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# Dendrochemical analysis of a tree-ring growth anomaly associated with the Late Bronze Age eruption of Thera

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ABSTRACT

The most marked tree-ring growth anomaly in the Aegean dendrochronological record over the last 9000 years occurs in the mid 17th century BC, and has been speculatively correlated with the impact of the Late Bronze Age eruption of Thera (Santorini). If such a connection could be proved it would be of major interdisciplinary significance. It would open up the possibility of a precise date for a key archaeological, geological and environmental marker horizon, and offer a direct tie between tree-ring and ice-core records some 3600 years ago. A volcanic explanation for the anomaly is highly plausible, yet, in the absence of a scientifically proven causal connection, the value of the proposed correlation is limited. In order to test the hypothesis, dendrochemical analysis via Synchrotron Radiation Scanning X-ray Fluorescence Microscopy (SXFM), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) was carried out on growth-ring series from four trees displaying the anomaly. Increases of sulfur, calcium, and rare earth elements following the onset of altered growth, plus concentration spikes of zinc and hafnium in the first affected growth-ring provide promising new evidence in support of a volcanic causal factor. Although a volcanic association is implied, the new data are not sufficient to prove a link to the exact eruption source.



## 1. Introduction

During the Late Bronze Age a major explosive eruption of the Aegean volcanic island of Thera (Santorini) propelled a layer of ash and pumice across the eastern Mediterranean (Guichard et al., 1993). The known and speculated impact of this event ranges from the burial of local towns and villages (Doumas, 1992, 1983), to tsunamis and the collapse of Minoan civilization on Crete (Bruins et al., 2008; McCoy and Heiken, 2000b), to a range of climatic disturbances around the globe (Grudd et al., 2000; Baillie and Munro, 1988). While many such assertions are themselves the subject of dispute (Eastwood et al., 2002; Pyle, 1997), it is the exact date of the eruption which continues to raise major controversy (Wiener, 2007; Bietak, 2003; Warren, 1999), as the volcanic deposition layer provides a unique stratigraphic time marker with potential to resolve the chronology of the eastern Mediterranean region.

Radiocarbon evidence puts the eruption between 1660 and 1600 BC (Manning et al., 2006; Friedrich et al., 2006). Whilst this evidence, produced by two independent research teams, is compelling, an *absolute* date, the actual year in which the eruption took place, would provide the most useful and appropriate starting point for any analysis of subsequent impact on society and climate. The dendrochronological record offers the potential for such absolute (precise and accurate) dating to a specific annual growth season.

Over the years, tree-ring records around the globe have yielded short-lived anomalous changes in growth connected via modern proxy to the impact of short-term perturbations in climate occasioned by Plinian volcanic eruptions (Robock, 2002; Robock and Mao, 1995). For the early Late Bronze Age period, two notable clusters of such growth anomalies occur.

In 1627/1628 BC narrow growth or frost events are found in North European (Grudd et al., 2000; Baillie and Munro, 1988) and North American (Salzer and Hughes, 2007; LaMarche and Hirschboeck, 1984) dendrochronological records. These have been correlated with acidity horizons in the GISP2 (Zielinski et al., 1994) and Dye 3 (Clausen et al., 1997) ice cores, and are supported by the

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1627–1600 BC date range (Friedrich et al., 2006) derived from an olive tree buried by eruption debris. The accuracy of this narrow date range has been questioned, however, due to major difficulties inherent in identifying annual growth increments in olive wood (Vinther et al., 2008).

Around 1645 BC, (within the broader radiocarbon range of Friedrich et al., 2006 and Manning et al., 2006), a second cluster of anomalous growth events includes North American, Siberian and Finnish ring width minima in 1652 BC and 1648/1649 BC, and a frost damaged bristlecone pine ring in 1653 BC (Salzer and Hughes, 2007; Hantemirov and Shiyatov, 2002; Eronen et al., 2002). Again, possible volcanic forcing is evidenced by correlation with a significant acidity horizon around 1642 ± 5 BC in the Greenland ice core record (Vinther et al., 2006, 2008).

While the relevance of any of these specific dates in relation to Thera will continue to be argued (e.g. Denton and Pearce, 2008), what can be agreed upon is that there is evidence to place both volcanic eruptions and climate perturbations at these two points in the early Late Bronze Age.

Within the 16th or early 15th century BC time range favored for the eruption by proponents of conventional archaeological dating (Wiener, 2003, 2007; Warren, 1999), such evidence is more sparsely distributed. Whilst a bristlecone pine ring width minimum in 1597 BC may link with a minor ice-core signal (Salzer and Hughes, 2007), this is not well substantiated. Minima in 1544 BC, 1524 BC and 1418 BC (with frost damage in 1419 BC) have no other proxy correlations, and the latter in particular is far outside the date range suggested by all radiocarbon evidence.

