

## Can tree-ring chemistry reveal absolute dates for past volcanic eruptions?

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### Abstract

Discussion of the significance of volcanically induced impacts on human history, the natural environment, and climate through the Holocene, has frequently stalled because of controversy concerning certain key volcanic eruptions and their precise relationships with the archaeological/environmental record. A major stumbling block in such debates is a failure to obtain precise and accurate dates for many of these key volcanic events. Most existing dates currently float against archaeological, historical, environmental, and climate data. A potential means to resolution lies with tree rings: these can be dated precisely by dendrochronology, are available from a wide range of loci around the world, and can record global climatic influences. It has been suggested that certain growth anomalies in dendrochronological sequences could offer “proxy” absolutely dated records of major, climatically effective, volcanic eruptions. However, this assertion has been widely disputed given the lack of a direct, positive, causal connection. The hypothesis that the required connection may be chemically encoded in individual annual growth rings from dated sequences is explored here both via review of existing literature on dendrochemical techniques, and by LA-ICP-MS chemical analysis of two tree ring sequences. It is concluded that dendrochemistry provides a promising means by which absolute dates may one day be attributed to key volcanic eruptions of pre-modern times.

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### 1. Introduction

Dendrochronological sequences built from precisely dated annual growth increments of certain tree species have been shown to record global and/or hemispheric climatic influences [29]. Over the past few decades there has been much speculation over causes of sudden, short term, growth anomalies in such sequences, where tree

growth was either so severely stunted that the annual ring or rings produced are only a few cells thick, or, where growth was extraordinarily enhanced for a short time. In such cases, where specific or local factors (e.g. canopy clearance, fires, insect attack, etc.) can be plausibly excluded, several instances of significant growth anomalies, thought to represent short term perturbations in climate, have been attributed as, or suggested to be, the effects of volcanism on the earth's atmosphere [6,7,11,19,30,31,46,47,56,79]. The mechanism evoked to explain these climatic shifts is that the sulphur dioxide based stratospheric aerosol generated by a major volcanic eruption, back-scatters incoming solar radiation and light, lowering ground temperatures

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for c. 1–3 years by small but significant amounts. The degree of impact varies with the size, type, and geographical location of the eruption, as well as time of the year and other concurrent climatic circumstances [1,14,60,64,72,74,76,80]. The argument for a causal connection between growth anomalies and eruptions is based on apparent correlations between the dates of specific anomalies with historically attested volcanism in the last few hundred years [11], and before this, with volcanically induced acidity spikes represented in polar ice core records [16,17,39,50,85,98]. However, over time, and especially beyond the last few centuries, the statistical correlation is less than decisive and the exact volcano-climate-tree growth linkage in individual cases is by no means universally agreed [12,13,66,71,77,97]. Many other circumstances apart from volcanic eruptions may cause anomalous tree growth, and skepticism about such linkages is justified in the absence of positive confirmation.

Volcanic acidity spikes in the annual layers of snow accumulation preserved in polar and other long-term ice records can sometimes be directly linked with specific volcanic eruptions via the chemical fingerprinting of associated volcanic glass shards [22,25,26,98]. Whilst recent advances in the detection of cryptotephra horizons and high resolution analysis of the NGRIP ice core [20] present encouraging prospects for an eventual long term, annual resolution record of volcanism, in general, dates beyond the last few hundred years are not at present absolute and can be rather problematic [83]. In contrast, well-replicated, absolute long tree-ring chronologies exist for a rapidly growing number of locations around the globe [24,32,51]. If it were possible to prove a causal connection between tree ring anomalies and specific volcanic eruptions as with the elemental signatures procured from ice layers and associated tephra shards (as suggested by numerous researchers in the 1980s e.g. Hughes [42]), then global dendrochronologies could be tapped to reconstruct an absolute history of volcanism for the Holocene and beyond with wide geographical coverage. The resulting record could be used to further refine and cross-calibrate with the ice core records tephra chronologies.

## 2. Dendrochemistry

The multi-elemental analyses of tree rings to produce dated sequences of palaeoenvironmental elemental change (dendrochemistry), has previously been used almost solely as a tool for reconstructing patterns of anthropogenic pollution [4,9,21,23,28,35,48,49,53,55,58,73,75,81,84,87,90,91,95,96]. However this approach can readily be applied to the volcanic signal research question.

