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LETTER

A millennium-long 'Blue Ring' chronology from the Spanish Pyrenees reveals severe ephemeral summer cooling after volcanic eruptions

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Abstract

'Blue Rings' (BRs) are distinct wood anatomical anomalies recently discovered in several tree species from different sites. While it is evident that they are associated with a cooling-induced lack of cell wall lignification, BRs have yet to be evaluated systematically in paleoclimate studies. Here, we present a continuous wood anatomical assessment of 31 living and relict pine samples from a high-elevation site in the central Spanish Pyrenees that span the period 1150–2017 CE at annual resolution. While most BR years coincide with cold summer temperatures and many BRs follow large volcanic eruptions, some were formed during overall warm summers. We also see a differential response between eruptions: the Samalas eruption is followed by 80% BRs in 1258, but only a modest signal is evident after the 1815 Tambora eruption, and there are no wood anatomical effects of the Laki eruption in 1783–1784. Apparently linked to a cluster of tropical eruptions in 1695 and 1696 CE, 85% BRs occurred in 1698. This new wood anatomical evidence is corroborated by the record of sulphur deposition in polar ice cores, and corresponds with catastrophic famine and unprecedented mortality in Scotland. The extremely rare occurrence of consecutive BRs in 1345 and 1346 marks the onset and spread of the Black Death, Europe's most devastating plague pandemic. In their ability to capture severe ephemeral cold spells, as short as several days or weeks, BR chronologies can help to investigate and understand the impacts of volcanism on climate and society.

1. Introduction

The summer cooling signatures of large volcanic eruptions have been intensively studied. Numerous factors influence the climate response to volcanism including eruption intensity and sulphur emission, source location, seasonal timing and climate sensitivity (Robock 2000, Oppenheimer 2011, Timmreck 2012, Esper et al 2013, Toohey et al 2019). Aside from recent eruptions, such as Pinatubo in 1991 (McCormick 1992, Russell et al 1996), for which

abundant direct observations are available, proxy data are needed to date and reconstruct the direct and indirect climatic effects of past volcanism (Gao et al 2008). Records of accumulated ice in Greenland and Antarctica represent the most reliable and longest archives of global volcanic sulphur emissions (Zielinski et al 1994, 1996, Zielinski 1995).

The available glacio-chemical records are, however, associated with variable and uneven dating uncertainties (Sigl et al 2015, Svensson et al 2020). Since volcanic sulphur excesses in ice cores are

widely used to derive the radiative forcing magnitude and timing in climate model simulations (Crowley 2000, Otto-Bliesner *et al* 2016), the precise dating of past eruptions is essential (Oppenheimer *et al* 2017, Büntgen *et al* 2017a), though often controversial (Dull *et al* 2019, Smith *et al* 2020). Even small dating errors will have significant effects on proxy-model comparisons (Anchukaitis *et al* 2012, Büntgen *et al* 2014, 2018, Esper *et al* 2015), and on investigations into the relationships between volcanism, climate and society (Sigl *et al* 2015, Büntgen *et al* 2016, 2020, Di Cosmo *et al* 2017, Oppenheimer *et al* 2018, Guillet *et al* 2020).

Tree ring-based reconstructions of regional to hemispheric summer temperature variability have been used to detect and quantify the climatic fingerprints of some of the largest volcanic eruptions during past centuries (Briffa et al 1998, Krakauer and Randerson 2003, Schneider et al 2015, Stoffel et al 2015, Wilson et al 2016, Anchukaitis et al 2017, Guillet et al 2017, Büntgen et al 2020). Maximum latewood density (MXD) is considered a more precise proxy for summer temperatures compared to tree-ring width (TRW) (Büntgen et al 2006, Schneider et al 2015, Stoffel et al 2015, Björklund et al 2019), which is subject to the effects of biological memory (Frank et al 2007, D'Arrigo et al 2013, Esper et al 2015). However, both parameters reflect an integrated response over most of the growing season (Fritts 1976, Briffa et al 2002, Büntgen et al 2011, Cuny et al 2014), and therefore do not express severe ephemeral cooling events lasting days or a few weeks only (see figure 4 and associated discussion in Büntgen et al 2017b for a better understanding of the biotic and abiotic factors of wood formation in Pinus uncinata at high-elevation sites in the central Spanish Pyrenees).

In addition to so-called 'Frost Rings' (FRs; collapsed and deformed early or latewood cells and rays) and 'Light Rings' (LRs; none or only a few layers of latewood cells), which can result from ephemeral cooling events during the growing season (Lamarche and Hirschboeck 1984, Filion et al 1986, Tardif et al 2020), 'Blue Rings' (BRs) are a newly discovered indicator of the degree of cell wall lignification that becomes visible in double-stained anatomical thin-sections (Piermattei et al 2015, Crivellaro et al 2018, Tardif et al 2020). Since cell wall lignification in wood seems to be thermally controlled (Gindl et al 2000, Körner et al 2019, Crivellaro and Büntgen 2020), we expect continuous BR assessments to provide additional insights into the climatic effects of past volcanism.

Here, we use wood anatomical and biochemical measurements of 31 annually-resolved and absolutely-dated pine TRW series from the upper treeline in the Spanish central Pyrenees to reconstruct the occurrence of BRs over the past 850 years. Through a comparison with different state-of-the-art wood anatomical, biochemical and spectroscopic

techniques (figure 1), we aim to explore the physiological and mechanistic processes relevant to the formation of BRs.

2. Materials and methods

Increment cores from 20 living trees and disc samples from 198 relict logs and snags of Mountain pines (Pinus uncinata Mill.) were collected at the upper treeline in the Spanish central Pyrenees. All trees in this remote northern limit of the Aiguestortes I Estany de Sant Maurici National Park grew above 2000 m asl $(\sim 42^{\circ}40'\text{N} \text{ and } 00^{\circ}50'\text{E})$. The TRWs of all samples were measured, cross-dated, and validated against existing, millennium-long TRW and MXD chronologies from the same region (Büntgen et al 2008, 2017b). In all samples, the occurrence of LRs and FRs was recorded, and a selection of 31 samples, evenly distributed across the past millennium, was made for the investigation of BRs. Wood anatomical thinsections of 15 μ m thickness were prepared (Gärtner and Schweingruber 2013, Gärtner et al 2015), and each sample was bleached with sodium/potassium hypochlorite to decolour cell walls and to remove undesired cell content. All microsections were stained with a blend of Safranin (red) and Astra Blue (blue) to visualise lignified and less lignified cell walls in red and blue, respectively. In this study, Astra Blue refers to a mixture of 0.5 g Astra Blue powder dissolved in 100 ml distilled water and 2 ml acetic acid, whereas Safranin refers to a mixture of 0.1 g Safranin powder dissolved in 100 ml distilled water. In our laboratory, we mix Astra Blue and Safranin at the proportion of 4:1 (i.e. four-times Astra Blue and one-time Safranin).