Irrespective of the actual date of the Thera eruption, for an absolute date for any volcanic eruption to ever be proven via the tree-ring width archive, a direct causal connection (as with sulfur and tephra in ice cores) is required between eruption and growth-ring. Dendrochemical analysis offers a potential means by which to investigate the feasibility of proving such a link. The principle that annual tree-rings can retain a sub-sample of the chemistry of the contemporary growth environment is well established (Watmough, 1999; Watmough and Hutchinson, 1996, 1999; Shortle et al., 1997; Robitaille, 1981) though controversial (Hagemeyer, 1993; Lövestam et al., 1990; Watmough, 1999; Zayed et al., 1992; Smith and Shortle, 1996). Whilst the various pathways and physiological controls determining element distribution in the xylem are highly complex and vary between species and with location, dendrochemistry can, and has, proved useful in reconstructing histories of environmental elemental change (Baes and McLaughlin, 1984; Symeonides, 1979; Bondietti et al., 1990; Guyette et al., 1989). Moreover, volcanic eruptions of known date have been traced in previous dendrochemical studies (Hall et al., 1990; Padilla and Anderson, 2002; Pearson et al., 2006, 2005), and a model formalizing the impact of sulfur dioxide-rich volcanic aerosol on metal uptake in trees has been suggested (Ünlü et al., 2005). The potential success of such studies relies upon a wide range of site and tree specific variables, not least of which is proximity to the erupting volcano. Ideally, therefore, the best chance of establishing a dendrochemical link for the Thera eruption would come from analysis of contemporary tree-rings, growing in sufficiently close proximity to the volcano to have received some portion of direct fallout from that event.

Unfortunately, as yet, there is no Aegean equivalent to the long, continuous, absolutely dated tree-ring series for the second millennium BC derived from German and Irish oaks, Swedish pines, or the bristlecone pines of the American southwest. Samples from the Aegean for this critical time period are limited to rare finds preserved at archaeological sites, cross-dated to build floating chronologies and then anchored in time by wiggle-matched radiocarbon dates, rather than by more conventional dendrochronological procedures. Nevertheless, The Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University has such unique samples from the early Late Bronze Age in its collection. Of these, 61 of at least 64 individual trees, represented in over 200 samples from Porsuk, SE Turkey (Fig. 1), display an exceptional short-lived (c. 7 year) growth spike which is by far the most significant growth anomaly to be found in over 9000 years of Aegean tree-rings. Although the exact provenance of the trees from Porsuk is unknown, it is almost certain that they grew c. 5 miles to the south of the site, in the Taurus Mountains, approximately 840 km downwind of Thera (Kuniholm et al., 1992), during the time frame in which, according to the radiocarbon evidence, the Minoan eruption of Thera took place.

The samples, retrieved from the foundations of a Hittite postern gate, preserved in a partially carbonized state in anaerobic conditions (Kuniholm et al., 1992, 2005), include *Juniperus*, *Pinus* and *Cedrus* sp. from two separate building phases. The trees represented range from 19 to 237 years old at the time of the growth spike indicating that the cause was wide ranging, impacting all trees in a mature forest ecosystem at the same point in time. The increase in growth is characterized by a rapid surge to between 200 and 700% of normal growth over the first 3 years, tailing back to previous levels in the next 3–4 years (Fig. 2).

Dendroecologically speaking, the most logical cause for an anomaly such as this would be a sudden, short-term improvement in growth conditions for these trees, specifically to a cooler, moister environment, possibly with increased cloud cover. Although the degree of climatic impact of the Thera eruption has been much argued in the literature (Pyle, 1997; Eastwood et al., 2002), even conservative estimates of sulfur dioxide emissions, the key volcanogenic factor influencing surface temperatures (Rampino and Self, 1982), are predicted to have resulted in 2 or 3 years of slightly warmer winters and cooler summers in high latitudes (Pyle, 1997). Such conditions could have extended the growth season, resulting in the observed short-term improvement in growth. This makes plausible the suggestion of Kuniholm et al. (1996) that this may be the Aegean equivalent to other European growth-ring anomalies attributed to the Thera eruption, especially in light of recent evidence suggesting the eruption may have been larger than previously estimated (Sigurdsson et al., 2006). Indeed, it is difficult to come up with an alternative hypothesis for the cause, given the very unique nature of the anomalous pattern. Short-term anthropogenic alteration of the water table, or thinning of smaller trees and shrubs (facilitating growth of the more mature trees) are possibilities, but are impossible to test further given the lack of exact provenance for the wood samples. The onset of the anomaly, starting with relatively dated ring 854, is currently radiocarbon dated to 1650 BC +4/−7 (Manning et al., 2003, 2001). Given the proximity to Thera, the nature of the growth pattern, and the coincidence of the date, a Theran causal hypothesis appears highly possible. Yet, in the absence of a provable causal connection, such conjecture is of somewhat limited use.

In this paper, high-resolution multi-elemental mapping via Synchrotron Radiation Scanning X-Ray Fluorescence Microscopy (SXFM) in combination with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Mass Spectrometry (ICP-MS) is used for a dendrochemical investigation of the tree-ring anomaly from Porsuk. The volcanic causal hypothesis is tested via an investigation to establish prospects for isolating an elemental marker signature which could be used to positively link the eruption of Thera, or some other event, with the change in growth pattern at this point in time.