The basic principle is that the chemical composition of the annually produced woody increment can act, at least partially, as an archive of the chemistry of the growth environment at the time of formation [2,18]. This is highly simplified however; many site specific influences and tree specific biological factors mediate the formation of the chemical record [18,82]. The underlying bed rock and soil chemistry, the depth of the substrate, the level of the water table, local wind directions, climate, aspect and slope can all determine not only background levels of elements available for uptake, but also exposure and response to various changes in environmental chemistry. Soil depth and chemistry in particular, can be fundamental in determining not only the availability of certain elements, but also the main uptake path via which a tree absorbs nutrients. A deep, fertile soil is likely to reduce sensitivity for recording short-term atmospheric elemental change by delaying uptake due to complex soil chemical interactions, and by encouraging dominant uptake of nutrients via the roots, potentially resulting in transportation of elements all around the xylem. In contrast, uptake through the leaves can result in rapid deposition in the most recently formed tree ring [52,93]. Therefore, it may be best to study samples predominantly of this uptake path, by selecting trees growing in poor, shallow, well-drained soils.

Tree specific biological factors such as migration of elements in the sapwood are relatively poorly understood, however a number of direct physiologically derived patterns or associations of elements have been observed in different tree species. These include: (i) overall radial distribution patterns which naturally decline or increase [3,5,9,28,36,37,45,61,63,70] (ii) changes in concentration at the boundary between the heartwood and sapwood [15,59,62,68,81,89,92,94,95] and (iii) concentrations of certain elements in particular anatomical components of a single tree ring [8,54,59,78,86]. Such patterns do not appear to be consistent for a particular element, but rather vary for the same element from species to species and are an essential consideration when interpreting any dendrochemical data set.

Irrespective of such complexities, dendrochemistry is a well-established technique with a wide range of work reported in the literature showing good correlation between the onset and cessation of known anthropogenic pollution events. This paper investigates the potential of using dendrochemistry to identify an elemental trace for a volcanic eruption in a dated tree ring. This is achieved by reviewing the evidence from dendrochemical studies to date, and by presenting encouraging new data derived from two modern test sequences covering the largest volcanic eruption of the last 200 years, Tambora, 1815 [64].

### 3. Hypotheses for a volcanic signature

If a volcanic eruption can be regarded as a pollution event dispersing a particular chemical signature into the environment at a specific time, then previous dendrochemical studies suggest that under the right conditions it may well be possible to detect some part of that signature in a contemporary tree ring sequence. More specifically, two hypotheses may be drawn from existing research as to the form of elemental volcanic signature one might hope to find.

The first hypothesis is that a direct sample of some unique part of the eruption chemistry (either from the gaseous cloud or as part of the physical loading of tephra) can be identified in individual tree rings. By linking the occurrence of unusual elements, combinations, and/or higher concentrations of particular elements known to be associated with a certain eruption, an actual chemical finger print could be provided which could be used to directly link absolutely dated tree rings with volcanic eruptions, ice core acidity profiles, and stratigraphic tephra horizons.

There are two studies which go some way towards supporting the viability of this hypothesis. Tendel and Wolf [88] found that certain trees can directly record an increase in levels of sulphur dioxide in the form of a corresponding increase in concentrations of sulphur (S) in contemporary growth rings. They found that this effect could apply in different tree species in a similar manner over a wide geographical area. More significantly, however, Hall et al. [38] found two anomalous rare earth elemental peaks in tree rings corresponding with eruptions of the Mount St. Helens volcano. The *Pseudotsuga menziesii* they sampled was growing 15 km northeast of the volcano and had received direct fallout of 15 cm of volcanic ash. Their analysis showed that anomalously high concentrations of rare earth elements; cerium (Ce), neodymium (Nd), lanthanum (La), samarium (Sm), gadolinium (Gd), lutetium (Lu), and thulium (Tm) occurred at AD 1478 and 1490—dates within a year of two known previous eruptions. Whether this type of response can be detected in terms of a wider ranging impact, utilising existing dendrochronologies, remains to be seen, but these two papers at least provide some indication that there are prospects for identifying some kind of directly linkable volcanic signature in tree rings.

