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Chemical Signals in Tree Rings from Northern Patagonia as Indicators of Calbuco Volcano Eruptions since the 16th Century

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Abstract: The Calbuco volcano ranks third in the specific risk classification of volcanoes in Chile and has a detailed eruption record since 1853. During 2015, Calbuco had a sub-Plinian eruption with negative impacts in Chile and Argentina, highlighting the need to determine the long-term history of its activity at a high-resolution time scale to obtain a better understanding of its eruptive frequency. We developed a continuous eruptive record of Calbuco for the 1514–2016 period by dendrochemical analysis of *Fitzroya cupressoides* tree rings at a biennium resolution using inductively coupled plasma–mass spectrometry. After comparing the chemical record of 20 elements contained in tree rings with historical eruptions, one group exhibited positive anomalies during (Pb/Sn) and immediately after (Mo/P/Zn/Cu) eruptions, with a Volcanic Explosivity Index (VEI) $\geq$ 3, and so were classified as chemical tracers of past eruptions (TPE). The tree-ring width chronology also exhibited significant decreases in tree growth associated with eruptions of VEI $\geq$ 3. According to these records, we identified 11 new eruptive events of Calbuco, extending its eruptive chronology back to the 16th century and determining a mean eruptive frequency of ~23 years. Our results show the potential to use dendrochemical analysis to infer past volcanic eruptions in Northern Patagonia. This information provides a long-term perspective for assessing eruptive history in Northern Patagonia, with implications for territorial planning.

Keywords: dendrochronology; volcanic eruptions; inductively coupled plasma–mass spectrometry; *Fitzroya cupressoides*

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1. Introduction

Along the vast Chilean portion of the Circum-Pacific ring of fire, nearly 90 volcanoes are active, resulting in a high exposure to volcanic hazards [1]. To develop hazard maps and risk mitigation planning nationwide, accounts of regional eruption records must be obtained to accurately determine eruptive frequency and recurrence rates. Volcanoes located in Patagonia (38°–55° S) have scarce or no historical eruptive records due to difficulties in access, a rainy climate, dense vegetation cover, and rare outcrops of volcanic deposits that prevent detailed study of eruptive history. Conversely, from the tephrochronology in soils it is possible to date volcanic events, and lacustrine records can provide complementary information across multi-millennial time frames [2–4]. However, ^{14}C dating has low temporal resolution, which limits precise estimates of eruptive frequency and recurrence rates.

An alternative and complementary method for dating past volcanic eruptions is by tree rings. Volcanic eruptions can generate tree growth anomalies, resulting in the narrowing or even absence of annual rings [5–8] as a consequence of physical damage to the leaves and stems of trees [9] and/or low temperatures induced by emissions of aerosols [10]. In Chile, tree growth anomalies have been observed in *Nothofagus* forests after the massive tephra fall following the eruption of the Cordón Caulle volcano in 2011 [11]. However, growth anomalies in tree rings may also be related to other types of disturbances such as insect defoliation [12], earthquakes [13,14], floods [15], fires [16], herbivore activity [17], and stand dynamics, thereby complicating its simple association with volcanic eruptions.

Because tree rings result from interactions between biological and physical environmental factors, they can be used to study and monitor environmental variations related to chemical anomalies [18]. As volcanic eruptions generate physical and chemical changes in the soil and atmosphere that determine tree growth anomalies, they can also produce anomalies in the concentrations of chemical elements within tree rings. Hence, chemical analysis of tree-ring sequences appears to be complementary in dating past volcanic eruptions at a high-resolution timescale [19]. The application of dendrochemistry in the study of volcanic eruptions is based on two hypotheses: a direct and an indirect response. The direct response implies that a chemical signature (sulfur, phosphorus, silver, zinc, copper, iron, manganese, or rare earth elements) identified in the tephra generated by a volcanic eruption can enter directly into a tree and be identified in the tree rings. This entry of the elements contained in the tephra that are available to plants, such as S, Zn, Cu, Mn, Fe and P, occurs immediately [20,21], or later, when the tephra deposited in the soil becomes weathered (by the effect of water and biological agents in the soil) and the chemical bonds are broken, thus releasing chemical elements that can be absorbed by the roots. Another method of direct entrance into the tree is through the stomata of its leaves, which allow the absorption of chemical elements of the tephra deposited on the leaves or in suspension in the air. This may be the case for gaseous forms of sulfur absorbed directly by the trees through the stomata [22,23], resulting in a characteristic geochemical signature in tree rings that can be related to the existence of tephra fall. However, it has been observed that the entry of metals into the tree through the leaf stomata can be faster than through the roots [24].

An indirect response can be observed through the relationship of tephra and nutrient uptake since tephra might modify soil pH after a volcanic eruption [25], which in turn alters the availability of nutrients in soil for tree absorption, decreasing or increasing the chemical concentrations in tree rings [19]. The decrease in soil pH will depend on the amount of SO_2 emitted during the eruption that is dispersed in the eruptive column and is deposited in a dissolved form in the tephra [26]. Finally, the effect of tephra fall on the chemistry and possible signal of the trees would also be variable according to: (1) the characteristics of the eruption, such as its magnitude and the amount (thickness), granulometry, and chemical composition of deposited tephra; (2) the atmospheric characteristics (climate) that influence the wind dispersion of the eruptive column and the weathering of the deposited tephra; (3) site characteristics such as location, distance from the volcanic source, topography (slope favors the erosion of the tephra), and the physico-chemical characteristics of the soil (such as pH, cation exchange capacity, presence of mycorrhizal fungi).

Dendrochemical studies identify temporal variability in the environment by using advanced analytical techniques to measure the content of chemical elements present in annual tree rings. The methods used to determine volcanic signatures in tree rings include inductively coupled plasma–mass spectrometry (ICP–MS) [22,23,27–29], laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) [19,30,31], synchrotron scanning X-ray fluorescence microscopy (SXFM) [32], and neutron activation analysis (NAA) for isotopic concentration measurements [32]. Some examples of volcanic eruption dating using dendrochemical analysis include the detection of high concentrations of rare earths (cerium, neodymium, lanthanum, samarium and lutetium) in trees from Mount St. Helens during the years 1478 and 1490 [22], increases in sulfur and phosphorus in trees from the Paricutín volcano during 1943 and 1952 [23], increases of sulfur, calcium, rare earths, zinc, and hafnium in tree rings during the eruption of the Thera volcano [28], increases of barium, copper, and zinc following the eruptions of the Laki (1783), Tambora (1815), and Krakatoa (1883) volcanoes [19], and elevated phosphorus content related to the Mount Hood eruption in 1781 AD [31]. Despite the significant advances achieved during the last decade, progress is still needed in dendrochemistry research of volcano activity, as some studies have been inconclusive [27] or were developed only after large-scale eruptions [30]. In spite of the usefulness of dendrochemical studies as indicators of volcanic eruptions and tracers of pollution, this approach could have some limitations due to possible lateral mobility of chemical elements through the wood and the adjacent annual rings due to physiological processes in the living wood [33–35]. Thus, the possible mobility from sapwood to heartwood could affect the element distribution. However, dendrochemical studies have been demonstrated to be very useful to track past volcanic eruptions, and the development and application of this technique is still in progress; thus, more studies are necessary to refine it and achieve a better understanding.