## 2. Methods

Samples of *Juniperus* sp. were taken from the archive of the Aegean Dendrochronology Project where they had previously been

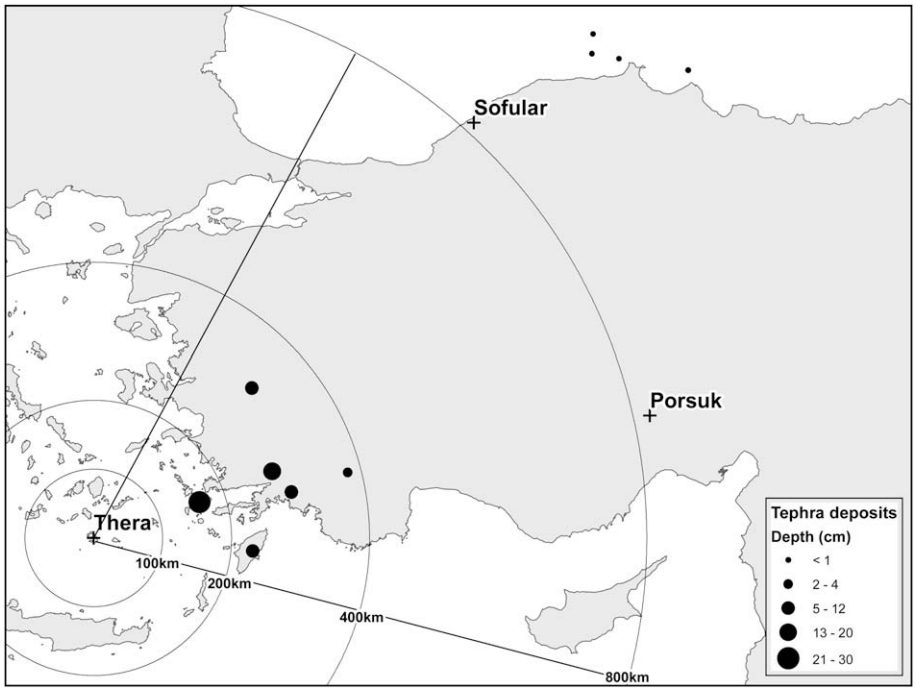


**Fig. 1.** Distance from Thera to Porsuk with known tephra deposition and approximate tephra spread based on data from Eastwood et al. (2002), Sullivan (1988), Guichard et al. (1993), McCoy and Heiken (2000a), and Momigliano (2000). At Sofular Cave, Frisia et al. (2008) report a large spike in sulfur from a speleothem record, which they attribute to the Bronze Age eruption of Thera.

dated both by dendrochronological methods and radiocarbon wiggle-match dating (Manning et al., 2001; Kuniholm et al., 1996). Sections of rings covering the growth anomaly at relative year 854 were extracted with a sterile steel scalpel. Prior to chemical analysis, these subsamples were re-measured and re-surfaced with a sledge microtome to produce a flat, uncontaminated sampling surface. Intensity variations of a suite of elements were measured via SXFM at the F3 bending-magnet beamline at the Cornell High Energy Synchrotron Source. Incident X-ray energies between 10 and 19 keV were selected to maximize the fluorescence of the widest possible range of elements. A 0.3% bandpass monochromatic X-ray beam, using a 15 Å d-spacing $Mo/B_4C$ multilayer double-bounce monochromator was used. The beam was collimated to 1 mm and then focused to 30 μm using a single-bounce capillary focusing optic (Bilderback et al., 2007). To preserve spectral integrity, shields of molybdenum metal were placed around each sample to attenuate fluorescence from anything but the sample. The energy spectra were recorded using a Vortex-90EX single-element energy-resolving silicon-drift detector and multichannel analyzer. Each energy spectrum was collected and analyzed using PyMCA (Solé et al., 2007), a purpose-designed, open-source software package which deconvolves overlapping peaks, determines peak areas and mass fractions for individual elements, and provides an interface for interpretive analysis.

Area scans for four different *Juniperus* sp. trees (C-TU-POR-1, 3, 26 and 167) were made to investigate the physiological distribution of elements within the wood structure, and the spatial/temporal distribution of elements in the growth-rings in and around the anomaly. In addition, individual tree-rings from two of the Porsuk samples were prepared and analyzed via ICP-AES (C-TU-POR-3 and 26) and ICP-MS (C-TU-POR-26) according to methodologies and calibration procedures described in Pearson et al. (2006) and Pearson (2006), in order to detect the widest possible range of elements for interpretation.

Aims were to investigate the temporal/spatial elemental distribution of the wood to assess, first: if the sample appeared to be contaminated by the chemistry of the burial environment; and second: assuming the samples were suitable for further analysis, to compare any elemental change detected at the anomaly between each sample.

## 3. Results

The combination of the three analytical methods resulted in detection of a range of over 30 elements, with some detectable by only one method (e.g. sulfur (S) via ICP-AES or the rare earth elements (REE) via ICP-MS) and others (e.g. calcium (Ca)) replicated by all methods allowing for intercomparison of data series for the same element.