Far more evidence exists to support the second hypothesis, which relates to a somewhat less provable link with volcanism. This is that a volcanically induced increase in global or local environmental acidity levels would increase availability of other elements in the soil, or on the bark and leaves and result in an increase or decrease in concentrations of those elements in contemporary tree rings. Evidence to support this can be drawn from a wide range of studies on the impact of acid rain — a common by-product of both anthropogenic and

volcanic pollution. Rising soil acidity, due to increased precipitation of sulphuric or nitric acid from anthropogenic pollution sources, can lead to alterations in the relative availability of nutrients and ions in the soil, and preferential up take and translocation within trees (see Table 1). Where the effect on the soil is prolonged or the original soil chemistry is more susceptible to leaching, a corresponding decrease in the availability of certain elements may occur. A time lag may be associated with this response, the extent of which would depend on the degree of acidic pollution, the natural buffering capacity and depth of the soil, and the particular species of tree. However, acid precipitation has also been shown to enhance susceptibility to adsorption through the bark and leaves [44,52,69] leading to an even more rapid response from trees where such uptake paths are dominant.

Confirmation that this hypothesis can be applied to a volcanic scenario has been provided by Padilla and Anderson [65]. In their study of a 350-year-old *Pinus ponderosa*, a series of rises or peaks in concentrations of barium (Ba), copper (Cu) and zinc (Zn) were observed around the time of the Laki (1783), Tambora (1815) and Krakatau (1883) eruptions. They attribute these results, as hypothesised, to a decrease in soil pH resulting from volcanically induced acid rain. The most convincing of the associations are Ba, Cu and Zn for Tambora and Cu for Krakatau. The claimed Laki association is less convincing as the date also coincides with a forest fire which could equally be responsible for increased concentrations. As the sequence was sampled at a resolution of 5 to 10 years, and not all these increments are labelled on the given graphs, there is some ambiguity with regard to how accurately the observed increases correlate with the eruption years. However, the results are encouraging and if replicated at higher resolution would greatly improve prospects for a dendrochemical resolution to the problem of dating past volcanism, even though this type of response could only be used as a proxy indicator rather than to establish a causal connection.

Both Padilla and Anderson [65] and Hall et al. [38] used solution ICP-MS for their analyses. The main problems with this technique for the analysis of tree rings at annual resolution are a lengthy sample preparation procedure, which, in the separation and digestion of individual growth increments, destroys relatively large quantities of original sample and provides numerous opportunities for contamination. A potential alternative is to use a laser ablation sample induction system (LA-ICP-MS). Whilst problems currently exist in terms of calibration for this technique [96] and its small sample size in relation to potentially heterogeneous biological samples, they are seemingly outweighed by the capacity for rapid, high resolution, largely non-destructive multi-elemental analysis of long

Table 1  
Reported elemental response to increased environmental acidity in different tree species