The stained microsections were first washed with water and then with ethanol at increasing concentrations (Gärtner et al 2015), and finally embedded under a cover glass with a permanent hardener. In this study, we define a complete BR as a tree ring in which we are able to visually detect a distinct layer of completely blue cell walls (figure 1(C)), whereas a partial BR (pBR) is characterized by a non-continuous layer of blue cell walls and/or by only blue inner layers of cell walls. It is evident that the lack of cell wall lignification is always stronger in BRs compared to pBRs. However, in both cases, we can assume that the bluer the cell walls, the less lignified they are (Gerlach 1984, Piermattei et al 2015, Ghislan et al 2019, Crivellaro and Büntgen 2020, Tardif et al 2020).

In order to compare our new BR record against pine growth and summer temperature, we used the existing TRW and MXD chronologies, as well as the mean May–June and August–September temperature reconstruction from the same site (Büntgen *et al* 2017b). As a proxy for volcanic forcing of large-scale climate variability, we use the annual sums obtained from monthly-resolved estimates of stratospheric aerosol optical depth (SAOD) over the

Northern Hemisphere (NH) extra-tropics ($>30^\circ$ N), derived from polar ice core records (Toohey and Sigl 2017). Superposed epoch analysis (SEA; see Rao *et al* 2017 for methodological details) was used to quantify regional to hemispheric warm-season temperature variation and volcanic forcing for those years in which (i) at least 20% of the observations for that year contain BRs (n = 38), (ii) at least 20% pBR (n = 47), and (iii) all years in which either 20% BRs or pBRs occurred (n = 71).

Owing to their exceptionally good preservation and continuous timespan from 1320-1850 CE (figure S1 (available online at https://stacks.iop. org/ERL/15/124016/mmedia)), three relict pine samples were selected for an additional inspection of intra- and inter-annual changes in wood polymer composition (see supplementary materials for details), as well as to probe further the physiological and mechanical drivers of different cell anatomical properties. Lumen area and cell wall thickness were measured in BR years, as well as in the three years before and after each BR using the image analysis software ROXAS (von Arx and Carrer 2014). Intra- and inter-annual wood density profiles values for the same sequences were obtained from the Walesch 2003 x-ray densitometer (Schweingruber et al 1978, Eschbach et al 1995), as well as from digital scans processed by the CDendro/CooRecorder software (version 9.3.1—Cybis Elektronik and Data; Björklund et al 2019).

Since neither the anatomical nor the image-based wood density surrogates provide quantitative measures of the lignin content in cell walls, we applied Raman spectroscopy. First, ~ 0.5 mm thick blocks were measured to acquire low-resolution Raman images across several consecutive rings, followed by high-resolution imaging of the tree rings 1335, 1338 and 1345 on 10–20 μ m thin-sections at 0.3 μ m lateral resolution to define changes in wood polymer composition (Agarwal 2006, Gierlinger and Schwanninger 2006, Gierlinger *et al* 2012). While removing possible disturbance signals due to cosmic rays and applying a baseline correction, the full Raman spectrum was recorded from 650–1750 cm⁻¹ (see supplementary materials for details). We focussed on spectral bands at \sim 1600, 1637 and 1652 cm⁻¹ that are representative of changes in lignin, pinosylvin (Belt et al 2017, Felhofer et al 2018) and resin acids, respectively (see supplementary material for a detailed description of the Raman spectroscopic procedure).

3. Results

A total of 120 BRs and 177 pBRs were identified in 31 living and relict pine samples between 1170 and 2017 CE (figure 2; table S1). Only three samples were completely devoid of BRs, and another three samples contained only one BR. Sample size ranged from two trees at the record's beginning and end, to 15 trees

in the mid-15th century (figure 2(B)). The occurrence of BRs generally coincides with low MXD and narrow TRW (figure 2(C)). The relative and absolute occurrence of BRs per year ranges from 7%-100% and from 1-11 cases, respectively. The most pronounced anatomical signal during the past 850 years is found in 1698 CE, when 11 out of 13 trees contained BRs (figure 2; table 1). There are 38 and 47 years in which more than 20% of the total number of rings are either BRs or pBRs, respectively (figure 3; table S1). Like BRs and pBRs, the highest frequency of FRs and LRs occurs in the middle of the 16th and 17th centuries (figure 3). LRs are most abundant in 1576, 1587, and 1552 CE, and LRs in 1698 and 1714 coincide with BRs. The wood formed in 1714 not only exhibits BRs and LRs but also a high frequency of FRs in the latewood. Latewood FRs are characteristic features in 1587 and 1480, whereas the highest frequency of earlywood FRs occurs in 1523 and 1516 CE (figure 3).

Most of the BRs and pBRs coincide with relatively cold summers (figure 4(B)), often following large volcanic eruptions (figure 4(C); tables 1, S1). Cooling in the mid-13th century, as well as around 1700, and again in the early-19th century, coincides with an increase in the intensity and frequency of BR and pBR years. The longest BR-free periods, 1180-1224 and 1835-1884, coincide with intervals of comparatively low SAOD. The timing of several known equatorial eruptions, including those of Samalas and Kelut (Indonesia), Huaynaputina (Peru), Tambora (Indonesia), Cosigüina (Nicaragua) and Krakatau (Indonesia) in 1257, 1586, 1600, 1815, 1835 and 1883, respectively, coincides with substantial BR and pBR frequencies in the following years 1258, 1587, 1601, 1816, 1835 and 1884/85 CE. However, the cell wall lignification of highelevation pines in the Pyrenees does not appear to have responded to the prominent high-latitude eruptions of Katla and Laki (both Iceland), or Katmai (Alaska) in 1210, 1783/84 and 1912, respectively. While the vast majority of BRs and pBRs are discrete, consecutive BRs and pBRs only occur in 1345/46, 1674/75 and 1808/1809, timings that also parallel significant, though yet unidentified, eruptions recognised in glacio-chemical records (figure 4(C); tables 1, S1).