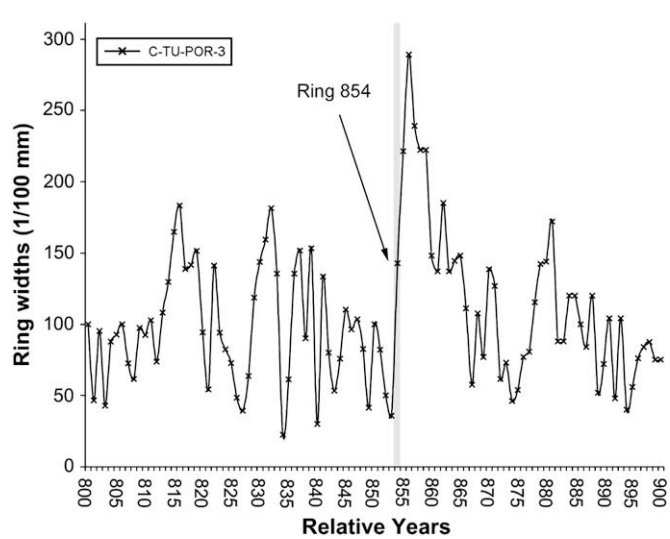


**Fig. 2.** Example of the Porsuk growth-ring anomaly in tree C-TU-POR-3 (191-year sequence).

SXFM elemental maps were produced for potassium (K), Ca, manganese (Mn), iron (Fe), copper (Cu), bromine (Br), rubidium (Rb) and strontium (Sr). Other key elements (e.g. hafnium (Hf), REE) are present in insufficient levels in the wood to be detected by this technique. Observable correlations between element distribution and macro/microscopic characteristics of the wood samples made it possible to discern where elemental changes were most clearly reflecting the chemistry of the cell structure rather than possible contamination in the burial environment. For example, higher intensity Ca, Br, Rb and Sr in the latewood of the growth-rings shows physiological dominance rather than some sort of post burial contaminant. In contrast, correlation of these same elements with dramatically higher intensities towards the outer edge of some of the samples showed the deleterious impact of carbonization and external contamination on any potential elemental record within the tree-rings (see C-TU-POR-1, Fig. 3).

For each of the four samples from Porsuk, increases and/or decreases in intensity for a range of elements occur at the ring 854 growth anomaly. For C-TU-POR-26 and C-TU-POR-3 additional increases, decreases or spikes in concentration were detected via ICP-AES and ICP-MS.

C-TU-POR-1 showed the least discernible elemental response, largely due to high levels of external contamination. This is shown in Fig. 3 for Ca. Significantly higher Ca intensity towards the exterior of the sample makes it difficult to discern a more subtle increase in the latewood of ring 854 and in ring 855.

Ca was the most responsive element detectable by SXFM at the growth-ring anomaly. In all samples a slight increase (c.10%) can be observed at or immediately following the anomaly. This was best defined in C-TU-POR-3 (Fig. 3) where both earlywood and latewood of ring 854 show a 22% increase in Ca intensity preceded by a series of uncontaminated, elementally unresponsive rings. In C-TU-POR-26 both K and Ca show an increase following the onset of the growth anomaly which corresponds with a depletion of Cu, Br, Rb, and Sr. The response for Ca is shown in Fig. 3. Although there are other rings in the sequence prior to ring 854 where higher intensity Ca can be observed, following ring 854 all latewood Ca shows over a 10% increase. A similar increase can be observed in the earlywood, though this is not consistent for all rings following 854. C-TU-POR-167 shows a similar response for K and Ca, however Br, Rb, and Sr are also increased in this sample.

ICP-AES analysis of C-TU-POR-3 and 26 replicated the observed increases/decreases in essential elements detected by SXFM. In addition, a short-term increase in zinc (Zn) and more sustained increase in sulfur (S) were shown following ring 854 in both samples (Fig. 4). ICP-MS analysis of C-TU-POR-26 replicated the observed increases/decreases in essential elements detected by ICP-AES. It also showed increases of rare earth elements (REE) in rings 856 and 857, and unusual elements such as selenium (Se) and yttrium (Y) from ring 855 onwards. Of particular note is a spike of Hf in ring 854 (Fig. 5).

## 4. Discussion

The elemental changes observed in the four trees from Porsuk from the onset of the growth-ring anomaly are not entirely consistent. Whilst the majority of elements appear to increase at or following ring 854, that change is not equally strong in all trees, nor does it affect all elements in the same way at exactly the same time. In the absence of any means to prove the exact growth provenance of the material it is not possible to address these inconsistencies further as they are likely to reflect localized, micro-site specific variables.

The key point is, whilst the exact type of the elemental change is not replicated in each tree, some degree of change occurs for most elements, in all the trees, from the onset of the growth anomaly. This was replicated via three separate analytical methods. The fact that the change is slightly different in individual trees indicates a response to external elemental variability, impacted by a wide range of micro-site/tree specific factors (e.g. soil depth, chemistry, or the age of the tree), rather than some type of physiological effect common to *Juniperus* sp. in response to more favorable growth conditions. This is supported by the fact that where longer sequences were analyzed (e.g. Fig. 4), the change can be observed to extend beyond the physical anomaly into the resumed regular growth. The implication of all this is that, when considering the probable cause of the ring 854 growth anomaly, we are looking not only for a change in environmental conditions which caused a short-term improvement in growth, but also an event which caused a significant change in environmental chemistry.