Element	Response	Species
Al	Increase	<i>Quercus rubra</i> L.
Al	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
Al	Increase	<i>Picea rubens</i> Sarg.
Al	Increase	<i>Pinus sylvestris</i> L.
As	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
As	Increase	<i>Acer saccharum</i> Marsh.
Ca	Decrease	<i>Quercus rubra</i> L.
Ca	Decrease	<i>Quercus robur</i> L.
Ca	Decrease	<i>Fagus sylvatica</i> L.
Ca	Increase	<i>Acer pseudoplatanus</i> L.
Ca	Increase	<i>Picea rubens</i> Sarg.
Cd	Increase	<i>Abies religiosa</i> H.B.K. & Cham
Cd	Increase	<i>Juniperus virginiana</i> L.
Cl	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
Co	Increase	<i>Acer saccharum</i> Marsh.
Cr	Increase	<i>Acer saccharum</i> Marsh.
Cu	Increase	<i>Pinus sylvestris</i> L.
Cu	Increase	<i>Acer pseudoplatanus</i> L.
Cu	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
Fe	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
K	Decrease	<i>Fagus sylvatica</i> L.
K	Decrease	<i>Quercus robur</i> L.
K	Increase	<i>Pinus sylvestris</i> L.
Mg	Decrease	<i>Fagus sylvatica</i> L.
Mg	Decrease	<i>Quercus rubra</i> L.
Mg	Increase	<i>Picea rubens</i> Sarg.
Mg	Increase	<i>Acer pseudoplatanus</i> L.
Mg	Increase	<i>Picea abies</i> (L.) H.Karst.
Mg	Increase	<i>Picea rubens</i> Sarg.
Mn	Increase	<i>Abies balsamea</i> (L.) Mill.
Mn	Increase	<i>Acer pseudoplatanus</i> L.
Mn	Increase	<i>Acer saccharum</i> Marsh.
Mn	Increase	<i>Quercus rubra</i> L.
Mo	Decrease	<i>Juniperus virginiana</i> L.
Na	Increase	<i>Tsuga canadensis</i> (L.) Carrière
Ni	Increase	<i>Acer saccharum</i> Marsh.
Ni	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
P	Decrease	<i>Acer pseudoplatanus</i> L.
Pb	Increase	<i>Acer pseudoplatanus</i> L.
Pb	Increase	<i>Pinus sylvestris</i> L.
Pb	Increase	<i>Abies religiosa</i> H.B.K. & Cham
Pb	Increase	<i>Juniperus virginiana</i> L.
Rb	Increase	<i>Pinus sylvestris</i> L.
S	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
S	Increase	<i>Acer saccharum</i> Marsh.
Si	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
Sr	Decrease	<i>Quercus prinus</i> L.
Sr	Increase	<i>Acer pseudoplatanus</i> L.
Zn	Increase	<i>Acer saccharum</i> Marsh.
Zn	Increase	<i>Pinus contorta x banksiana</i> (Loud.) Lamb.
Zn	Increase	<i>Abies balsamea</i> (L.) Mill.

Compiled from Refs. [9,10,21,27,28,33,34,40,41,43,49,52,57,68,70,81,87,95]. The table illustrates primarily how certain elements in certain species of tree respond to increased environmental acidity. In doing so, it also illustrates the complexity of response, and how the same element can behave differently in different species. This variability reflects the external and internal influences on a particular tree, for example the original chemical composition of the soil and species-specific growth requirements.

sequences of individual tree rings. The minimum ablation radius is around 30  $\mu\text{m}$ , a particular advantage for analysis of narrow ring anomalies, rare samples requiring preservation and where only narrow increment core samples are available. A high-resolution pilot study was carried out in order to assess the potential of this analytical method, with a primary aim of ascertaining whether the Tambora eruption of AD 1815, could be detected in or around the 1815 growth increment in wood from one of the world's long-term tree-ring chronologies.

#### 4. High resolution pilot study – methodology

A sample of absolutely dated *Pinus sylvestris* from Sarikamiş, Turkey (40.33N, 42.33E, 2600 m), was obtained from the Aegean Dendrochronology Project tree-ring collections (SRK-12) courtesy of Peter Ian Kuniholm and Maryanne Newton. *Pinus* sp. have been used successfully in dendrochemical studies and it was hypothesised that the regular, coniferous, structure of this species would produce a more representative analysis via LA-ICP-MS. The sample was taken from a high altitude location with very rapidly draining soils, conditions likely to emphasise any potential elemental response in the tree rings to atmospheric pollution. A short test sequence of early and late wood (AD 1805–1818) was analysed. This was followed by a further extended sequence of early and late wood (AD 1788–AD 1828).

Sub-samples of each core were mounted to fit the dimensions of the laser sampling chamber and fresh sampling surfaces were cut with an acid washed microtome blade prior to analysis. It was found that this method produced more effective results than either mechanical sanding or laser rastering the surface, both of which produced loose material or crushed the cell structure. Cutting a fresh surface immediately prior to analysis provides clean access to a defined cell structure.