Given the existence of various active volcanoes and useful tree species for dendrochronological studies, Northern Patagonia offers an opportunity for assessing volcanic eruption signals in tree rings and backtracking eruptive records. The Calbuco volcano ranks third in the specific risk classification of active volcanoes in Chile [1] and has a detailed historical eruption record after the foundation of the nearby city of Puerto Montt during the mid-19th century. In the Andean forests of this region, the long-lived *Fitzroya cupressoides* species is present. This tree species has been extensively used for dendrochronological studies including climate reconstructions and ecological studies [36–39]. Currently, there are more than 20 millennial length tree-ring chronologies of *F. cupressoides* in the region that can be used as a reference series to date and develop new records near the Calbuco volcano. Based on the tephra fall during Calbuco eruptions, that would have produced chemical anomalies in the annual growth rings of *F. cupressoides* of adjacent forests, this study aims to develop a dendrochemical record as a high-resolution proxy for identifying Calbuco eruptions during the last 500 years—testing a new approach for studying volcanic activity in Chile. The specific goals of this study are: (a) to develop dendrochemical records of 20 elements at biennium scale contained in *F. cupressoides* tree rings during the last 500 years near the Calbuco volcano, (b) to examine the potential relationship between chemical signals in *F. cupressoides* tree rings and documented Calbuco eruptions, (c) to date Calbuco eruptions during the last 500 years, inferred from distinctive chemical and tree-growth anomalies in *F. cupressoides* tree rings, and (d) to determine the eruptive frequency of the Calbuco volcano based on a reconstructed activity record inferred from the dendrochemical record.

2. Materials and Methods

2.1. Geological Setting and Eruptive History of Volcanoes in Southern Chile

The volcanic arc of the Andes is the product of the subduction of the Nazca plate underneath the South American plate at a velocity of 7–9 cm/yr [40]. There are nearly 90 active volcanoes located throughout the Central and Southern Andes of Chile [1]. Since AD 1900, about 200 eruptions have been recorded in Chile, many of these affecting human populations and infrastructure. The largest historical eruptions in Chile have been Quizapu 1932 [41], Hudson 1991 [42,43], Láscar 1993 [44], Chaitén 2008 [45], and Cordón Caulle 2011 [46]. Except for the Lascar volcano, these volcanoes are located in the Southern Andes. The southern part of the Southern Andes volcanic arc is directly related to the Liquiñe-Ofqui Fault Zone (LOFZ), which weakens the continental crust and helps the magma ascend [47–49].

Calbuco is an active stratovolcano located in the Southern Andes volcanic arc, Northern Patagonia of Chile (41°20′ S/72°37′ W; 2,003 m a.s.l.), 30 km northeast of Puerto Montt (Figure 1). According to the Chilean Geological and Mining Survey, Calbuco ranks third in the specific risk classification of active volcanoes in Chile [1], which is based on the dangers and exposure of human populations to eruptions of national volcanoes. This volcano has formed over the last ~300,000 years [50], and the historical record (Table 1) indicates more than 11 eruptive cycles since AD 1792 [51,52], with an eruptive frequency of 19 years. The historical eruption record is detailed and reliable after 1853, when the nearby city of Puerto Montt was founded. These eruptive cycles mean volcanic activity periods are generally integrated by two or more eruptions (or explosions), and that their activity is effusive and explosive, with tephra dispersion mainly drifting northeast and east due to predominantly westerly winds. The eruptions are primarily of andesitic composition with violent sub-Plinian eruptive behavior that includes pyroclastic and lava flows, domes, spines, blasts and lahars [53]. The most recent eruption of the Calbuco volcano occurred in April 2015 (Figure 2); it was sub-Plinian, with a Volcanic Explosivity Index (VEI) of ~4 [54–56]. It generated pyroclastic density currents, lahars, and tephra fall, causing many impacts in Chile and Argentina such as damage to infrastructure, and agricultural and livestock activities, as well as suspending regional air traffic for a few weeks [57]. The tephra mostly affected areas northeast of the volcano (Figure 1), such as the Ensenada village nearly 15 km away, which was covered by tephra deposits of 20–30 cm thick [54].

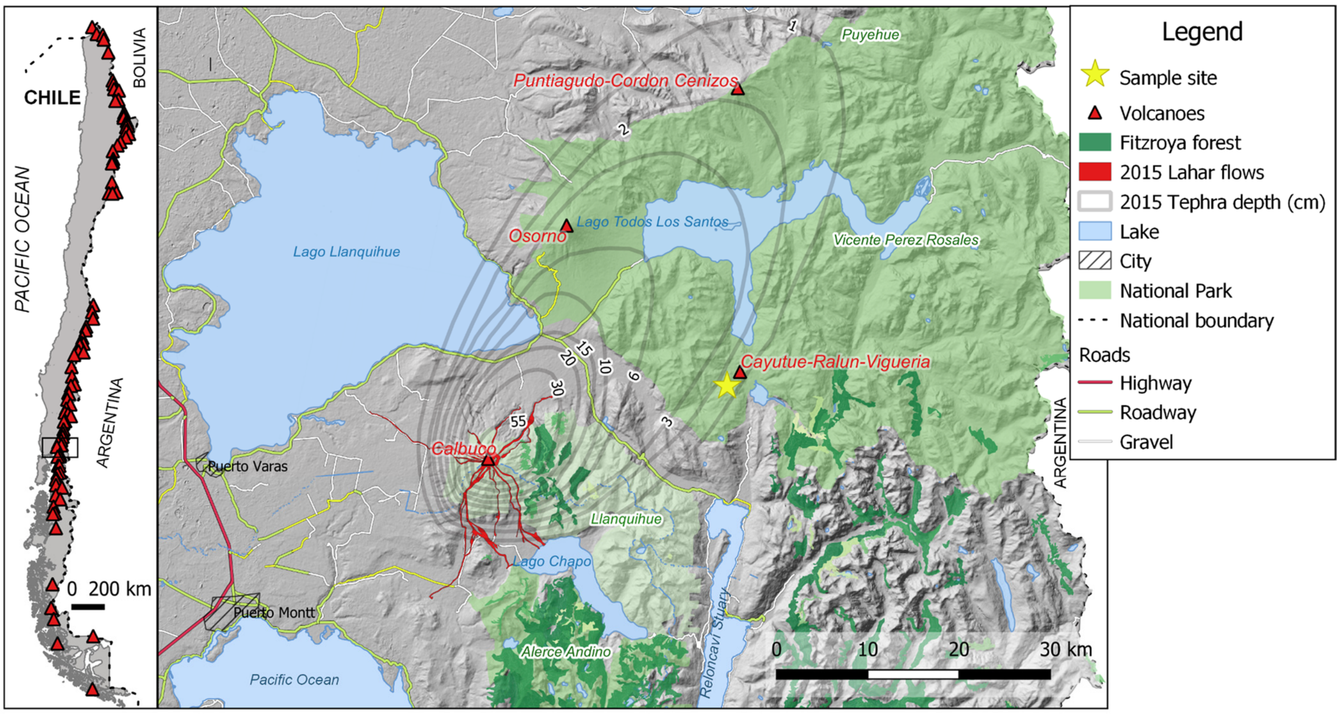

Figure 1. Map of study area indicating Calbuco volcano and the *F. cuppressoides* sampling site. The lahar flows and tephra deposition (cm depth) during the Calbuco eruption of 2015 [54] are indicated with red lines and isopachs, respectively. On the left is a map of Chile indicating the location of active volcanoes in red triangles.

