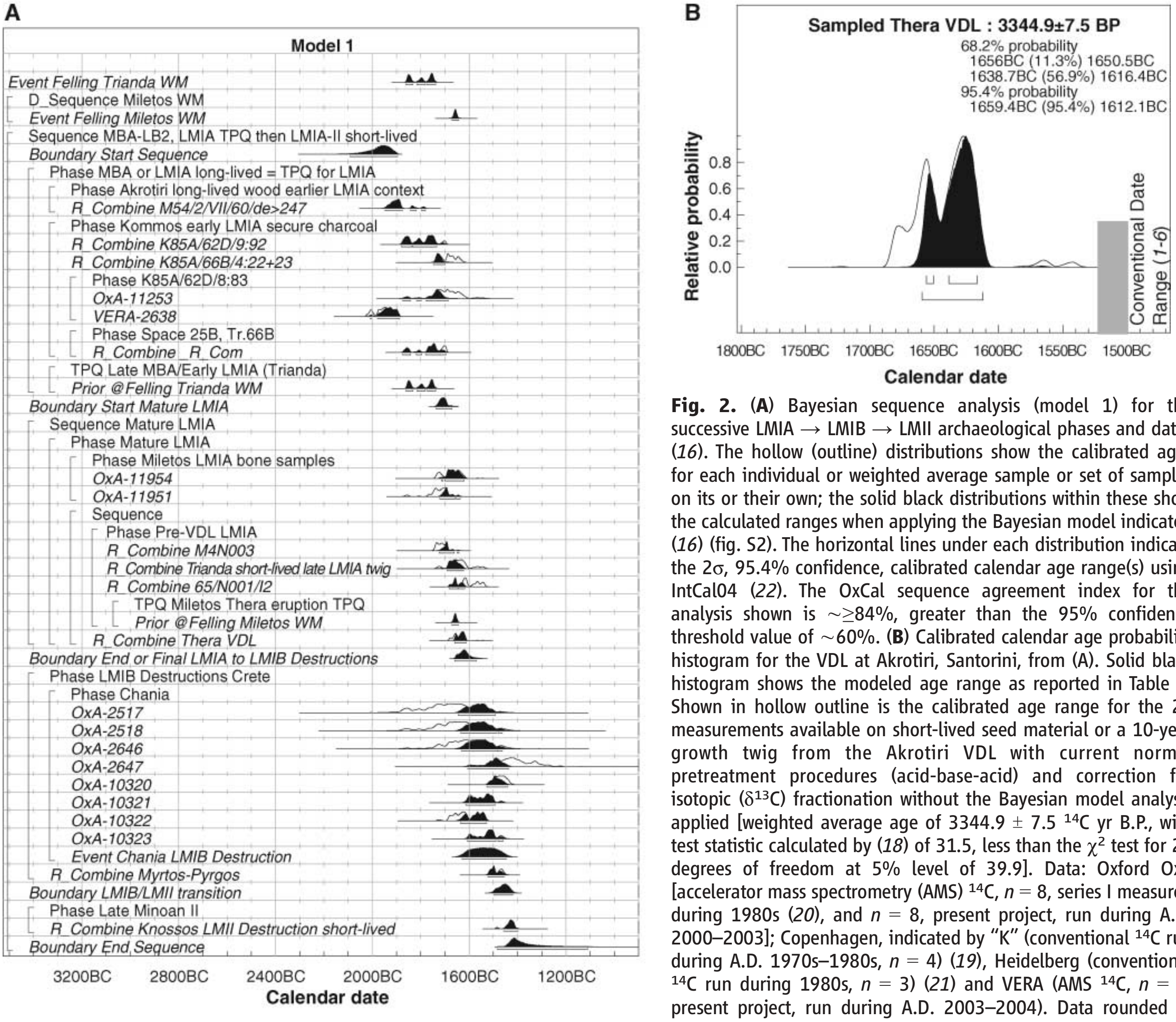

Fig. 2. (**A**) Bayesian sequence analysis (model 1) for the successive LMIA → LMIB → LMII archaeological phases and dates (*16*). The hollow (outline) distributions show the calibrated ages for each individual or weighted average sample or set of samples on its or their own; the solid black distributions within these show the calculated ranges when applying the Bayesian model indicated (*16*) (fig. S2). The horizontal lines under each distribution indicate the 2σ, 95.4% confidence, calibrated calendar age range(s) using IntCal04 (*22*). The OxCal sequence agreement index for the analysis shown is $\sim\geq 84\%$, greater than the 95% confidence threshold value of ~60%. (**B**) Calibrated calendar age probability histogram for the VDL at Akrotiri, Santorini, from (A). Solid black histogram shows the modeled age range as reported in Table 1. Shown in hollow outline is the calibrated age range for the 28 measurements available on short-lived seed material or a 10-year growth twig from the Akrotiri VDL with current normal pretreatment procedures (acid-base-acid) and correction for isotopic ($\delta^{13}C$) fractionation without the Bayesian model analysis applied [weighted average age of 3344.9 ± 7.5 ^{14}C yr B.P., with test statistic calculated by (*18*) of 31.5, less than the χ^2 test for 27 degrees of freedom at 5% level of 39.9]. Data: Oxford OxA [accelerator mass spectrometry (AMS) ^{14}C, $n = 8$, series I measured during 1980s (*20*), and $n = 8$, present project, run during A.D. 2000–2003]; Copenhagen, indicated by "K" (conventional ^{14}C run during A.D. 1970s–1980s, $n = 4$) (*19*), Heidelberg (conventional ^{14}C run during 1980s, $n = 3$) (*21*) and VERA (AMS ^{14}C, $n = 5$, present project, run during A.D. 2003–2004). Data rounded to one decimal place. The total probability of a calibrated calendar age later than ~1600 B.C. is less than 3%. The gray bar shows the conventional date range for the VDL of 1525–1500 B.C. (*1*–*6*).