The demonstrated increase in S provides a working hypothesis for increases and decreases in other elements at the anomaly. Studies of the impact of anthropogenically induced acid rain on forest ecosystems (Bondietti et al., 1989; DeWalle et al., 1991; Shortle and Bondietti, 1992) have shown that depending on the concentration of sulfuric deposition and the buffering capacity of the soil at any particular site, other elements (in particular Ca or Mn) can be mobilized and more freely incorporated in the xylem. Where acidity levels are particularly high or sustained, Al can be mobilized, binding to the fine root tips and blocking out other elements (Shortle et al., 1997).

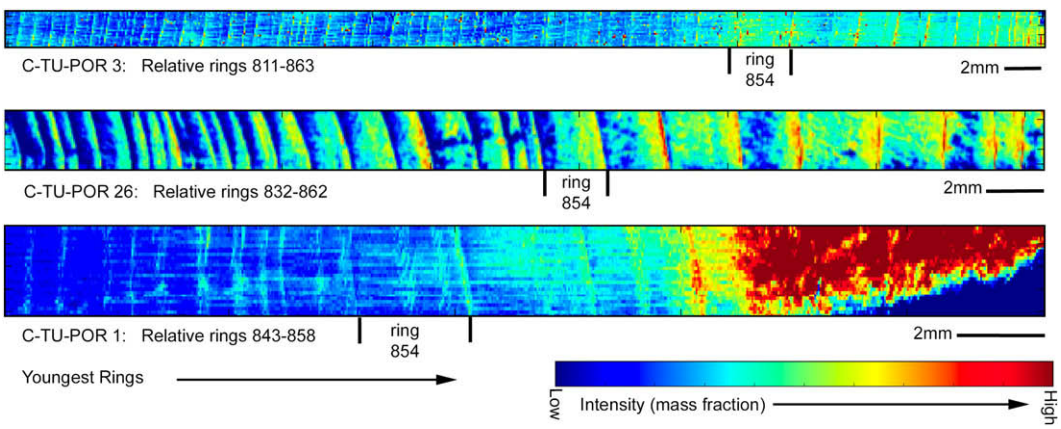


**Fig. 3.** Maps of Ca intensity for sample C-TU-POR-1, 3, and 26. Relative year 854 is currently dated 1650 BC +4/−7.

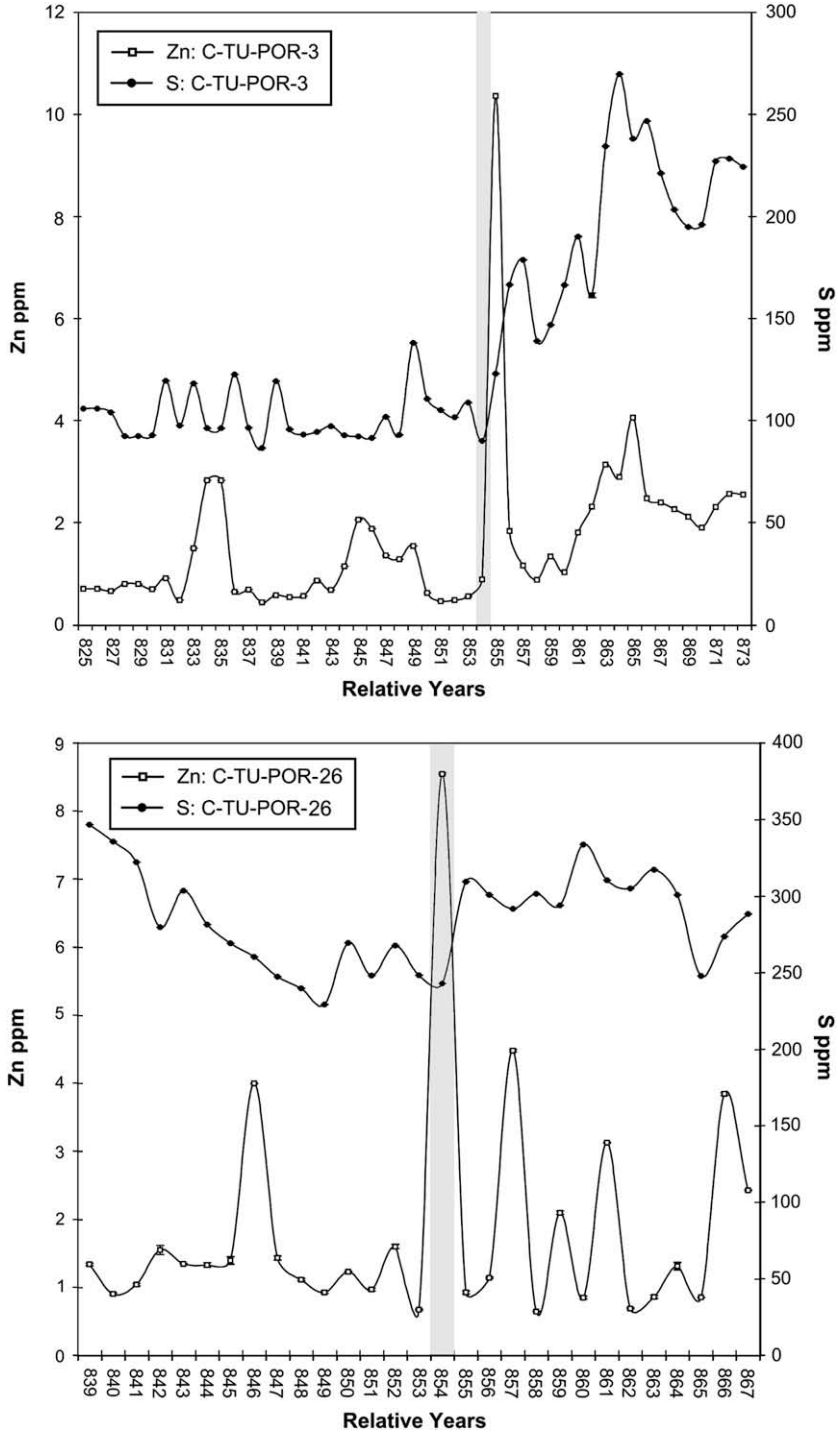


**Fig. 4.** S and Zn in samples C-TU-POR-3 and 26 via ICP-AES. For both samples S rises after ring 854 (marked by vertical line), and a large spike of Zn occurs in ring 854/855.

So increases and decreases in elements observed in the Porsuk trees can be explained by a sudden influx of acid and its effect on micro-site specific variables for each of the trees. The distinct increase in S concentrations shown in Fig. 4 indicates a large influx of S to the forest system, while increased Ca, Mn, and Sr (e.g. Fig. 5) may indicate mobilization of these elements in response to that increased acidity. Whilst a forest fire might result in similar changes in environmental chemistry (Bondietti et al., 1989), the growth-ring pattern is not consistent with the impact of such an event, nor were any fire scars found in the Porsuk samples. Given the approximate date of the anomaly, the most logical source of sulfuric deposition would be volcanic, and given its proximity, Thera would seem the most likely candidate. Yet S alone does not prove a connection with the Minoan eruption. Likewise, the spikes of Zn (see Fig. 4) and Zr, whilst indicating an