Analysis was carried out using a quadrupole, Thermo Elemental PlasmaQuad ICP-MS in conjunction with a Cetax LSX-100 laser (Nd:YAG pulsed with Q-switch) operating at 266 nm. These were driven by PQVision version 4.1.2 and Cetac laser system version 1.20, with a high resolution CCD camera system for observation of the sample during analysis. Due to a lack of matrix matched calibration standards for the laser ablation analysis of wood samples, alternative calibration steps were put in place. NIST SRM 610 glass wafers (proven to be homogenous and spiked with up to 61 trace elements at nominal concentrations of 500, 610 and 50  $\mu\text{g g}^{-1}$ , see [67]) were run intermittently throughout analyses as a calibration standard and to monitor changes in instrumental output. Replicate analyses of the gas passing through the sample chamber were made before

analysis of sample sets, and mean blank values were calculated for each element. These values were then subtracted from each run of each sample for all elements. The only data not to be blank subtracted were the NIST 610 data for carbon 13 ( $^{13}\text{C}$ ). As there is no C in NIST,  $^{13}\text{C}$  in the air was used as a value for calibration. The lower limit of detection was calculated as three times the standard deviation of the replicate gas blank analyses. All values less than the lower limit of detection were discarded to leave values of  $3\sigma$  or higher. A combined correction factor  $(100/\text{Deg of Ionisation}) \times (100/\text{Isotopic Abundance})$  was applied to adjust for differences in isotopic abundance and varying degrees of ionisation in the argon plasma. All elements in each sample were then ratioed to the  $^{13}\text{C}$  in that sample.  $^{13}\text{C}$  was selected as an internal standard as it is less abundant than the  $^{12}\text{C}$  isotope, and so produces the more reliable mass signal. NIST discs were ratioed to the  $^{13}\text{C}$  which was retained from the gas blank. All values were then calibrated to an arbitrarily selected data set of “master NIST averages” so that day-to-day variation in instrumental detection would not prevent the linkage of data sets from different days of analysis. The calibration factor was produced by dividing the overall mean from the Master NIST data by the overall mean of the NIST ablations for specific days of analysis. Data are presented as ratios to  $^{13}\text{C}$ . While accurate concentrations data cannot be produced without a matrix matched calibration standard, these data allow comparison between precise differences in concentrations from one year to another.

## 5. Discussion

For the initial test sequence from 1805 to 1818 out of the 30 elements analysed, only aluminium (Al), Mn, nickel (Ni), Zn, Cu, Strontium (Sr), cadmium (Cd), Ba,

La and rubidium (Rb) were above detection limits, however, of these, several elements produced promising results when considered against the background of known physiologically derived distribution patterns. Figs. 1 and 2 provide examples of the two types of elemental anomaly observed around 1815. In Fig. 1 the early and late wood sequence for Al and Zn shows a marked heterogeneity of the tree rings around 1815. This is indicated by the size of the error bars which reflect differences between the three runs of a single sample ablation: the larger the bar, the greater the variation in tree-ring chemistry only a few microns apart. The fact that the bars are small and stable for the rest of the sequence suggests that the chemistry of the tree rings is more homogenous overall with some kind of elemental disturbance occurring around 1815 (the slight offset in effect can be explained by the effects of translocation). Some studies have reported high concentrations of particular elements within individual tree rings [54,55,59,86]. In particular, Sunden et al. [86] observed highly concentrated clusters of specific elements in small patches within certain rings. It is possible that the data disturbance identified around 1815 is derived from the presence of this type of feature, which may be induced by sudden, large scale mobilisation of divalent cations due to acidic deposition on soils. Fig. 2 shows just the early wood values for Zn and Cu. Here a peak in the ratio pattern can be seen for both elements, indicating that concentrations are much higher in 1815, as well as slightly more heterogeneous. This rise in concentrations fits more conventionally with a causal hypothesis relating to increased environmental acidity.