at Akrotiri was abandoned just before the eruption, should either date the eruption within a year or two or set a close tpq for the eruption a few years later. It is consonant with the independent date of 1627–1600 B.C. at 2σ confidence (1621–1605 B.C. at 1σ) from ^{14}C WM dating of an olive tree killed by the eruption (*29*) (Table 1 and fig. S8). Moreover, our data on short-lived samples from immediately before the eruption yield a contemporary to slightly older age range, demonstrating that this olive tree was last alive around or shortly after the final harvest year represented at Akrotiri, and thus its last preserved ring (bark) provides the best current date for the eruption.

The conventional dates for the LMIA to II phases and for the Santorini eruption ~1525 to 1500 B.C., based on Egyptian contexts and associations, are inconsistent with our findings. This suggests either a defect in the conventional linkages to the Egyptian historical chronology in the mid–second millennium B.C. or a failing in the Egyptian chronology itself. Because the Egyptian historical chronology is widely considered relatively robust and in the 14th century B.C. (Amarna period) it correlates well both with the independent Mesopotamian historical chronology and ^{14}C evidence (*30*–*32*), the problem more likely relates to the interculture linkages in the mid–second millennium B.C. [or, less likely, some chronological flaw affecting specifically mid–second millennium B.C. Egyptian dates (*16*)].

These findings imply that some previously hypothesized dates and associations for the Santorini eruption are now not likely. Suggested dates from tree-ring growth anomalies (*6*, *33*–*36*) remain as yet hypotheses lacking causal connection. The growth anomaly in a group of Aegean trees dated 1650 +4/–7 B.C. (*36*) now seems a little too early to be associated with Santorini. The question of the possibility of a relationship with the 1628 to 1627 B.C. tree-ring growth anomaly widely attested in the Northern Hemisphere (*33*–*35*) remains open but is challenged by the narrow date in (*29*). There is no positive evidence in favor of the suggestion of a 1525 or 1524 B.C. date (*6*), and it is incompatible with our findings and those of (*29*). Suggested dates ~1645 B.C. or otherwise from ice-core evidence (*8*, *37*–*39*) are unlikely or unclear