influx of new chemistry to the growth environment (or rapid mobilization of these elements in the soil), cannot be directly linked to a particular source. The only potential indicators detected for which a specific volcanic origin might be more directly hypothesized are the Hf spike (e.g. see Fig. 5), which occurs in ring 854, and the increase in REE, Se and Y following the onset of the anomaly. Hf occurs with Zr in zircon crystals in silicate rich igneous rocks. The bedrock of the Taurus Mountains is

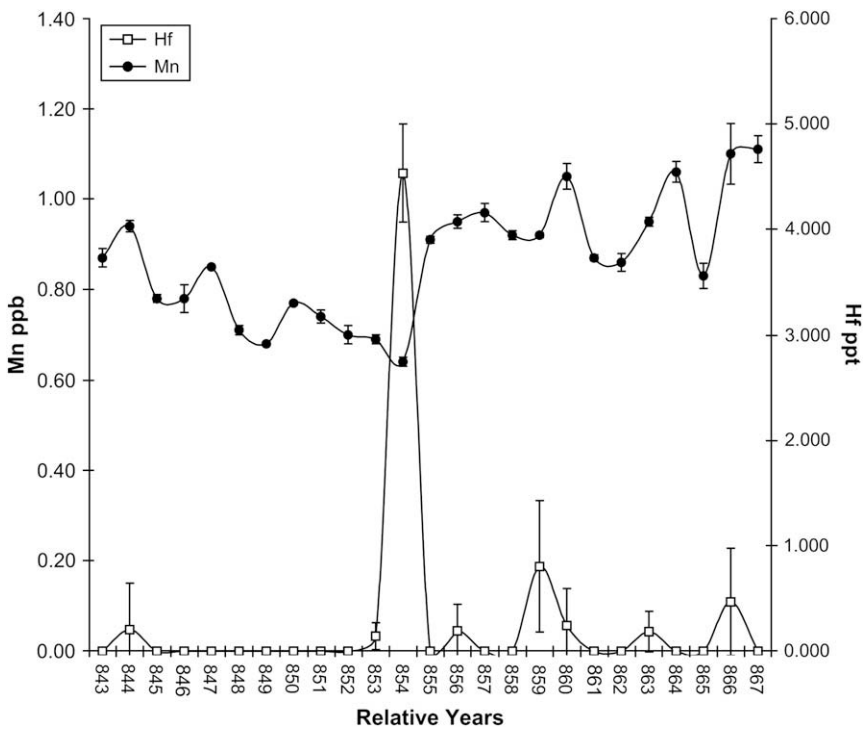


**Fig. 5.** Hf and Mn in sample C-TU-POR-26 via ICP-MS. Hf spikes in ring 854, with concentrations partially above detection in the following rings, indicating a sudden influx of this element into the growth environment around the time ring 854 was formed. Mn shows an increase from ring 855 and may be indicative of the impact of increased environmental acidity.

calcareous, made up of sedimentary (limestone) and/or metamorphic (marble) facies. Given the rareness of Hf, its mode of formation, and the sudden, short-term increase, a volcanic origin seems a likely possibility. Hf has been measured in the Minoan eruption deposits by numerous research teams (Steinhauser et al., 2006; Eastwood et al., 1999; Huber and Bichler, 2003; Bichler et al., 2003), and zircons have been reported as part of the finer wind-blown fraction of the tephra (Vitaliano and Vitaliano, 1974). Equally it is difficult to offer an alternative explanation (other than the influx of new geological material) for an increase in the REE and unusual elements such as Se and Y. Whilst REE are common in the earth's crust, they tend to be of higher concentration in more acidic rocks. Whilst it could be argued that the observed increase reflects the impact of increased environmental acidity on REE availability in the soil/regolith, fresh deposition of acidic volcanic ash seems more probable. For example, Hall et al. (1990) found increased REE indicative of known deposition from an eruption of Mt St Helens.