Results from the SEA confirm that most of the BRs and pBRs were formed during exceptionally cold summers over the western Mediterranean Basin (figure 5; table S2), which in turn tend to coincide with increased volcanic forcing that triggered longer-term summer cooling at the hemispheric-scale. Significant (p<0.001) and sharp regional May–June and August–September temperature depressions of $-1.59~^{\circ}\text{C}~(\pm 0.66~^{\circ}\text{C}), -1.39~^{\circ}\text{C}~(\pm 0.65~^{\circ}\text{C})$ and $-1.30~(\pm 0.69~^{\circ}\text{C})$ coincide with 38 BR years, the 47 pBR years and the 71 combined instances, respectively. For the same years, SAOD exhibits the

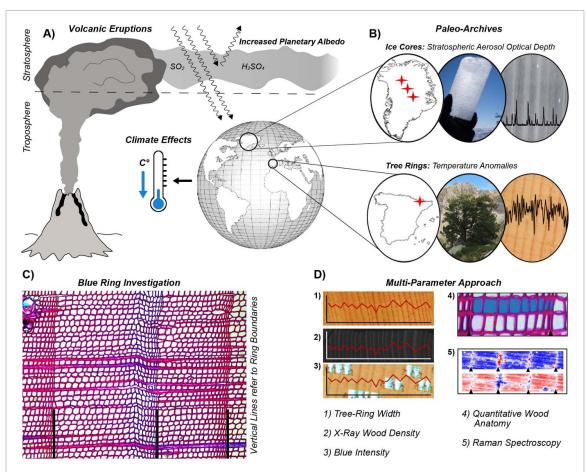


Figure 1. Study design. (A) Depending on their location, intensity, seasonality and sulphur yield, volcanic eruptions may cause severe ephemeral summer cooling. (B) Ice cores and tree rings can provide unique insights into sulphur emissions and temperature depressions caused by volcanic eruptions that occurred long before the period of intensive monitoring. (C) In this study, we apply anatomical thin-sectioning and double-staining on 31 wood samples from living and relict pines that were $collected \ at \ the \ upper \ treeline \ in \ the \ central \ Spanish \ Pyrenees \ to \ develop \ the \ first \ continuous \ BR \ chronology \ back \ to \ 1170 \ CE \ (see$ methods for details). (D) On a selection of three relict pine samples that contain BRs, five different parameters were investigated: (1) tree-ring width, (2) wood density, (3) blue intensity, (4) wood anatomy, and (5) Raman spectroscopy (see supplementary materials for methodological details).

Table 1. Blue Ring ranking. The highest occurrence of BRs and pBRs in decreasing order and associated with volcanic eruptions that possibly caused the anatomical features. For each year, the total number of samples (No. Samples), the total number of BR and pBRs, as well as the percentage of BRs and pBRs are shown together with the available information on historical volcanic eruptions that occurred in the same year or the year before BR formation.

Year	No. Sample	No. BRs	No. pBRs	% BRs	% pBRs	Volcanic Eruption	Eruption Location	Estimated Eruption Date
1698	13	11	0	85	0			
1258	5	4	1	80	20	Samalas	Indonesia	1257
1714	13	8	1	62	8			
1233	2	1	0	50	0			
1298	8	4	0	50	0			
1288	7	3	4	43	57			
1675	14	6	4	43	29			
1587	12	5	1	42	8	Kelut	Indonesia	1586
1835	12	4	4	33	33	Cosigüina	Nicaragua	20 Jan 1835
1809	13	4	5	31	38			
1345	11	2	7	18	64			
1601	10	1	3	10	30	Huaynaputina	Peru	19 Feb 1600
1884	10	1	2	10	20	Krakatau	Indonesia	26 Aug 1883
1816	13	0	4	0	31	Tambora	Indonesia	10 Apr 1815

0.29 (\pm 0.60), 0.52 (\pm 0.60) and 0.38 (\pm 0.56). The SEA patterns confirm common knowledge (figure 5):

largest and most significant (p < 0.05) increases of MXD-based temperature reconstructions capture severe summer cooling and rapid recovery, and the SAOD record reflects the approximate timing

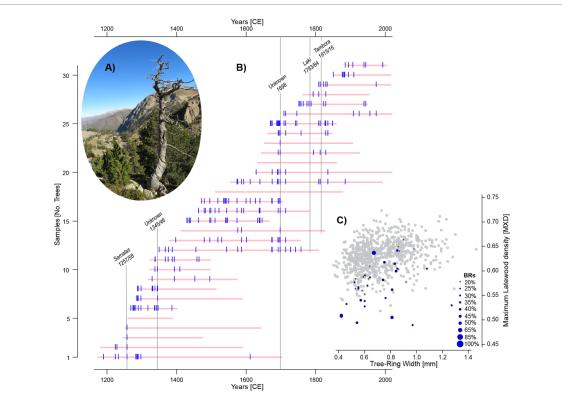


Figure 2. Blue Rings in the Spanish Pyrenees. (A) Example of a relict Mountain pine (*Pinus uncinata* Mill.) at the upper treeline in the central Spanish Pyrenees treeline (above 2000 m asl). (B) Horizontal pink lines show the time span of each of the 31 pine samples (see figures 3 and 4 for the number of samples in each year), with the vertical blue lines referring to the occurrence of BRs. Grey vertical lines in the background highlight the most important volcanic eruptions that are discussed in this study. (C) Comparison between the raw maximum latewood density values (MXD; g cm⁻³) and the raw tree-ring width values (TRW; mm) in 420 series from our sampling location (Büntgen *et al* 2017b) against the BR years (superimposed as blue dots). The size of the blue dots reflects the percentage of BRs identified in a particular year (20%–100%).

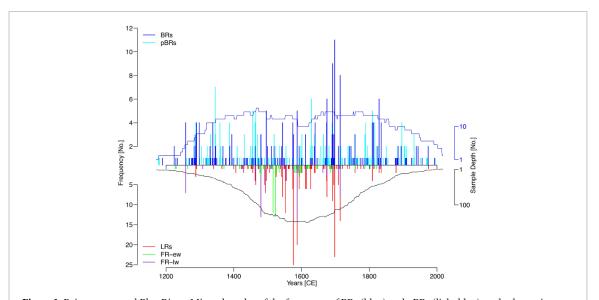


Figure 3. Pointer years and Blue Rings. Mirror bar plot of the frequency of BRs (blue) and pBRs (light blue), and other pointer years: light rings (LRs—red), frost rings in earlywood (FRs-ew—green) and in latewood (FRs-lw—violet) from 1170–2017 CE. The frequency expressed as a total number represented in the left *y*-axes differ from the occurrence of BRs and pBRs (1–12) and the other pointer years (1–25). The sample depth represented in the right *y*-axes differs from the occurrence of BRs and pBRs (1–31 samples) and the other pointer years (1–198 relict logs or snags discs).

of volcanic forcing but dating uncertainty must be considered.