In order to substantiate the initial findings, a longer sequence was run to see the 1815 disturbance in a wider context. The second sub-sample was taken from a different depth within the main sample. Again only 10 elements were reliably above detection. The results in

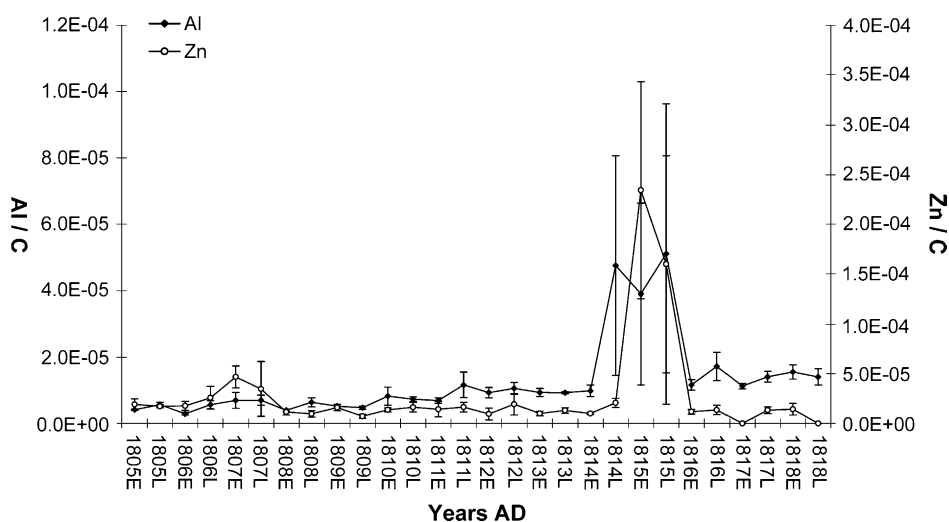


Fig. 1. LA-ICP-MS analysis of a sample of *Pinus sylvestris*, early and late wood sequence, for Al and Zn for AD 1805–1818.

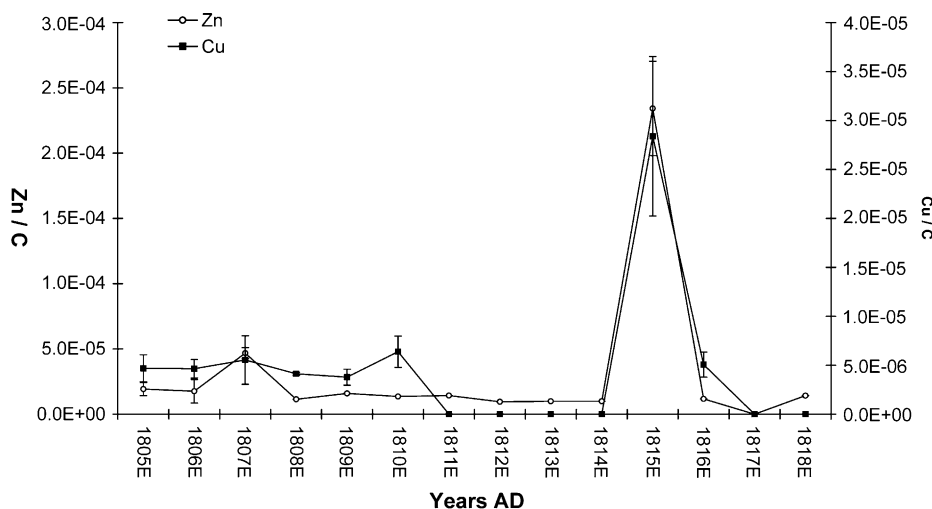


Fig. 2. LA-ICP-MS analysis of a sample of *Pinus sylvestris*, early wood data only, for Zn and Cu for AD 1805–1818.

the context of the longer sequence look even more promising, with an anomalous rise for most elements around 1815 standing out as a distinct event against a natural pith to bark pattern which does not cross the heartwood/sapwood boundary. No correlations were found between the tree ring width and elemental patterns. Fig. 3 shows an example for Al and Ca. Promising though these data may appear, it should be noted that the second sequence did not statistically replicate the first. This can be illustrated by comparing the data for Al in Figs. 1 and 3. The first possible explanation for this underlines a key consideration for any dendrochemical study: i.e. there can be considerable variation of elemental concentrations in the same yearly growth increment both around the ring, and at various heights in the trunk. This is a critical consideration in the design of any dendrochemical study, which should aim to sample from several heights and along different

radii within the trunk, in order to present fully substantiated data representing the average and/or replicated chemistry of the tree rings. Another explanation (also relating to this) may lie with the analytical technique. As laser ablation only samples a small sub-sample of each tree ring, a reliably replicable result is greatly dependant on a good degree of homogeneity displayed by the tree rings in relation to the sample size. This illustrates a possible limitation for the future use of the LA-ICP-MS technique on tree ring sequences without extensive repeated sampling – and points to use of, for example, solution ICP-MS as a more efficient and representative sampling technique. Nonetheless, it is surely significant that the most prominent changes in pattern occur at the same time for both sequences for the majority of the elements detected, and that this time happens to coincide with the largest volcanic eruption of the last 200 years.