It is with the REE that the main plausible potential exists to actually prove a link between a tree-ring and a specific volcanic eruption. These elements have unique ratios depending on source formation conditions and are widely used to provenance geological materials (e.g. Steinhauser et al., 2006; Eastwood et al., 1999). Unlike the essential elements which have specific functions in the xylem and so are likely to undergo a degree of fractionation as they are incorporated into the wood, it is hypothesized that the REE would be more passively incorporated. If so, it is possible that a signature ratio of the original source of the REE could be retained in the wood, and could then be used to fingerprint against known tephra geochemistry from possible eruption sources. Given that trees generally do not passively absorb elemental chemistry and that geochemical tephra provenance itself is a complex and difficult technique (Pearce et al., 2007), establishing such a link represents a significant challenge. In this study, while increases in several REE were clear following ring 854, an insufficient number were consistently above detection for any attempt at fingerprinting to be made.

Whilst further replication of the observed signatures is required for all elements, these data imply that the Porsuk growth anomaly was caused by an acid-producing environmental event which also resulted in the introduction of new geological material to the growth location. The presence of Hf and the REE in particular indicates a volcanic origin. This interpretation makes it possible to offer an alternative explanation for the Porsuk growth anomaly. Rather than the indirect, albeit well-established effect of sulfur dioxide on climate (Robock and Mao, 1995), it seems plausible that the growth anomaly was caused by more direct volcanogenic impact, a type of fertilization effect, either from tephra deposition, or due to the soil/chemical impact of volcanogenic acid. Alternatively it is possible that acidic/tephra deposition was sufficient to harm less established or lower lying vegetation, temporarily improving conditions for well-established trees until the ground cover recolonized. Fig. 6 compares the Porsuk growth anomaly with two similar growth perturbations, one resulting from anthropogenic fertilization, one from improved growth conditions due to destruction of ground cover following the 1912 AD Katmai eruption.

As the exact provenance of the wood samples from Porsuk is unlikely to be established, it is difficult to investigate this hypothesis further (i.e. by locating and characterizing a potential eruption horizon in the exact growth location stratigraphy). It is likely that the trees received some direct deposition of tephra as their approximate growth location lies within the north-easterly axis of tephra dispersal reconstructed from tephra horizons in Turkey and the Greek islands (Eastwood et al., 2002; Fig. 1). Even so, given the reported depth of such horizons in various locations much closer to Thera, it is unlikely that the volume of deposition at over 800 km would have been sufficient to cause much disruption to other vegetation. In terms of the purely physical impact of tephra