Figure 2. Eruption of the Calbuco Volcano during 22 April 2015. In the foreground is the city of Puerto Montt by the Pacific coast (founded in 1853), and in the background to the east are the Andes. Note the eruptive plume of the volcano in a west–east direction as a result of persistent westerly winds. The *F. cupressoides* sampling forest is located just behind the volcano under the eruptive plume. Photo credit: MAV Drone, César Santana https://www.facebook.com/mavdrone/ (accessed on 12 November 2019).

Table 1. Historical eruption records of the Calbuco volcano [50–52].

Year AD	VEI [1]	Ashfall	Feature	Reference
1792	?	?	Possible explosive eruption	[58]
1845	?	?	Possible eruption	[59]
1893–1895	4	yes	Sub-Plinian eruption with pyroclastic and lahar flows	[60]
1906–1907	2	yes	Minor explosive eruptions with ash emission	[61–63]
1911–1912	2	yes	Small eruption with dome and spine growth	[64]
1917	3	yes	Phreato-Plinian eruption with lava and lahar flows	[65]
1929	3	yes	Phreato-Plinian eruption; lava emission	[66,67]
1932	2	yes	Short-term and intense explosive eruptive activity	[68]
1945	2	yes	Explosive eruptive activity	[69]
1961	3	yes	Sub-Plinian eruption with lava and lahar flows	[70–72]
1972	2	yes	Weak eruption with pyroclastic emission	[73]
2015	4	yes	Sub-Plinian eruption with pyroclastic and lahar flows	[54,56]

[1] VEI: Volcanic Explosivity Index [55].

Other volcanoes located near the Calbuco volcano are Osorno (2652 m a.s.l) and the Cayutué minor eruptive center [74,75] next to the Todos Los Santos Lake. The Osorno stratovolcano has had 12 well-documented eruptions during the 18th and 19th centuries, all of them occurring with only effusive non-explosive eruptive activity, with the most recent lava eruption occurring in 1835 [51,76]. Calbuco and Osorno are large stratovolcanoes with different eruptive behaviors [77], with Calbuco being much more active and characterized by producing large eruptions with an explosive behavior, generating high eruptive columns with tephra fall and pyroclastic flows [53], while Osorno has a non-explosive effusive behavior with lava emission and reduced tephra fall [78,79]. In addition to their different eruptive styles, both volcanoes possess distinctive geochemical characteristics, with Calbuco producing exclusively andesitic products (58% SiO_2) while Osorno is characterized by products of basaltic to andesite-basaltic composition (50–56% SiO_2) [80]. On the other hand, there is variability in the contents of trace elements such as Zn (64–102 ppm), Cu (33–56 ppm), and Pb (7–41 ppm) in tephra from the Calbuco volcano [77,81], while the products from the Osorno volcano have similar ranges of Zn (62–108 ppm, 79 ppm in 1835), higher Cu (63–92 ppm; 85 ppm in 1835) and lower Pb (5–19 ppm) [82–85].

2.2. *Fitzroya Cupressoides Forests*

Fitzroya cupressoides, commonly known as Alerce, is an endemic and evergreen conifer tree species of temperate rainforests of Chile and Argentina. It can reach 5 m in diameter and up to 50 m in height, being the second longest-living tree species in the world, able to reach more than 3600 years old (Figure 3) [37]. It grows in Northern Patagonia, mainly in Chile (39°50′–43° S) along the Andes, the Coastal Range, and the Central valley between sea level and 1,200 m altitude [86]. The climate in the distribution range of *F. cupressoides* is a temperate humid oceanic type with a mild Mediterranean influence during summer, characterized by a high annual precipitation that varies from 2000 mm in the northern range and intermediate depression to more than 5000 mm above 700 m a.s.l. on the windward side of the mountains, where there is commonly snow during the winter [86,87].

Figure 3. Old-growth forest of *F. cupressoides* with millennial individuals in the Andes of Northern Patagonia, Chile. At the left appears a *F. cupressoides* tree-ring sequence with its distinct annual rings growing from the bottom up. White dots are positioned every 10 years.

F. cupressoides forests grow in areas with shallow soils, poor drainage, and low fertility, where competition with other tree species is low [86,88,89]. In the Coastal Range, it is associated with *Nothofagus nitida*, *Drymis winteri*, *Saxegothaea conspicua*, and *Podocarpus nubigena* tree species. In the Andes Range, it is mainly associated with *Nothofagus betuloides,* and occasionally with *Nothofagus pumilio* in higher altitudes. In medium and low altitudes, it grows with *N. nitida*, *Laureliopsis philippiana*, and *S. conspicua*. It has also been observed in areas with poor drainage in both mountain ranges with the conifer *Pilgerodendron uviferum* [86,89,90]. The tree rings of *F. cupressoides* have been extensively studied, providing excellent dendrochronological records utilized for ecological [88], ecophysiological [91], and paleoclimatic studies [37,38].

2.3. Tree-Ring Sampling Site

The *F. cupressoides* sampling forest was selected based on: (i) location east of the Calbuco volcano under the general tephra dispersion zone, due to persistently westerly winds, (ii) being composed by ancient *F. cupressoides* individuals in a region where this species has been historically heavily cut down, (iii) accessibility to the site in the Andean region. According to this, our sampling site was a forest located 28 km NE of Calbuco between 800 and 1000 m a.s.l., near the Cayutué Lake at 41°15′ S and 72°16′ W in the Vicente Pérez Rosales National Park and 60 km NE of the city of Puerto Montt in the Los Lagos District (Figure 1). The climate of the study area is described as a temperate rain climate with an annual precipitation of more than 5000 mm [91]. Temperatures vary seasonally from an average of 15.3 °C in January to 7.6 °C in July. Soil in the study area has poor drainage, composed of coarse and fine tephra from the Calbuco and Osorno volcanoes and the Cayutué eruptive center (Figure 4), and the slope in the study area is low to moderate. During the 2015 Calbuco eruption, it was estimated that 1–2 cm of ash fell in the area of our sampling forest, but in situ measurements made during our sampling determined an ash fall of 5 cm in thickness (Figure 1). Prior to the 2015 eruption, the soil of the Cayutué forest exhibited four separate tephra deposits from Calbuco from over the last 2000 years (Figure 4). The tephra deposits were associated with petrographic and geochemical characteristics of volcanic sources. The origins of tephra deposits were the Calbuco and Osorno volcanoes and a massive scoria sequence of the Cayutué eruptive center. Two orange deposits were correlated with Cal12 and Cal13 tephra units dated to 1800 and 1200 years BP, respectively [81].