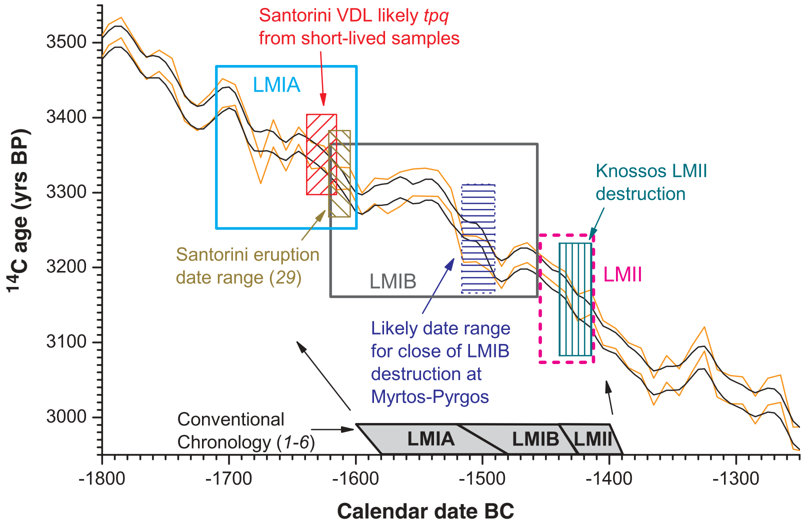

Fig. 3. Schematic representation of the ^{14}C-derived Aegean early Late Bronze Age archaeological chronology summarized in Table 1, Fig. 2, and (*29*) shown against the Northern Hemisphere ^{14}C calibration curve [IntCal04 from (*22*) shown in black as a ±1σ range, and IntCal98 from (*23*) shown in orange as a ±1σ range]. The chronology shows the 1σ ranges, or most likely subelement thereof, from Table 1 for events and a midpoint approximation for the transitions between phases. The latter is only a very approximate guide. Some complications are not addressed (and are not represented in our ^{14}C evidence): for example the suggestion of a short post-Santorini-eruption final phase of LMIA (*1*) (which might move the start of LMIB lower, to around 1600 B.C.), and the transition date between LMIB and LMII is flexible and not well defined. The previous conventional Aegean chronology derived from the standard interpretation of the archaeological and art-historical associations (*1*–*6*) is shown below. The new ^{14}C-derived chronology both begins the Late Bronze Age ~100 years earlier than previously accepted and also substantially lengthens the LMIA and (especially) LMIB and LMII cultural phases.

Table 1. Typical Bayesian analysis outcomes for model 1 (average 10 runs). The 2σ, 95.4%, confidence calibrated calendar date ranges B.C. calculated by the analysis shown in Fig. 2 are listed for a number of the key transitions or events or phases within the LMIA to LMII archaeological sequence. The 1σ (68.2% confidence) ranges with IntCal04 (*22*) are also shown in the first row of data marked with asterisks. Data rounded to the nearest whole year. Typical data given (each computer run of the model varies very slightly, with variation usually ≤2 years; quoted probabilities also vary slightly by run). Results against the IntCal98 ^{14}C calibration data set, which was derived from similar underlying data but by a different modeling procedure (*23*), are also shown; the outcomes are very similar, which demonstrates the robustness of the conclusions irrespective of such minor changes in calibration data set. We further show results for (i) model 1 without any data from Santorini included, and the VDL calculated as an event within the sequence (fig. S5). The modeled placement for the VDL is entirely complementary with the data from Santorini, demonstrating that no offset effect applies to the Santorini data, which may therefore be used with confidence. (ii) Model 1 adding the Santorini olive tree WM information (*29*) (eruption event 1627–1600 B.C. at 2σ). The bottom row shows the conventional archaeologically derived dates (*1*–*6*) for comparison.

	Transition to mature LMIA	Felling date Miletos oak	Akrotiri VDL	Transition end LMIA to LMIB	Myrtos-Pyrgos close of LMIB destruction	Knossos LMII destruction
Model 1, IntCal04 (*22*)	1737–1673 1722–1695*	1671–1644 1664–1652*	1660–1612 1656–1651 (11.3%)* 1639-1616 (56.9%)*	1659–1572 1647–1644 (3.1%)* 1642–1603 (65.1%)*	1522–1456 1517–1491 (58.1%)* 1475–1467 (10.1%)*	1457–1399 1439–1414*
Model 1, IntCal98 (*23*)	1733–1665	1669–1646	1661–1605	1660–1567	1522–1487 (65.3%) 1482–1451 (30.1%)	1489–1480 (3.6%) 1452–1394 (91.8%)
Model 1, no Santorini data, IntCal04 (*22*)	1728–1643	1672–1645	1668–1585	1661–1553	1522–1456	1487–1481 (1.3%) 1457–1400 (94.1%)
Model 1, adding (*29*) data (fig. S8), IntCal04 (*22*)	1737–1673	1671–1644	1654–1649 (3%) 1645–1611 (92.4%) 1σ: 1633–1617*	1626–1562	1522–1457	1487–1480 (1.5%) 1458–1400 (93.9%)
Conventional chronology (*1*–*6*)	1600/1580		1525/1500	1520/1500/1480	1440/1430/1425	1400/1390