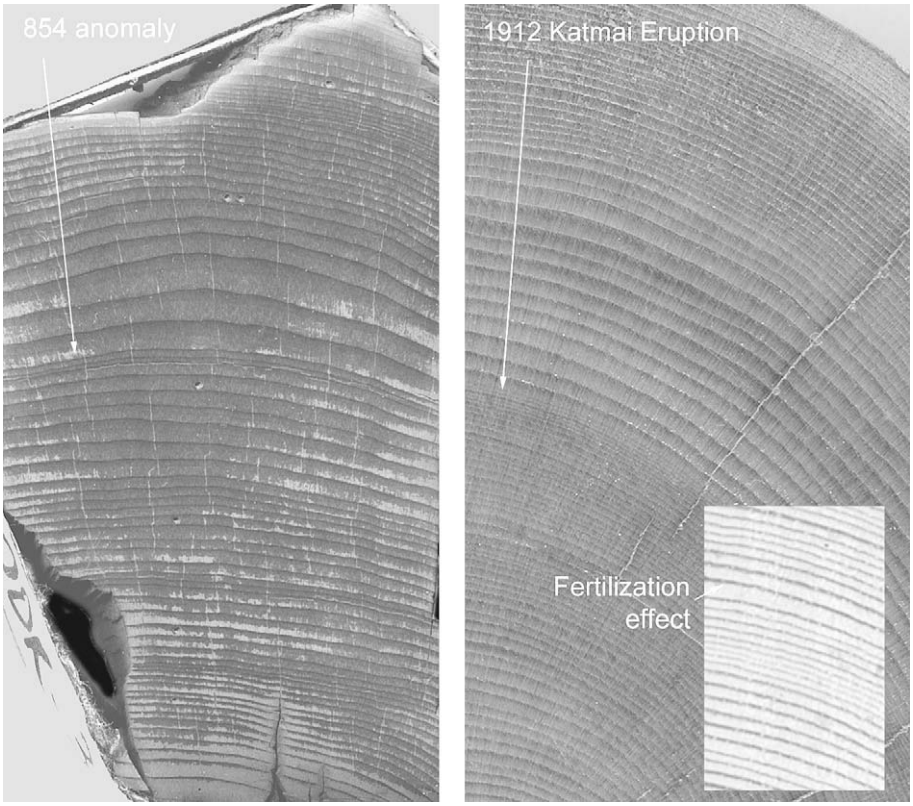


**Fig. 6.** Left: The 854 anomaly in sample C-TU-POR-3; right: a similar (though extended) growth-ring anomaly from a tree which grew c. 30 km from Katmai Volcano, Alaska. The tree in question was inundated with a few feet of pumice following the 1912 AD eruption of Novarupta, attributed to Katmai. The pumice killed or suppressed low vegetation cover, enhancing conditions for established trees (Peter Ward, personal communication). Inset: a short growth anomaly from a single application of fertilizer to a tree in an experimental forest.

deposition, it has been reported that a negative effect on grasses requires over 0.5–2.5 cm of deposition (Blong, 1984), and in excess of 15 cm is required (Rees, 1970) to begin to damage shrubs. It seems highly unlikely that the volume of deposition possible at Porsuk would have been sufficient to make a physical impact, unless it be via an improvement to the moisture retention capacity of the soil. This would fit with the observed growth anomaly, the larger rings reflecting short-term increased moisture, tailing off rapidly as the ash weathered into the soil. The weathering process would release new elemental components into the soil, but if the previous hypothesis is correct, and the change in chemistry at the growth anomaly was incidental to the actual cause, the observed elemental response would be likely to begin as the tephra broke down, i.e. as the growth response returned to normal. Instead the elemental response represents a significant change in environmental chemistry at the onset of the growth anomaly. It is this fact, along with the significant concentration change, which makes a potential fertilization effect from the addition of volcanic by-products (acidic deposition in particular), the more probable cause.

The impact of acidic volcanic output on vegetation has been well recorded in the literature (e.g. Grattan and Pyatt, 1994). It is possible that altered soil acidity made it difficult for certain ground cover to grow, lessening competition for mature trees, but it is the potential impact of nutrient release from increased acidity, in combination with a slight influx of new mineralogically enriched material, which fits best with the derived elemental evidence from the Porsuk trees. A recent study (Frisia et al., 2008) provides speleothem evidence for a major sulfate peak in the early Late Bronze Age (which the authors attribute to the Thera eruption), from a cave in northwestern Anatolia. The cave is located further to the north than Porsuk, but at approximately the same distance from Thera (see Fig. 1) and provides independent evidence of widespread S deposition across the region. Given this evidence, it seems reasonable to conclude that the root cause of the Porsuk growth-ring anomaly is not the indirect impact of an eruption on climate, but rather a direct impact from volcanogenic deposition. If this is the case, the Porsuk anomaly should no longer be cited as evidence for the climatic impact of the eruption (though the new evidence does not rule out climatic fluctuation as a further contributing factor).

This conclusion has parallels with that of Eastwood et al. (2002), who identified enhanced lake eocosystem productivity resulting from deposition from the Minoan eruption at a site 400 km east–northeast of Thera. The case is further strengthened by comparison with an early study of *Pinus* sp. growth-ring anomalies (including anomalously wide rings) resulting from eruptions of Paricutin volcano in Mexico (Eggler, 1967). In the study, where site-specific factors could be investigated and an eruption history was known, a combination of all the previously proposed impact factors was concluded to have resulted in similar anomalous growth. Furthermore, Cronin et al. (1998) report that as little as 0.25 mm of tephra can result in significant additions of S, much of which is immediately available to plants, with the remainder becoming available via oxidation within 2 months of deposition. Whilst all eruptions differ, this indicates potential at least for the observed growth ring response to reflect accurately the year of deposition (subject to element mobility in the xylem).

## 5. Conclusions

For the first time we present direct evidence in support of a volcanogenic cause for the growth-ring anomaly beginning with relative ring 854 in trees from the Anatolian dendrochronological

record. We do not use this to claim once and for all a positive causal connection between the Thera eruption and this sequence of tree-rings, but the presence of a replicable elemental change in all four trees, including significant increases in S and Hf at the onset of the growth-ring anomaly, provides convincing evidence that a volcanic eruption was the primary cause. Given the approximate growth location of the trees and the current date of the anomaly, the most logical source would be the Minoan eruption of Thera. These data can be cited as new proxy evidence to add to that of other paleo-environmental archives which place the date for the Minoan eruption in the mid-late 17th century BC.

Future work will aim to extend the annual resolution sequence over the wider time period within which most scholars agree the eruption must have occurred. For the data collected in this study, covering the years around both 1650 BC and 1628 BC, the only replicable indication of major elemental change was found at relative ring 854. If it could be demonstrated that this elemental change is unique over several hundred years (as is true of the actual growth anomaly), this would provide further evidence to improve the credibility of the proposed link with the largest volcanic eruption in the region at this time. Furthermore, if the observed increase in Hf could be replicated in a larger number of samples, and the REE increase substantiated to a point where it was possible to attempt geochemical fingerprinting, then potential may still exist to link the Minoan eruption with a tree-ring date.

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