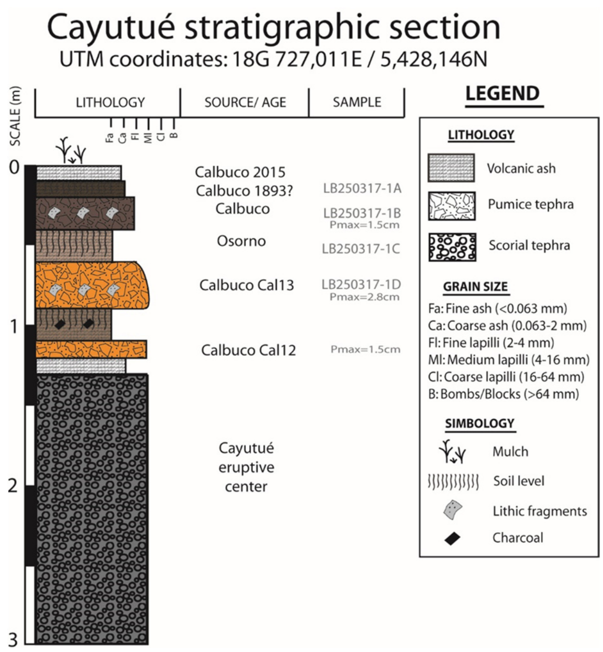

Figure 4. Stratigraphic section of the study site in the Cayutué forest with tephra deposits.

The fieldwork was done during March 2017 by sampling 15 trees, with 2 cores per tree of healthy dominant *F. cupressoides* individuals, utilizing increment borers of 5 mm in diameter. Core samples were prepared following standard dendrochronological techniques [92]. Tree rings were visually cross dated to the year of ring formation [93] and measured under a binocular stereoscope with 0.001 mm precision using a Velmex system. Following the Schulman convention for the Southern Hemisphere [94], dates were assigned for annual rings to the year in which radial growth started. The cross-dating quality and measurement accuracy of the tree ring samples were checked with COFECHA software [95], and corroborated with the neighboring *F. cupressoides* chronology from the Lenca site (40 km), which included 119 cross-dated trees covering the last 4,084 years [38].

2.4. Dendrochemical Analysis

After tree-ring dating was finished, the cores of 10 trees were selected to develop a dendrochemical chronology with a 2-year resolution by pooling two consecutive annual rings (one biennium) for the period between AD 1514–2016. All selected tree cores covered the entire 1514–2016 interval. Sample preparation for the analysis was done by cutting the tree cores under a binocular microscope into segments of two years using sterile ceramic knives over an acrylic table, as well as isopropyl alcohol to clean all materials. Each 2-year wood segment was polished with diamond tools to remove the surface that was in contact with extraction and sanding tools. Once cut, the 2-year samples from each of the ten trees were placed in labeled tubes, forming a 2-year composite sample and reaching the 50 mg minimum mass needed for chemical analysis. Thus, we obtained 252 composite samples at a 2-year resolution covering the period AD 1514–2016. Subsequently, the samples were sent to be measured at the Arizona Laboratory for Emerging Contaminants (ALEC) at the University of Arizona. Grouping samples from different trees has the disadvantage of not being able to evaluate the similarity of chemical signals between different individuals. In this work we chose this approach as it eventually integrates the group signal into a sample, helps to provide the minimum mass for analyses, and allows lower costs—thus a longer period of years can be covered in the final registry.

In ALEC, the samples were dried to a constant weight and weighed into pre-cleaned, pre-weighed, metal-free polypropylene trace centrifuge tubes. They were then predigested with 3 mL of 70% nitric acid (HNO_3) for 24 h at room temperature, then fully digested at 90 °C in a heater block for 2 h. Following digestion, the sample tubes containing the digested material were reweighed to calculate dilution factors. A 1.5-mL aliquot of digestate was gravimetrically diluted by a factor of approximately 10 with ultrapure 18.2-megaOhm/cm water and spiked with three internal standards: beryllium (20 ppb), indium (10 ppb), and bismuth (5 ppb). Then, the liquid samples were analyzed by inductively coupled plasma–mass spectrometry (ICP–MS; model Agilent 7700x) along with standards (pine needles and apple leaves) and blanks. Results were expressed as $\mu g\ g^{-1}$ of dry weight of wood. A total of 20 elements were measured: beryllium (Be), boron (B), aluminum (Al), silicon (Si), phosphorus (P), titanium (Ti), manganese (Mn), nickel (Ni), copper (Cu), zinc (Zn), germanium (Ge), zirconium (Zr), niobium (Nb), molybdenum (Mo), silver (Ag), cadmium (Cd), tin (Sn), antimony (Sb), barium (Ba), and lead (Pb). For each of these elements, the minimum detection limit reached low parts per billion (less than 0.05 ng/mL). The ICP–MS method is extremely efficient and has the capacity to develop simultaneous analysis of most elements in the periodic table, providing the greatest possible range of elements from which to evaluate potential volcanic eruption signals [32].

To determine the capacity of chemical elements to act as Tracers of Past Eruptions (TPEs), we evaluated the potential signals of the historical eruptive events (Table 1) in the time series of the measured set of 20 elements using a Superposed Epoch Analysis (SEA) [96] utilizing the EVENT routine [97]. SEA is one of the most classic event analyses in dendrochronological studies, typically used to test the significance of a mean response of a time series (e.g., dendrochemical series or ring-width chronologies) to certain events such as volcanic eruptions [8]. Departures from the mean values of the analyzed time series for specified years during event years and specified years after each event are averaged to a superposed relative epoch. In the case of the measured chemical series, SEA compared the variations of the chemical element time series with a list of the historical eruptive events of the Calbuco volcano. As the time resolution of the chemical element data has a 2-year (biennium) resolution, for each eruptive event a 6-biennium window (periods of two years) is considered, including 1 pair of years leading up to and 5 pairs of years following the event. The 6-biennium windows for all the events are overlaid and averaged to obtain the mean pattern of each chemical element related to the eruptive events. To determine if the dendrochemical series for the event years were significantly different from randomly selected sets of other years, 1000 Monte Carlo simulations were used to select sets of years from the dendrochemical series to estimate significance for the departures from the mean values of the original time series. SEA computation is based on scaled values of the original time series, and 95% confidence intervals are computed for the scaled values for each year in the superposed epoch. The historical Calbuco eruptions vary in magnitudes classified by the Volcanic Explosivity Index (VEI, Table 1). For the SEA, we utilized the following historical eruptive events for VEI $\geq$ 2: 1892–1893, 1906–1907, 1910–1911, 1916–1917, 1928–1929, 1932–1933, 1944–1945, 1960–1961, 1972–1973, and 2014–2015 (2-year resolution), and for VEI $\geq$ 3: 1892–1893, 1916–1917, 1928–1929, 1960–1961, and 2014–2015. Chemical elements that exhibited significant positive concentration anomalies associated with historical eruptions events were selected as chemical TPEs.