Agreement between BRs, pBRs and reduced TRW and MXD is confirmed by the continuous intra- and

inter-annual assessment of three relict wood samples (figures S1, S2). Both, the cell lumen area and cell wall thickness in the latewood of BR years in these samples are reduced in comparison to fully lignified rings

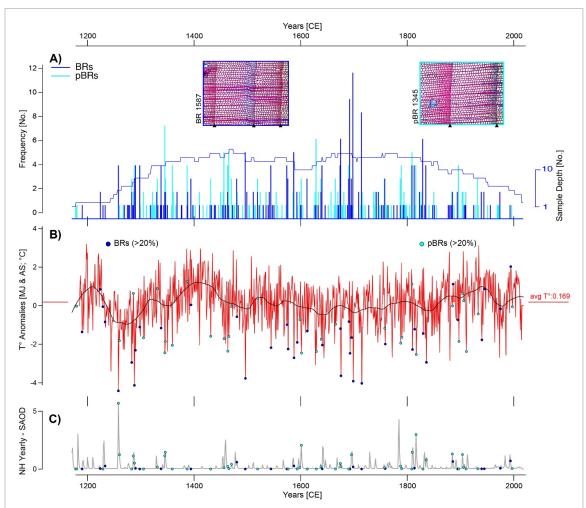


Figure 4. Blue Rings, temperature anomalies and volcanic eruptions. (A) Number of Blue Rings (BRs—blue vertical bar) and partial Blue Rings (pBRs—light blue vertical bar) through time from 1150 to 2017, and sample depth (black line). A microscopic magnification of double stained anatomical sections of BRs and pBRs is shown. (B) Reconstructed summer temperature (May–June—August–September) (red line) from 1186–2014 for maximum latewood density (MXD) expressed as temperature anomalies from the instrumental reference period 1961–1990 (Büntgen et al 2017b), and (C) the yearly stratospheric aerosol optical depth (SAOD) for the Northern Hemisphere extra-tropics $30-90^{\circ}$ N (Toohey and Sigl 2017). The black line imposed in the reconstructed summer temperature shows the smoothing line of 10%. Blue and light-blue circle represents the occurrence of BRs and pBRs $\geqslant 20\%$, respectively.

(figures S3, S4). Interestingly, the latewood of BRs is characterised by thin cell walls (figure S5), whereas the cell wall thickness in fully lignified rings usually increases towards and throughout the latewood. The Raman spectroscopy reveals differences in resin acids and the phenolic combination of pinosylvin and lignin between BRs and fully lignified rings (figure S6). The most distinct Raman signals for pinosylvin (at 1637 cm⁻¹) and resin acids (at 1652 cm⁻¹) are found in the cell walls and cell corners of the pBRs in 1338 and 1345 CE (figure S7).

4. Discussion and conclusions

This study strongly suggests that BRs and pBRs can be considered as a new indicator of severe ephemeral cold summer temperatures, with BRs formed at lower summer temperatures than pBRs. Moreover, our findings suggest that BR and pBR occurrence is not limited to a few trees nor influenced by tree age. The highest frequency of BRs, pBR, as well as FRs and LRs occurred during the coldest period of the Little Ice Age in the Pyrenees (Büntgen et al 2008, 2017b, Morellón et al 2011) (figures 3, 4). Moreover, we found significant agreement between BRs and low MXD (figure 2(C)), because cell wall thickening is compromised during cold growing seasons (Filion et al 1986, Schweingruber 1993, Vaganov et al 2006), and cell wall lignification is limited by temperature (Gindl et al 2000, Crivellaro and Büntgen 2020). However, the Walesch-based relative MXD values are not directly associated with the lignin content of the cell walls (Schweingruber et al 1978, Büntgen et al 2017b). What remains to be explained are those few years where BRs and pBRs are associated with high MXD and positive (reconstructed) temperature departures (figures 2(C), 4(B)). In such instances, we can only speculate on what might be responsible for inhibiting lignin deposition. The first explanation is that short and late-growing season

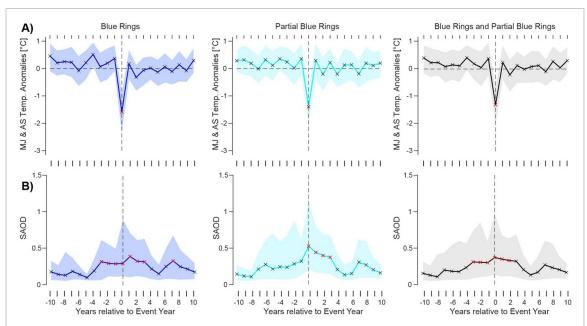


Figure 5. Blue Rings, temperature anomalies and volcanic eruptions. Superposed Epoch Analysis (SEA) of the Blue Ring (BR) and partial Blue Ring (pBR) years ($\geq 20\%$) against (A) the MXD-based summer temperature reconstruction from the Pyrenees (Büntgen *et al* 2017b), and (B) the yearly stratospheric aerosol optical depth (SAOD) of the Northern Hemisphere extra-tropics between 30−90°N (Toohey and Sigl 2017). The year zero (0) refers to the occurrence year of BRs (blue), pBRs (light blue), and the combination thereof (black), and the corresponding shadows refer to the upper and lower confidence intervals. Crosses represent mean values, whereas red crosses indicate significant anomalies (p < 0.001 in A and p < 0.05 in B). Please note that we decided to not calculate the SEA relative to the 10 years before the event to avoid spurious negative values in the SAOD timeseries.

cold spells affect the occurrence of BRs and pBRs (Piermattei *et al* 2015), but do not have a meaningful negative effect on either MXD or TRW. This could be the result of a week or even a few days of anomalously cold-wet conditions during summer affecting the newly developed cells.

Another potential explanation for the observed positive temperature response may involve the role lignin plays in enhancing the mechanical strength of cell walls, enabling plants to grow tall and transport water to great heights (Niklas 1992, Meents et al 2018). Such a line of inquiry will eventually lead back to how environmental conditions trigger auxin production (Mroue et al 2018), and what amounts of auxin are required for regulating lignin production, much of which we just do not know for many species and locations. What is abundantly clear is these anomalous warm-season BR observations represent a reliable indicator, manifest by the number of times they are found in different samples in the same year, of a rare condition that in the Pyrenees have occurred less than a dozen times in the past 800 years. Whether the responsible conditions are endogenous or exogenous, including possible drought stress at the upper treeline (Galván et al 2015), remains to be explored. A good position from which to start this exploration would be armed with a contiguous BR chronology from temperature sensitive trees at a location where daily, possibly even hourly climate data are available.