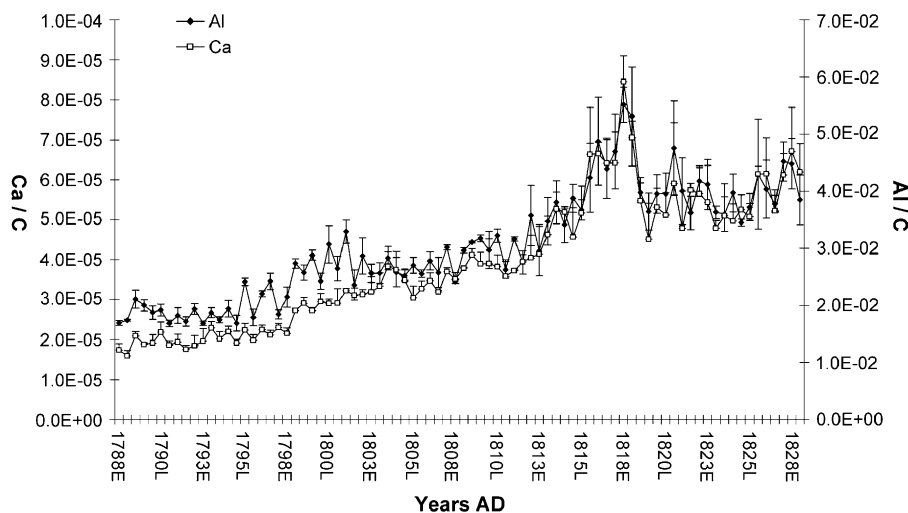


Fig. 3. LA-ICP-MS analysis of a sample of *Pinus sylvestris*, early and late wood sequence, for Al and Ca for AD 1788–1828.

## 6. Conclusions

LA-ICP-MS was found to have great potential for the rapid, high resolution, largely non-destructive, multi-elemental analysis of tree ring sequences as specifically required for this research question. However, it is currently limited by difficulties with calibration, failure to detect a wide range of elements, and problems with replication of sequences due to xylem heterogeneity. Further developmental work is required, or an alternate technique must be sought.

Further research on the main research question should focus on very specifically designed studies, which take into full consideration all aspects of the history of the sample in question and previously observed physiologically derived patterns of elements and ring width. These studies should be on suitable samples of wood, grown in marginal, dry environments and preserved in cold or dry (non-contaminating) conditions (for example from the North American *Pinus aristata* chronology). The focus should be on elucidating an elemental signature which can be directly linked to a specific eruption as opposed to the secondary effect of environmental acidification put forward to explain our datasets. Much work in addition is needed to understand the physiological processes associated with such a response.

Data should be substantiated by replication where possible from several sampling points in the same tree and the same sequence from a number of trees.

Given the right tree, the right growth environment, and the right environmental conditions, dendrochemical studies have shown that annual concentrations of specific elements in tree rings can directly reflect changes in external environmental chemistry. It seems there is now good evidence from both the existing literature and these new data sets to indicate that this technique can be applied to the detection of volcanically induced changes in environmental chemistry. This association is likely however to be extremely difficult to define and quantify. Whether or not (and how) a particular eruption shows up in the chemistry of a tree ring relies upon a massive number of variables, many of which may not be understood for dendrochronological samples covering the most significant eruptions of archaeological time. Nevertheless, with a rigorous programme of research, using carefully selected samples, and continuously improving analytical techniques, it now appears that there are good prospects that tree-ring chemistry may one day reveal absolute dates for volcanic eruptions from the world's major dendrochronological sequences.

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