Dates of past eruptions during the pre-historical period 1514–1848 were inferred by the co-occurrence of concentration values of the selected chemical TPE above the 90th percentile of each chemical series for at least $\geq$ 2 TPE, either during the same biennium or immediately adjacent; the latter to account for the possible lateral mobility of elements between neighboring rings. Finally, the eruptive frequency was calculated assuming a Poisson distribution for volcanic eruptions [98]. The probability of a volcanic event is defined as 1-exp (-λt) in a determined time interval t, where the eruption rate λ is the number of eruptions in a total time interval, and the eruptive frequency (or recurrence) is the mathematical inverse of the eruption rate.

2.5. Analysis of Ring Width Patterns

To develop the tree-ring width chronology, each *F. cupressoides* ring-width series was standardized to remove non-climatic variability due to tree aging trends or forest disturbances. Each measured ring width of year *t* was divided by the year *t* value of a fitted negative exponential curve or straight line to get a tree-ring index [93]. A standard ring-width chronology was calculated, averaging the detrended tree-ring series by means of a bi-weight robust mean using ARSTAN44 program [99]. Chronology variance through time was stabilized using the method described by Osborn et al. [100]. The quality of the tree-ring chronology was assessed by using the Expressed Population Signal (EPS) statistic. To evaluate the potential signals of past eruptive events in the *F. cupressoides* ring-width chronology, we used a superposed epoch analysis (SEA) [96]. For each eruptive event, a six-year window was considered, including the eruption year and five years following the event. Additionally, we computed correlation analyses to identify possible relationships between *F. cupressoides* growth patterns, and maximum temperature and precipitation using a regional meteorological record composed of La Ensenada, Osorno, and El Tepual weather stations during the AD 1950–2016 period.

3. Results and Discussion

3.1. Dendrochemical Anomalies

The concentrations of twenty elements from *F. cupressoides* tree rings covering 500 years over the period AD 1514–2016 (Be, B, Al, Si, P, Ti, Mn, Ni, Cu, Zn, Ge, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, and Pb) were used to determine the capability of chemical elements to act as tracers of past eruptions. The response of six chemical element concentrations (Pb, Sn, Mo, Cu, P, Zn) associated with historical records of eruptions clearly showed positive concentration anomalies during and after historical VEI $\geq$ 3 eruptions of Calbuco (Figure 5). These six elements were named as chemical tracers of past eruptions (TPEs) and were classified into (1) co-eruptive signals: Pb and Sn, which exhibited positive anomalies in the biennium of the eruptions, and (2) post-eruptive signals: Mo, Cu, P and Zn, which exhibited positive anomalies during the biennium following the eruptions.

The increases in P, Zn, and Cu concentrations in the years of eruptions is consistent with observations made by Sheppard et al. [23,31] for the eruptions of Paricutin (1943–1952) and Mt Hood (1781), and by Padilla and Anderson [29], Pearson et al. [19], and Pearson et al. [28] for the increases in Zn and Cu for the eruptions of Santorini (3,600 BP), Laki (1783), Tambora (1815), and Krakatoa (1883). The co-eruptive TPE (Pb and Sn) that showed an increase in concentration in the year of the eruption would enter the tree quickly directly as nanoparticles through the leaves after being affected by falling tephra, which is a faster entry mechanism than through the roots [24]. While the late response (two to three years later) shown by the post-eruptive TPE may be due to the fact that the chemical elements would most probably enter the tree through the roots, either as direct input from the tephra deposited in the soil after the eruption (i.e., Zn, Cu, and P that may be available to plants [20,21]), or indirectly when the fall of tephra triggers a decrease in soil pH [25] that induces a change in the bioavailability of elements already contained in the soil, but which were not bioavailable to plants such as Zn and Cu [19,29]. This effect on pH would depend on the amount of SO_2 emitted during the eruption, dispersed with the eruptive column and deposited in dissolved form with the tephra [26]. The release of chemical elements from the tephra into the soil occurs with greater velocity in tephra less than 10 cm thick in a period of years, generating a renewal of the soil [20]. Also, fine ash decomposes and releases nutrients faster than coarse ash or lapilli, because it has a greater specific surface area exposed to weathering agents [101]. In addition, mycorrhizae in tree roots can break bonds and increase the bioavailability of nutrients [102]. Therefore, the direct contribution of elements into the tree from deposited tephra will occur more rapidly in sites affected by fine ash less than 10 cm thick [25,26,101].

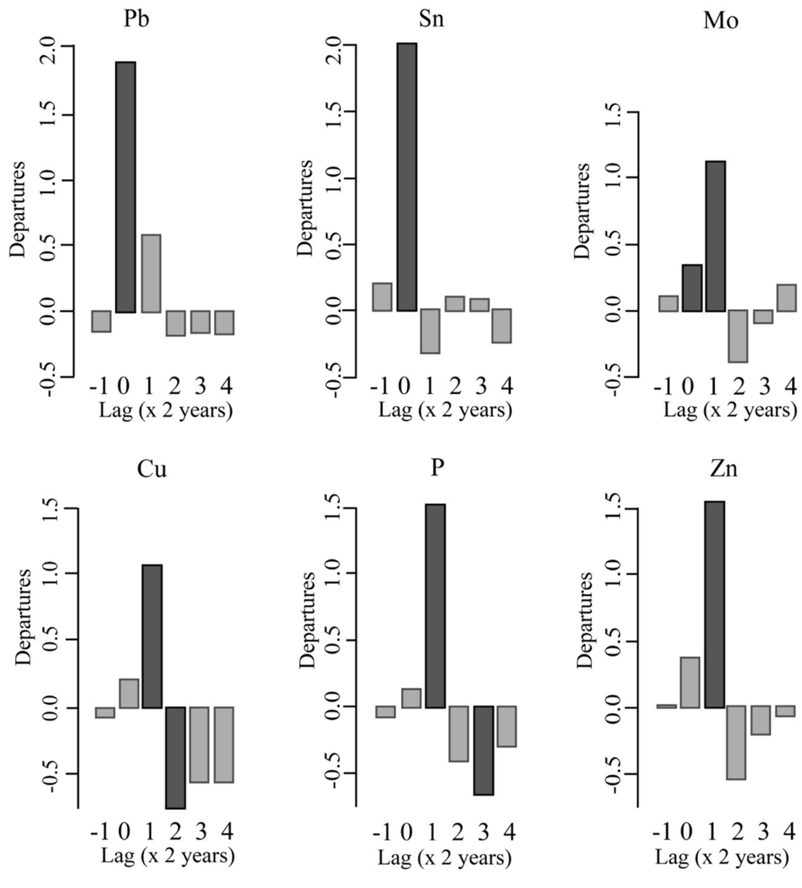

Figure 5. Superposed epoch analysis (SEA) comparing the normalized departures (z-scores) of chemical tracers of past eruptions (TPE: Pb, Sn, Mo, Cu, P, and Zn) contained in biennium portions of *F. cupressoides* tree rings corresponding to the Calbuco eruptions with a VEI $\geq$ 3 for the period 1850–2016 AD. The *X*-axis represents a set of 6 biennia equivalent to 12 years, from 2 years before the eruption to 9 years following it. Black bars represent significant confidence levels at 95% after 1000 Monte Carlo iterations.