Another source of possible uncertainty is related to the fact that the qualitative double-staining

technique with Safranin and Astra Blue, while a reliable indicator (Baldacci-Cresp et al 2020) is not a direct measure of cell wall lignification. Our results from Raman spectroscopy are not conclusive either (figures S6, S7). Beside lignin, other aromatic compounds such as pinosylvin, the spectral properties of which partly overlap with those of lignin (Felhofer et al 2018), were also detected in the cell walls. However, Raman imaging revealed an increase of phenolic extractives (pinosylvin and resin acids) in the BRs and pBRs of 1338 and 1345 CE. This finding raises the question whether the synthesis of these compounds might be a protective response to climatically-driven stress or aromatic moieties unrelated to lignification. Raman spectroscopy captured and envisaged extractive phenolic content in the lumen, walls and corners of the analysed cells (figure S7), which is consistent with the findings of Belt et al (2017) and Felhofer et al (2018). Pinosylvin is a plant secondary metabolite belonging to the stilbene family (see the molecular structure in figure S7(D)). This metabolite is an effective fungicide that occurs in pine heartwood (Hovelstad et al 2006) and is known to accumulate in cells in response to cold climates (Erdtman and Rennerfelt 1944, Joosen et al 2006, Chong et al 2009, Felhofer et al 2018). Moreover, trees can reduce the consumption of nutrients in response to external stressors, which increases the rate of secondary metabolite production (Rudman 1966, Stewart 1966). The high level of additional phenolic compounds that we measured in BR years might result from an increase of metabolic products due to a decreased

demand for nutrients during cold summer events (Metsämuuronen and Sirén 2019). Despite much progress, we still lack a comprehensive understanding of the processes involved in cell wall lignification and secondary metabolite production in trees (Donaldson 1991, Gindl and Grabner 2000, Ramakrishna and Ravishankar 2011, Crivellaro and Büntgen 2020).

In conclusion, our continuous wood anatomical assessment of 31 living and relict pine samples from a high-elevation, treeline site in the central Spanish Pyrenees (Büntgen et al 2008, 2017b) shows that the majority of BR years since 1150 CE coincide with cold summer temperatures. While many BRs follow large volcanic eruptions, such as 80% BRs in 1258 after Samalas (Vidal et al 2016, Guillet et al 2017), some were formed during overall warm summers as in 1232/33 and 1883/84 in which neither TRW nor MXD exhibit negative anomalies. The eruptions of Tambora in 1815 (Oppenheimer 2003) and Laki in 1783 (Thordason and Self 1993) had only moderate and almost no effects on the formation of BRs in the Pyrenees, respectively (table S1). These findings do not contradict our understanding of the spatial extent of the post-Tambora 'year without a summer' that was most pronounced in central Europe but less over the Iberian Peninsula (Trigo et al 2009, Büntgen et al 2017b), as well as the climatic effect of Laki (D'Arrigo et al 2011, Schmidt et al 2012) that had almost no effect on the formation of MXD in the Pyrenees (Büntgen et al 2017b). The highest concentration of 85% BRs occurs in 1698 CE. This distinct wood anatomical anomaly at the end of the 17th century likely resulted from a cluster of yet unidentified tropical eruptions (Sigl et al 2015, Toohey and Sigl 2017), and is corroborated by bi-polar sulphur ice core peaks in 1695/96 (Irawan et al 2009). The cold summer of 1698 in the western Mediterranean basin also corresponds with catastrophic famine and unprecedented mortality in Scotland (D'Arrigo et al 2020). The occurrence of two consecutive BRs in 1345 and 1346, which is a very rare phenomena in our new timeseries (table S1), coincides with the onset and establishment of the Black Death (Ziegler 1969, Twigg 1984); Europe's most devastating plague pandemic caused by Yersinia pestis (Stenseth et al 2008, Schmid et al 2015).

Based on their sensitivity to abrupt cooling of several weeks or even days during the growing season, BRs offer a new high-resolution archive for refining the dating of ice core records. We consider BRs can improve the dating accuracy of past volcanic eruptions, because they can capture very short cold spells and are not affected by biological memory, a condition indicative of TRW (Frank *et al* 2007, Franke *et al* 2013). Moreover, BRs can help to identify possible short-term associations between volcanism, weather and society. We are also convinced that BRs are skilful for disentangling the volcano-climate-human nexus on sub-seasonal time-scales, because

agricultural productivity, and thus societal vulnerability, can depend on short-term weather extremes (Brázdil et al 2005, Battipaglia et al 2010), which are generally not captured in variations of the more classical TRW and MXD parameters. The fact that differences exist in climate responses to volcanic eruptions—both in space and in time—underlines the benefit of combining evidence from different treering parameters (Büntgen 2019). Achievements at the interface of quantitative wood anatomy and dendroclimatology are expected to improve the spatial coverage of BR records for the past millennium in both hemispheres, and even over the past 2000 years at a few sites. The combined, high-resolution, wood anatomical and dendrochronological insights should be compared against spatiotemporally explicit early instrumental and documentary evidence to gain deeper understanding of the timing and climatic forcing of yet unidentified eruptions and their source volcanos, such as the eruption(s) in 1345(6) that likely caused cooling at the onset of Europe's Black Death, or the possible cluster of eruptions between around 1808 and 1813 that possibly added to the exceptional temperature depression in the aftermath of the Tambora eruption in 1815 CE. In case of the 1808-1809 mystery eruption (Dai et al 1991, Chenoweth 2001, Cole-Dai et al 2009, Guevara-Murua et al 2014), our wood anatomical evidence would suggest that cooling reached the Pyrenees before November, because latewood formation and subsequent cell wall lignification are known to occur between September and October when high-elevation pines in the central Spanish Pyrenees recycle non-structural carbohydrates from the beginning of the growing season in May and June (Camarero et al 1998, Büntgen et al 2017b).