given recent critical discussions of associations, provenience of volcanic glass shards recovered, and the exact dates of the relevant ice-core layers (*39–41*). This age is also a little old given our findings and especially those in (*29*). Other work has argued that this 1645 B.C. record may instead reflect an eruption of Aniakchak (*40*). Allied with previous arguments for Santorini's relatively modest SO_2 output (*42*), the search for Santorini tephra in Arctic ice-core records should now focus on some of the (smaller) volcanic signals particularly in the late 17th century B.C., such as that of ∼1622 to 1618 B.C. (Dye 3 ice core or Greenland Ice Core Project ice cores) (*37*).

Our findings are consonant with the so-called "high" Aegean chronology, which suggests a reinterpretation of some of the cultural linkages (*10*, *13*). The chronology places the formation and high point of the New Palace period of Crete (Middle Minoan III to LMIA), the linked Shaft Grave period of the Greek mainland (late Middle Helladic and Late Helladic I), and the closely associated Middle Cypriot III–Late Cypriot IA phase on Cyprus all before ∼1600 B.C. These phases are thus contemporary with the world of the later Middle Bronze Age of the Levant and into the Second Intermediate Period in Egypt [∼1650 or 1640 to 1540 or 1530 B.C., when northern Egypt was controlled by a Canaanite dynasty with links to the Levant (*43*)], not the earlier New Kingdom (18th Dynasty, ∼1540–1295 B.C.) period of Egypt as long thought (regarding especially LMIA, Late Helladic I, and Late Cypriot IA). This chronology, and the 100-year shift in associations, in turn implies a reevaluation of previous culture-history and art-history assumptions and frameworks. For example, the well-known wall paintings unearthed at Akrotiri, Thera (*44*) need to be assessed in terms of contemporary 17th century B.C., and not later 16th century B.C., work in the east Mediterranean and Levant.

The difference between the Aegean ^{14}C-based dates and archaeological dates is not constant across the second millennium B.C. Instead, by the LMII phase (late 15th century B.C.) the ^{14}C and archaeological dates are close, and other work indicates good agreement between them for the 14th to 13th centuries B.C. (*32*, *45*, *46*). Our evidence is compatible with the well-established conventional linkages between Old Palace (Middle Minoan, MM, IB to II) Crete and 12th and 13th Dynasty Egypt in the 19th and 18th centuries B.C. (*1*, *2*, *7*). The period (MMIII through LMII), originally interpolated between well-based archaeological associations linked with the Middle Kingdom (19th–18th centuries B.C.) and Amarna (mid–14th century B.C.) periods, alone needs revision, and LMIA to II is here suggested to date within the bounds ∼1710–1410 B.C. (from likely 1σ ranges in Table 1 and Fig. 3) instead of ∼1600 or 1580 to 1400 or 390 B.C. (*1–6*). (MMIII is left to be interpolated as a relatively short phase lying in the mid– to late 18th century B.C.) The date range for the later LMIB destruction horizon at Myrtos-Pyrgos 1522–1456 B.C. (2σ) and the likely LMIB-LMII transition ∼1450 B.C. (Figs. 2 and 3) are consistent with the long-held correlation of part of this ceramic phase (or its mainland coeval phase of Late Helladic IIA) with the early New Kingdom in Egypt (which begins ∼1550 or 1540 B.C.) and into the reign of Tuthmosis III (1479–1425 B.C.) (*1–3*, *5*, *7*, *11*). However, our dates show that the overall LMIB and LHIIA phases began earlier, and so were much longer, than previously thought. The overall New Palace period of Crete (MMIII to LMIB), when the island dominated Aegean trade and culture, is thus found to be a very long era (>250 years) (Fig. 3).

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