3.2. Ring-Width Patterns

A ring-width standard chronology was developed from thirteen selected cross-dated series of ten individuals of *F. cupressoides* from the Cayutué forest, covering the period

AD 855–2016 (Figure 6). The Cayutué chronology exhibits high temporal variability at interannual, decadal, and multidecadal scales, demonstrating that *F. cupressoides* growth at the Cayutué site can record environmental fluctuations at multiple time scales. Regarding the eruption signals in the *F. cupressoides* ring-width chronology, a significant decrease of growth is observed in years where eruptions had a VEI $\geq$ 3 (Figure 6), while there are not significant signals for eruptions of VEI $\geq$ 2. Foliar damage caused by the tephra fall in the Cayutué forest indicates that past Calbuco eruptions of higher VEI have influenced *F. cupressoides* growth in this site, which is a phenomenon previously described in other forests around Calbuco [103] and worldwide that were affected by volcanic eruptions [5–7,9,11,104,105]. Given this result, we utilized the ring-width chronology as a complementary indicator of past eruptions along with co-occurrence of anomalous concentration values of chemical TPEs for at least $\geq$ 2 TPE during the pre-historical period 1514–1848.

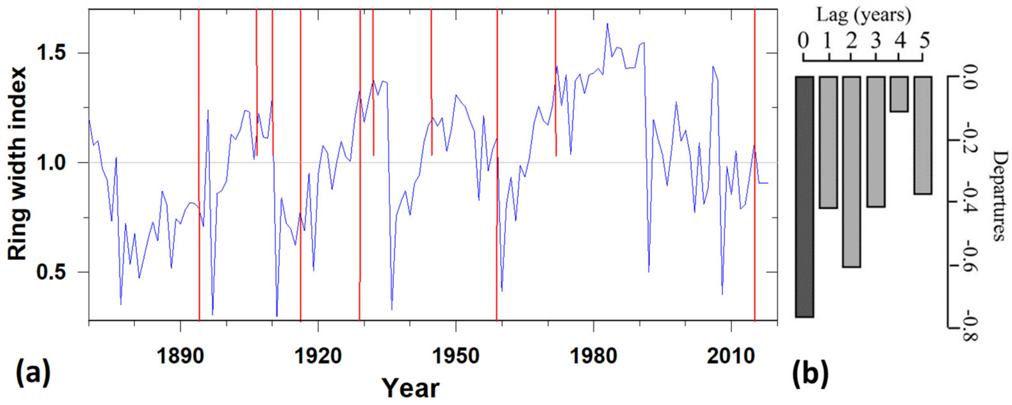

Figure 6. (**a**) The standard annual *F. cupressoides* tree-ring-width chronology of the Cayutué site during the period of the historical eruption record of the Calbuco volcano from 1850 to 2016 AD. Vertical long and short red lines indicate historical eruptions with a Volcanic Explosivity Index of $\geq$3 and =2, respectively, according to Petit-Breuilh [51], Sellés and Moreno [50] and the Global Volcanism Program [52]. (**b**) Superposed epoch analysis (SEA) comparing the *F. cupressoides* normalized treering index departures (z-scores) during the Calbuco eruptions of VEI $\geq$ 3 for the period 1786–2016 AD. The *X*-axis represents a set of 6 years (the eruption year and 5 years following it) and black bars represent the significant confidence level at 95% after 1000 Monte Carlo iterations.

Concerning the climate signals in the *F. cupressoides* chronology during the 1950–2016 period, a negative correlation was found between the chronology and temperature during the summer period (January to March), and a positive correlation for the chronology and precipitation during January. These results imply that years with extreme low values of ring-width chronology could be partially due to extreme warm and dry summers. These climate-growth correlations are consistent to previous *F. cupressoides* tree-ring studies in Chile [37,91].

3.3. Tree-Ring Signals and Eruptive Record

3.3.1. Historical Eruptions

By reviewing the distribution of the TPE elements and comparing it with the years of documented eruptions of the Calbuco volcano, it is possible to distinguish that the most significant positive chemical anomalies, especially Pb, occurred after the two biggest eruptions of the Calbuco volcano (VEI 4), i.e., in AD 1893–1894 and 2015 (Figure 7). During the years of these eruptions the dendrochronological records show negative anomalies in *F. cupressoides* growth and a significant increase in Pb, and increases of a lesser extent in Sn, P, Mo, Zn, and Cu. Moreover, there is stratigraphic and descriptive evidence of tephra deposition in the Cayutué forest for both eruptive events (Figure 4). The 1917 eruption (VEI 3) produced abundant SO_2 emissions and had east and northeast dispersion [51,65], therefore it must have affected our study site with ash fall, which is clearly manifested in the tree rings with a decrease in growth, a considerable increase in Zn concentration, and a moderate increase in Sn, Pb, P, and Cu. For the 1961 eruption (VEI 3), which had an eastern and northeastern dispersion, the signal in the rings is less evident, with a decrease in growth and weak dendrochemical signals. The 1929 eruption (VEI 3) is not clearly identified in the tree-ring records. This may be due to the fact that this event is mentioned as a phreatomagmatic eruption, i.e., rich in water vapor, but emitting little new volcanic material [51,66,67].

In the case of the VEI 2 eruptions, a minor response is identified after the 1932 eruption consisting of an increase in Zn in the year of the eruption and an increase in Mo and Cu 3–4 years later. In addition, two years after the 1945 eruption there is an increase in Cu and Zn. In contrast, there are no growth nor elemental concentration anomalies associated with the VEI 2 eruptions of 1906, 1909, 1910, and 1972. This indicates that the *F. cupressoides* tree-ring width and chemistry registries would not record most VEI 2 eruptions, since these would generally not generate ash fall nor affect trees at the distance of our study site. The possible eruption of 1792 [58] does not show any increase in TPE concentrations; on the contrary, elemental concentrations are very low, which may be due to the fact that it was a low explosive eruption, with VEI 2 or less, which did not generate tephra fall in the forest under study. The historical source of this eruption is unreliable because the accounts of it do not offer a detailed description and were obtained 50 years after the year of the supposed event from people far away from the volcano, and may even have been confused with the eruption of the Osorno volcano in 1790–1791 [51]. Prior to the mid-19th century, it is difficult to find reliable historical sources to corroborate volcanic activity because human presence at that time was rare and records were only documented by travelers [51], thus the evidence from the ring-width and chemical anomalies in our dendrochronological records would be a valuable proxy of the eruption activity.