Last but not least, we encourage intensified efforts to improve our understanding of the physiological mechanisms behind the lignification process in plant cell walls (Meents et al 2018), and of the possible connections between cell wall lignification and temperature (Piermattei et al 2015, Crivellaro and Büntgen 2020, Tardif et al 2020). The feasibility of such work, however, critically depends on the quality and availability of both, suitable wood samples, as well as in situ meteorological measurements.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

- Agarwal U P 2006 Raman imaging to investigate ultrastructure and composition of plant cell walls: distribution of lignin and cellulose in black spruce wood (*Picea mariana*) *Planta* 224 1141–53
- Anchukaitis K J et al 2012 Tree rings and volcanic cooling Nat. Geosci. 5 836–7
- Anchukaitis K J *et al* 2017 Last millennium Northern Hemisphere summer temperatures from tree rings: part II, spatially resolved reconstructions *Quat. Sci. Rev.* **163** 1–22
- Baldacci-Cresp F, Spriet C, Twyffels L, Blervacq A-S, Neutelings G, Baucher M and Hawkins S 2020 A rapid and quantitative safranin-based fluorescent microscopy method to evaluate cell wall lignification *Plant J.* 102 1074–89
- Battipaglia G, Frank D C, Büntgen U, Dobrovolny P, Brázdil R, Pfister C and Esper J 2010 Five centuries of Central European temperature extremes reconstructed from tree-ring density and documentary evidence *Glob. Planet. Change* 72 182–91
- Belt T, Keplinger T, Häninen T and Rautkari L 2017 Cellular level distributions of Scots pine heartwood and knot heartwood extractives revealed by Raman spectroscopy imaging *Ind. Crops. Prod.* **108** 327–35
- Björklund J et al 2019 Scientific merits and analytical challenges of tree-ring densitometry Rev. Geophys. 57 1224–64
- Brázdil R, Pfister C, Wanner H, von Storch H and Luterbacher J 2005 Historical climatology in Europe—the state of the art Clim. Change **70** 363–430
- Briffa K R, Osborn T J, Schweingruber F H, Jones P D, Shiyatov S G and Vaganov E A 2002 Tree-ring width and density around the Northern Hemisphere: part 1, local and regional climate signals *Holocene* 12 737–57
- Briffa K R, Schweingruber F H, Jones P D, Osborn T J, Shiyatov S G and Vaganov E A 1998 Reduced sensitivity of recent tree-growth to temperature at high northern latitudes Nature 391 678–82
- Büntgen U *et al* 2011 Causes and consequences of past and projected Scandinavian summer temperatures, 500–2100 AD *PloS One* 6 e25133
- Büntgen U *et al* 2016 Cooling and societal change during the late antique little Ice Age from 536 to around 660 AD *Nat. Geosci.* 9 231–6
- Büntgen U *et al* 2017a Multi-proxy dating of Iceland's major pre-settlement Katla eruption to 822–823 CE *Geology* 45 783–6
- Büntgen U *et al* 2017b New tree-ring evidence from the Pyrenees reveals western Mediterranean climate variability since medieval times *J. Clim.* **30** 5295–318
- Büntgen U *et al* 2018 Tree rings reveal globally coherent signature of cosmogenic radiocarbon events in 774 and 993 CE *Nat. Commun.* 9 3605

- Büntgen U 2019 Re-thinking the boundaries of dendrochronology *Dendrochronologia* 53 1–4
- Büntgen U et al 2020 Prominent role of volcanism in Common Era climate variability and human history Dendrochronologia 64 125757
- Büntgen U, Frank D C, Nievergelt D and Esper J 2006 Summer temperature variations in the European Alps, AD 755–2004 *J. Clim.* 19 5606–23
- Büntgen U, Frank D, Grudd H and Esper J 2008 Long-term summer temperature variations in the Pyrenees *Clim. Dyn.* 31 615–31
- Büntgen U, Wacker L, Nicolussi K, Sigl M, Güttler D, Tegel W, Krusic P J and Esper J 2014 Extra-terrestrial confirmation of tree-ring dating *Nat. Clim. Change* 4 404–5
- Camarero J J, Guerrero-Campo J and Gutiérrez E 1998

 Tree-ring growth and structure of *Pinus uncinata* and *Pinus sylvestris* in the central Spanish Pyrenees *Arct. Alp. Res.*30 1–10
- Chenoweth M 2001 Two major volcanic cooling episodes derived from global marine air temperature, AD 1807–1827 *Geophys. Res. Lett.* 28 2963–6
- Chong J, Poutaraud A and Hugueney P 2009 Metabolism and roles of stilbenes in plants *Plant Sci.* 177 143–55
- Cole-Dai J, Ferris D, Lanciki A, Savarino J, Baroni M and Thiemens M H 2009 Cold decade (AD 1810–1819) caused by Tambora (1815) and another (1809) stratospheric volcanic eruption *Geophys. Res. Lett.* 36 L22703
- Crivellaro A and Büntgen U 2020 New evidence of thermally-constraint plant cell wall lignification *Trends Plant Sci.* **25** 322–4
- Crivellaro A, Reverenna M, Ruffinatto F, Urbinati C and Piermattei A 2018 The anatomy of 'Blue Ring' in the wood of *Pinus nigra LES/WOOD* **67** 21–28
- Crowley T J 2000 Causes of climate change over the past 1000 years *Science* **289** 270–7
- Cuny H E, Rathgeber C B, Frank D, Fonti P and Fournier M 2014 Kinetics of tracheid development explain conifer tree-ring structure New Phytol. 203 1231–41
- D'Arrigo R, Klinger P, Newfield T, Rydval M and Wilson R 2020 Complexity in crisis: the volcanic cold pulse of the 1690s and the consequences of Scotland's failure to cope *J. Volcanol. Geotherm. Res.* 389 106746
- D'Arrigo R, Seager R, Smerdon J E, Legrande A N and Cook E R 2011 The anomalous winter of 1783–1784: was the Laki eruption or an analog of the 2009–2010 winter to blame *Geophys. Res. Lett.* **38** L05706
- D'Arrigo R, Wilson R and Anchukaitis K J 2013 Volcanic cooling signal in tree ring temperature records for the past millennium *J. Geophys. Res.* **118** 9000–10
- Dai J, Mosley-Thompson E and Thompson L G 1991 Ice core evidence for an explosive tropical volcanic eruption 6 years preceding Tambora *J. Geophys. Res. Atmos.* **96** 17361–6
- Di Cosmo N, Oppenheimer C and Büntgen U 2017 Interplay of environmental and socio-political factors in the downfall of the Eastern Türk Empire in 630 CE Clim. Change 145 383–95
- Donaldson L A 1991 Seasonal changes in lignin distribution during tracheid development in *Pinus radiata* D. Don *Wood Sci. Technol.* **25** 15–24
- Dull R A et al 2019 Radiocarbon and geologic evidence reveal Ilopango volcano as source of the colossal 'mystery' eruption of 539/40 CE Quat. Sci. Rev. 222 105855
- Erdtman H and Rennerfelt E 1944 The pinosylvin-phenolic content of pine heartwood; its determination and its antiseptic action towards wood-destroying fungi *Svensk*. *Papper.* **47** 45–56
- Eschbach W, Nogler P, Schär E and Schweingruber F 1995 Technical advances in the radiodensitometrical determination of wood density *Dendrochronologia* 13 155–68
- Esper J, Schneider L, Krusic P J, Luterbacher J, Büntgen U, Timonen M, Sirocko F and Zorita E 2013 European summer temperature response to annually dated volcanic