Since the late 1980s, there has been a sustained increase in the Zn, Cu, Mo, P, and Mn dendrochemical series (Figure 7), for which there are no documented eruptions of the Calbuco volcano. Environmental and/or physiological factors could explain these patterns. One possibility is that the concentration patterns of these elements are controlled mainly by translocation processes between sapwood and heartwood [33]. Another possibility would be the contribution of anthropogenic air pollution to our sampling site from the nearby metropolitan area of the city of Puerto Montt, located 50 km southwest in line with the prevailing winds.

Puerto Montt has experienced exponential growth, registering one of the highest population increases in Chile during recent decades along with the development of several large industries, especially after 1979 when it became the capital of the Lake District region [106]. This demographic and economic growth has also led to an increase in motor vehicle traffic whose emissions contain Mo, Mn, Cu, and Zn [107,108]. A recent chemical analysis of snow samples in the area of the Calbuco volcano from the nearby Osorno volcano demonstrated the presence of Cu and Zn associated with gaseous and particulate contaminants emitted from the surrounding urban area, which is one of the populated districts from southern Chile with high contaminant emissions [109]. In the case of P, another possible source would be the intensive use of fertilizers in the thousands of hectares of pasturelands located west of our sampling site, an area that is the main region of production of cattle for milk and meat in Chile. This P could be remobilized and transported by the predominantly westerly winds to the Andean forests of *F. cupressoides*, which have soils with low levels of P [110]. This phenomenon of P deposition from agricultural areas in neighboring regions has been widely described for other regions of the world [111–113]. Another significant source of P would be the use of firewood [114], which is the main source of heating in the nearby metropolitan area. A recent dendrochemical study in Chile documented an example of positive trends of chemical elements in tree rings during recent decades as a result of anthropogenic air pollution in central Chile [115].

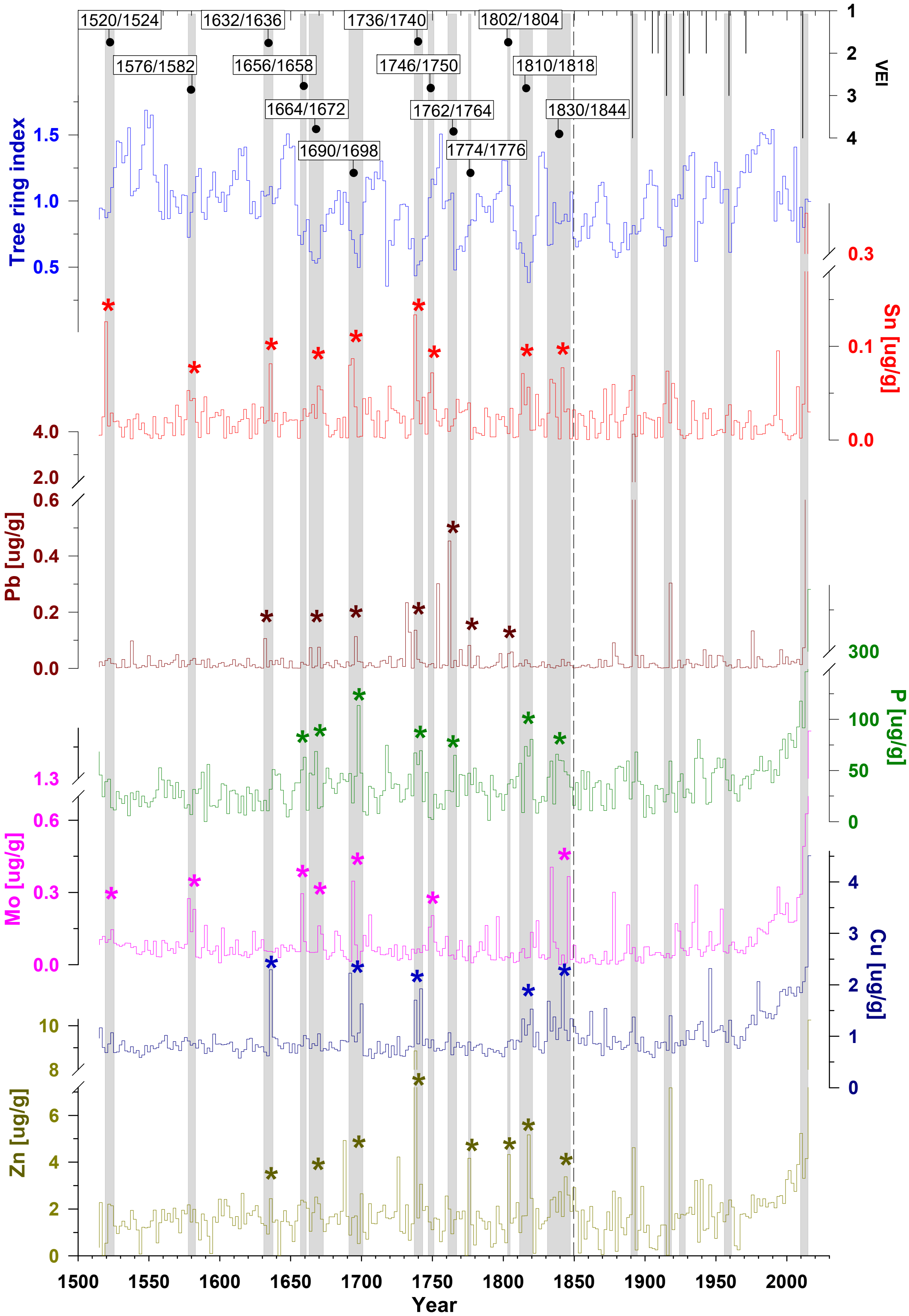

Figure 7. The Cayutué *F. cupressoides* dendrochemical (Sn, Pb, P, Mo, Cu, Zn) and ring-width chronologies. All registries have a biennium resolution. Vertical gray lines indicate the eruption dates of the Calbuco volcano during the historical period after 1850 (VEI ≥ 3 according to Petit-Breuilh [51], Sellés and Moreno [50], Global Volcanism Program [52]), and the possible dates of past eruptions during the 1514–1848 period inferred from the co-occurrence of concentration values of chemical TPEs above the 90th percentile of each chemical series for at least ≥ 2 chemical tracers, indicated by asterisks.

3.3.2. Possible Prehistoric Eruptions

Prior to 1850, we identify periods of co-occurrence of anomalies in the chemical concentrations of TPEs (Pb, Sn, Mo, Zn, Cu, and P; Figure 7) that would be associated with eruptions of the Calbuco volcano and, in some specific cases, of the Osorno volcano. Thus, we propose the following 11 unrecorded eruptive periods of Calbuco and 2 of Osorno that coincide with the described historical eruptions between 1575 and 1834–1835 [51,76]. In the rings of the years 1520/1524, an increase in Sn concentration, and to a lesser extent Mo, can be observed, together with relatively low values of ring width. Later, in the year 1576/1582 a decrease in ring width is distinguished, accompanied by an increase in Sn and Mo concentrations, which could be associated with the eruption of the Osorno volcano in 1575 [51,76]. During 1632/1636, an increase in Cu and Sn concentration, and to a lesser extent in Pb and Zn, can be observed, and the ring widths show relatively normal values. During the period 1656/1658, there is a peak of P and Mo together with low values in the ring-width chronology. In 1664/1672, the TPE records shows an increase in concentrations of Sn, Pb, P, Mo, and to a lesser extent Zn, along with low values in the ring-width chronology. In the period 1690/1698, there is clear signal with a decrease in tree growth and an increase in the concentrations of Sn, Pb, P, Mo, Cu, and Zn. During 1736–1740, a decrease in tree growth together with an increase in the concentration of Sn, Pb, P, Zn, and Cu can be observed. This chemical anomaly could indicate an explosive eruption of VEI 3 or 4 that correlates with the brown Calbuco andesitic-basaltic tephra found in Cayutué soil (Figure 4). In 1746–1750, there is an increase of Sn and Mo, but no signs of tree growth decline, which may indicate a possible eruption with low amounts of tephra fallout. During 1762/1764, the TPE records indicate peaks of Pb and P together with a sharp decline in tree growth in the following biennium. In 1774/1776, there is an increase of Pb and Zn, with a ring width below the mean but no signs of a strong growth decline. At the beginning of the 19th century in 1802/1804, there is an increase of Pb and Zn accompanied by the beginning of a downturn in tree growth. During the period 1810/1818, the TPE records indicate peaks in Sn, P, Cu, and Zn concentrations, together with a strong decline in tree growth, suggesting a major eruption. Finally, during the period 1830/1844, peaks occur in the concentrations of Sn, P, Mo, Cu, and Zn, and tree growth values are below average. This period could be associated with the eruption of the Osorno volcano of VEI 3, recorded by Charles Darwin in 1834-35, and the subsequent eruption of 1837 of VEI 2 [51,76,116]. Also, historical records for the 19th century indicate a "possible eruption" of Calbuco during 1845 [51,59]. Although the influence of signals from the Osorno volcano in our dendrochemical record cannot be ruled out, the eruptive behavior of Osorno is not too explosive (VEI $\leq$ 2), which would imply that it does not typically generate large eruptive columns with ash fall at long distances [78]. Therefore, most of the signs of past eruptions identified in this study would come from Calbuco, which is an explosive volcano and is precisely located for persistent southwest winds to reach our tree-ring study site. However, it would be useful to generate dendrochemical registries immediately northeast of Osorno to contrast with the present dendrochemical registries.

3.3.3. Eruptive Frequency

By means of the present dendrochemical analysis, the eruption record of the Calbuco volcano is complemented and extended back in time to the 16th century, increasing the total number of dated eruptions to 22 with 11 new events (Figure 7). Thus, the mean eruptive interval of the Calbuco volcano could be estimated to be about 23 years. From the analysis of the *F. cupressoides* tree rings developed in this work, we could infer that the Calbuco volcano would have presented three large eruptions (~VEI 4) in a period of 500 years, during 1736–1740, 1893–1895, and 2015, which would indicate an average frequency of ~170 years for this magnitude of event. Complementarily, tephrostratigraphy demonstrates only 5 events in the soil profile during the last 2000 years (Figure 4), demonstrating the utility of combining both methodological approaches. The eruptions in the historical record have a general frequency of 18 years, while the results of the eruptive frequency prior to

1853 is 30 years. We hypothesize that the low eruptive frequency of Calbuco before the historical record could be due to the tree-ring records not being capable of capturing small eruptions, registering events with VEI ≥ 3 more faithfully.

4. Concluding Remarks

This study presents the development of the first continuous multi-century dendrochemical record in the Southern Hemisphere, which is utilized to infer the past eruptive activity of the Calbuco Volcano in Northern Patagonia during the last six centuries. It shows that dendrochemistry can be a useful technique to accurately determine the date of past volcanic eruptions by analyzing selected chemical tracers of past eruptions. Our results show that after comparing the chemical record of the different elements with the historical record of the Calbuco eruptions, a group of elements exhibited positive anomalies during and after eruptions, thereby being classified as tracers of past eruptions (TPE). *F. cupressoides* is a sensitive tree species for detecting chemical changes in leaves/soil produced by tephra falls, and it has great potential for studying the dynamics of past volcanism in Northern Patagonia, becoming a new proxy to date such events. The *F. cupressoides* trees growing close to and east of Calbuco, under the route of the prevailing westerly winds in the Cayutué forest site, are sensitive to past volcanic eruptions that can be registered through both the chemical signals on tree rings and significant decreases in tree growth associated with large eruptions.

The variability of the TPE signals and tree-growth anomalies during the years of inferred eruptions would reflect changes in the eruptive magnitudes (VEI), the volcanic sources, the contents of chemical elements in the tephra that can generate a direct contribution to the tree, and the acidity of the tephra in response to the amount of SO_2 emitted by the volcano, which alters the availability of nutrients in the soil for plants. Therefore, the identification of possible years of eruptions should not be focused on a single response variable, but instead on the combined multiproxy analysis of co-occurrence of anomalies in the TPE concentrations and in the *F. cupressoides* ring widths. The selected chemical elements (Pb, Sn, Mo, Cu, P, Zn) identified as TPE are mostly attributable to the Calbuco volcano and a couple of events of the Osorno volcano. Co-eruptive signals include an increase in both Pb and Sn concentrations during the t and t+1 years after explosive eruptions of Calbuco. Post-eruptive signals also include increases in Mo, Zn, Cu, and P concentrations following eruptions during the t+2 and t+3 years. TPEs can be used to find unknown eruptions, evaluate the certainty of past historical records by dendrochemistry, and determine the relative magnitude of past eruptions. Accordingly, eleven new Calbuco eruptions were identified by these dendrochemical records from the Cayutué forest. Consequently, the historical eruption record for the Calbuco volcano is extended back to 16th century, and the total number of eruptions is increased to 22, having a mean eruptive frequency of 23 years.

Some limitations arise from our approach, since TPE would not register small eruptions, i.e., of VEI < 3. In addition, it is also possible that there is lateral mobility of certain elements between rings, which would decrease the temporal accuracy of the record. Complementary studies are needed to identify the chemical signal variations of each volcano in order to develop detailed spatial records in regions with several volcanoes, as well as to develop regional networks of dendrochemical records using composite and individual tree samples. The present study shows the potential for dendrochemical studies in *F. cupressoides* to develop chronologies of eruptive histories in forested locations, and to determine the return interval of volcanic eruptions, which are necessary for infrastructure and risk planning of inhabited areas. Finally, we recommend utilizing a multiproxy dendrochronological approach that includes the evaluation of dendrochemical series and ring-width anomalies, together with other proxies such us lake sediments, taking into consideration the mentioned possible limitations. This information may provide a complementary understanding of the long-term perspective of the eruptive history of volcanoes in northern Patagonia.

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