- eruptions over the past nine centuries *Bull. Volcanol.* **75** 736
- Esper J, Schneider L, Smerdon J E, Schöne B R and Büntgen U 2015 Signals and memory in tree-ring width and density data *Dendrochronologia* 35 62–70
- Felhofer M, Pratz-Mateu B, Bock P and Gierlinger N 2018 Antifungal stilbene impregnation: transport and distribution on the micron-level *Tree Physiol.* **38** 1526–37
- Filion L, Payette S and Boutin Y 1986 Light rings in subarctic conifers as a dendrochronological tool *Quat. Res.* 26 272–9
- Frank D, Büntgen U, Böhm R, Maugeri M and Esper J 2007 Warmer early instrumental measurements versus colder reconstructed temperatures: shooting at a moving target Quat. Sci. Rev. 26 3298–310
- Franke J, Frank D, Raible C C, Esper J and Brönnimann S 2013 Spectral biases in tree-ring climate proxies *Nat. Clim. Change* 3 360–4
- Fritts H C 1976 *Tree Rings and Climate* (New York: Academic)
 Galván J D, Büntgen U, Ginzler C, Grudd H, Gutiérrez E,
 Labuhn I and Camarero J J 2015 Drought-induced
 weakening of growth-temperature associations in
 Mediterranean high-elevation forests *Glob. Planet. Change*124 95–106
- Gao C, Robock A and Ammann C 2008 Volcanic forcing of climate over the past 1500 years: an improved ice core-based index for climate models *J. Geophys. Res.* 113 D23111
- Gärtner H, Banzer L, Schneider L, Schweingruber F H and Bast A 2015 Preparing micro sections of entire (dry) conifer increment cores for wood anatomical time-series analyses *Dendrochronologia* 34 19–23
- Gärtner H and Schweingruber F H 2013 Microscopic Preparation Techniques for Plant Stem Analysis (Remagen-Oberwinter: Verlag Dr. Kessel)
- Gerlach D 1984 Botanische Mikrotechnik (Stuttgart: Georg Thieme Verlag)
- Ghislan B, Engel J and Clair B 2019 Diversity of anatomical structure of tension wood among 242 tropical tree species *Iawa J.* **40** 1–20
- Gierlinger N, Keplinger T and Harrington M 2012 Imaging of plant cell walls by confocal Raman microscopy *Nat. Protocols* 7 1694–708
- Gierlinger N and Schwanninger M 2006 Chemical imaging of poplar wood cell walls by confocal Raman microscopy *Plant Physiol.* **140** 1246–54
- Gindl W and Grabner M 2000 Characteristics of spruce [*Picea abies* (L.) Karst] latewood formed under abnormally low temperatures *Holzforschung* 54 9–11
- Gindl W, Grabner M and Wimmer R 2000 The influence of temperature on latewood lignin content in treeline Norway spruce compared with maximum density and ring width *Trees* 14 409–14
- Guevara-Murua A, Williams C A, Hendy E J, Rust A C and Cashman K V 2014 Observations of a stratospheric aerosol veil from a tropical volcanic eruption in December 1808: is this the Unknown ~1809 eruption Clim. Past 10 1707–22
- Guillet S et al 2017 Climate response to the Samalas volcanic eruption in 1257 revealed by proxy records Nat. Geosci. 10 123–8
- Guillet S, Corona C, Ludlow F, Oppenheimer C and Stoffel M 2020 Climatic and societal impacts of a 'forgotten' cluster of volcanic eruptions in 1108–1110 CE Sci. Rep. 10 6715
- Hovelstad H, Leirset I, Oyaas K and Fiksdahl A 2006 Screening analyses of pinosylvin stilbenes, resin acids and lignans in Norwegian conifers *Molecules* 11 103–14
- Irawan D, Puradimaja D J, Notosiswoyo S and Soemintadiredja P 2009 Hydrogeochemistry of volcanic hydrogeology based on cluster analysis of Mount Ciremai, West Java, Indonesia *J. Hydrol.* **376** 221–34
- Joosen R V L, Lammers M, Balk P A, Brønnum P, Konings M C J M, Perks M, Stattin E, van Wordragen M F and van der Geest A H M 2006 Correlating gene expression to physiological parameters and environmental conditions

- during cold acclimation of Pinus sylvestris, identification of molecular markers using cDNA microarrays *Tree Physiol.* **26** 1297–313
- Körner C, Riedl S, Keplinger T, Richter A, Wiesenbauer J, Schweingruber F and Hiltbrunner E 2019 Life at 0° C: the biology of the alpine snowbed plant Soldanella pusilla *Alp. Bot.* **129** 63–80
- Krakauer N Y and Randerson J T 2003 Do volcanic eruptions enhance or diminish net primary production? Evidence from tree rings Glob. Biogeochem. Cycles 17 1118
- Lamarche V C and Hirschboeck K K 1984 Frost rings in trees as records of major volcanic eruptions *Nature* 307 121–6
- McCormick M 1992 Initial assessment of the stratospheric and climatic impact of the 1991 Mount Pinatubo eruption: Prologue *Geophys. Res. Lett.* 19 149
- Meents M J, Watanabe Y and Samuels A L 2018 The cell biology of secondary cell wall biosynthesis Ann. Bot. 11 1107–25
- Metsämuuronen S and Sirén H 2019 Bioactive phenolic compounds, metabolism and properties: a review on valuable chemical compounds in Scots pine and Norway spruce *Phytochem. Rev.* **18** 623–64
- Morellón M *et al* 2011 Climate changes and human activities recorded in the sediments of Lake Estanya (NE Spain) during the medieval warm period and little Ice Age *J. Paleolimnol.* **46** 423–52
- Mroue S, Simeunovvic A and Robert H S 2018 Auxin production as an integrator of environmental cues for developmental growth regulation *J. Exp. Bot.* **69** 201–12
- Niklas K J 1992 Plant Biomechanics: An Engineering Approach to Plant Form and Function (Chicago, IL: University of Chicago Press)
- Oppenheimer C 2003 Climatic, environmental and human consequences of the largest known historic eruption: Tambora volcano (Indonesia) 1815 *Prog. Phys. Geogr.* 27 230–59
- Oppenheimer C 2011 Eruptions that Shook the World (Cambridge: Cambridge University Press)
- Oppenheimer C et al 2017 Multi-proxy dating the 'Millennium Eruption' of Changbaishan to late 946 CE *Quat. Sci. Rev.* **158** 164–71
- Oppenheimer C, Orchard A, Stoffel M, Newfield T P, Guillet S, Corona C, Sigl M, Di Cosmo N and Büntgen U 2018 The Eldgjá eruption: timing, long-range impacts and influence on the Christianisation of Iceland *Clim. Change* 147 369–81
- Otto-Bliesner B L *et al* 2016 Climate variability and change since 850 CE: an ensemble approach with the community Earth system *Model Bull. Am. Meteorol. Soc.* **97** 735–54
- Piermattei A, Crivellaro A, Carrer M and Urbinati C 2015 The 'blue ring': anatomy and formation hypothesis of a new tree-ring anomaly in conifers *Trees* 29 613–20
- Ramakrishna A and Ravishankar G A 2011 Influence of abiotic stress signals on secondary metabolites in plants *Plant Signal. Behav.* **6** 1720–31
- Rao M P *et al* 2017 European and Mediterranean hydroclimate responses to tropical volcanic forcing over the last millennium *Geophys. Res. Lett.* 44 5104–12
- Robock A 2000 Volcanic eruptions and climate *Rev. Geophys.* **38** 191–219
- Rudman P 1966 Heartwood formation in trees *Nature* 210 608–10
- Russell P B *et al* 1996 Global to microscale evolution of the Pinatubo volcanic aerosol derived from diverse measurements and analyses *J. Geophys. Res.* **101** 18745–63
- Schmid B V, Büntgen U, Easterday W R, Ginzler C, Walløe L, Bramanti B and Stenseth N C 2015 Climate-driven introduction of the Black Death and successive plague reintroductions into Europe *Proc. Natl Acad. Sci. USA* 112 3020–5
- Schmidt A, Thordarson T, Oman L D, Robock A and Self S 2012 Climatic impact of the long-lasting 1783 Laki eruption:

- inapplicability of mass-independent sulfur isotopic composition measurements *J. Geophys. Res.* **117** D23116
- Schneider L, Smerdon J E, Büntgen U, Wilson R J S, Myglan V S, Kirdyanov A V and Esper J 2015 Revising midlatitude summer temperatures back to A.D. 600 based on a wood density network *Geophys. Res. Lett.* 42 4556–62
- Schweingruber F H Trees and Wood in Dendrochronology 1993 (Berlin: Springer)
- Schweingruber F H, Fritts H C, Braker O U, Drew L G and Schar E 1978 The x-ray technique as applied to dendroclimatology *Tree-Ring Bull.* **38** 61–91
- Sigl M et al 2015 Timing and climate forcing of volcanic eruptions for the past 2,500 years Nature 523 543–9
- Smith V Cet al 2020 The magnitude and impact of the 431 CE Tierra Blanca Joven eruption of Ilopango, El Salvador Proc. Natl Acad. Sci. USA 117 26061–8
- Stenseth N C, Atshabar B B, Begon M, Belmain S R, Bertherat E, Carniel E, Gage K L, Leirs H and Rahalison L 2008 Plague: past, present, and future *PloS Med.* 5 e3
- Stewart M 1966 Excretion and heartwood formation in living trees *Science* 153 1068–74
- Stoffel M *et al* 2015 Estimates of volcanic-induced cooling in the Northern Hemisphere over the past 1,500 years *Nat. Geosci.* **8** 784–8
- Svensson A *et al* 2020 Bipolar volcanic synchronization of abrupt climate change in Greenland and Antarctic ice cores during the last glacial period *Clim. Past* 16 1565–80
- Tardif J C, Salzer M W, Conciatori F, Bunn A G and Hughes M K 2020 Formation, structure and climatic significance of blue rings and frost rings in high elevation bristlecone pine (*Pinus longaeva* D K Bailey) *Quat. Sci. Rev.* 244 106516
- Thordason T and Self S 1993 The Laki (Skaftár Fires) and Grúmsvötn eruptions in 1783–1785 *Bull. Volcanol.* 55 233–63
- Timmreck C 2012 Modeling the climatic effects of large explosive volcanic eruptions *Wiley Interdiscip. Rev. Clim. Change* 3 545–64
- Toohey M, Krüger K, Schmidt H, Timmreck C, Sigl M, Stoffel M and Wilson R 2019 Disproportionately strong climate

- forcing from extratropical explosive volcanic eruptions *Nat. Geosci.* 12 100–7
- Toohey M and Sigl M 2017 Volcanic stratospheric sulfur injections and aerosol optical depth from 500BCE to 1900CE Earth Syst. Sci. Data 9 809–31
- Trigo R M, Vaquero J M, Alcoforado M-J, Barriendos M, Taborda J, García-Herrera R and Luterbacher J 2009 Iberia in 1816, the year without a summer *Int. J. Climatol*. 29 99–115
- Twigg G 1984 The Black Death: A Biological Reappraisal (London: Batsform Academic and Educational)
- Vaganov E A, Hughes M K and Shashkin A V 2006 Growth

 Dynamics of Conifer Tree Rings. Images of the past and Future
 Environments (Berlin: Springer)
- Vidal C M, Métrich N, Komorowski J C, Pratomo I, Michel A, Kartadinata N, Robert V and Lavigne F 2016 The 1257 Samalas eruption (Lombok, Indonesia): the single greatest stratospheric gas release of the Common Era Sci. Rep. 6 34868
- von Arx G and Carrer M 2014 ROXAS–A new tool to build centuries-long tracheid-lumen chronologies in conifers Dendrochronologia 32 290–3
- Wilson R et al 2016 Last millennium northern hemisphere summer temperatures from tree rings: part I: the long term context *Quat. Sci. Rev.* 134 1–18
- Ziegler P 1969 *The Black Death* (Wolfeboro Falls (NH): Alan Sutton Publishing)
- Zielinski G A 1995 Stratospheric loading and optical depth estimates of explosive volcanism over the last 2100 years derived from the Greenland Ice Sheet Project 2 ice core *J. Geophys. Res. Atmos.* **100** 20937–55
- Zielinski G A, Mayewski P A, Meeker L D, Whitlow S and Twickler M S 1996 A 110,000-yr record of explosive volcanism from the GISP2 (Greenland) ice core *Quat. Res.* 45 109–18
- Zielinski G A, Mayewski P A, Meeker L D, Whitlow S, Twickler M S, Morrison M, Meese D A, Gow A J and Alley R B 1994 Record of volcanism since 7000 BC from the GISP2 Greenland ice core and implications for the volcano-climate system *Science* 264 948–52