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# Dendrochemistry of White Mountain bristlecone pines: An investigation via Synchrotron Radiation Scanning X-Ray Fluorescence Microscopy

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[1] Synchrotron Radiation Scanning X-Ray Fluorescence Microscopy (SXFM) was used for the first spatially/temporally resolved investigation of the multielemental chemistry of bristlecone pine (*Pinus longaeva* D.K. Bailey). A new protocol was designed to apply this nondestructive method of analysis to this unique palaeoclimatological resource, extracting previously inaccessible dendrochemical information at subannual resolution from tree rings ranging from 1400 to 40 $\mu$m. The potential of *Pinus longaeva* was assessed for the reconstruction of multicentennial annual resolution sequences of elemental change, with specific focus on the identification of multielemental markers for major, climatically effective volcanic eruptions. Increases in calcium (Ca), strontium (Sr), manganese (Mn), and zinc (Zn) were identified in association with frost rings around AD1601, following the eruption of Huaynaputina, Peru, but these could not be directly attributed to volcanogenic changes in environmental chemistry. Elemental patterns for 500 years from five trees demonstrated little agreement indicating that, for the elements detected, this species may be unsuitable for temporal reconstructions of external chemistry. Further development of SXFM dendrochemical technique, however, offers much potential for future work.

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## 1. Introduction

[2] The underlying principle of dendrochemistry is that an annually produced growth ring can provide a time capsule of the environmental chemistry of the year in which it formed. In reality the chemical record preserved in this way may or may not be representative of external changes in environmental chemistry depending on site-specific factors and a whole range of physiological variables within the xylem. As a result there is much controversy over the reliability of a dendrochemical approach [*Lövestam et al.*, 1990; *Zayed et al.*, 1992; *Hagemeyer*, 1993; *Smith and Shortle*, 1996; *Watmough*, 1999]. Nevertheless, given the right tree and set of environmental variables, it has been demonstrated an effective technique for the reconstruction of histories of environmental elemental change [*Symeonides*, 1979; *Robitaille*, 1981; *Baes and McLaughlin*, 1984; *Guyette et al.*, 1989; *Bondietti et al.*, 1990; *Watmough and Hutchinson*, 1996, 1999; *Shortle et al.*, 1997; *Watmough*, 1999].

[3] The majority of studies have focused on reconstructing the timing and impacts of various types of anthropogenic pollution on the natural environment, but an alternative application is the detection of elemental indicators of volcanic eruptions in dated tree ring sequences [*Pearson et al.*, 2005; *Ünlü et al.*, 2005; *Pearson et al.*, 2006; *Pearson*, 2006]. Eruptions of known date have been linked with changes in elemental chemistry in *Pinus* sp. by *Padilla and Anderson* [2002] and *Pearson et al.* [2005], and in *Pseudotsuga* sp. by *Hall et al.* [1990]; however further substantiation of such linkages is required. An elemental signature for volcanism in tree rings would provide direct access to absolute, precise dates for past eruptions that are currently imprecisely dated. Such a connection would be of tremendous value to a wide range of palaeoclimatic and predictive studies in terms of assessing the true nature and duration of volcanic impacts on climate and human society [*Grattan*, 2006].

[4] Anomalous growth rings in tree ring records (correlated with acidity spikes in ice core chronologies) are a long established proxy for dating volcanic events [*Ferguson*, 1969; *LaMarche and Hirschboeck*, 1984; *Baillie and Munro*, 1988; *Salzer and Hughes*, 2007]. A key tree ring record in this regard, extending over 10,000 years, is that from *Pinus aristata* Engelm. and *Pinus longaeva* D.K.

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Bailey: the North American bristlecone pines. It has been hypothesized [*Cutter and Guyette*, 1993; *Pearson et al.*, 2005] that the marginal growth environment which makes these trees highly sensitive indicators of palaeoclimate also provides the optimum conditions for dendrochemical responsivity. Minimal soil depth, basic soil chemistry, and low ectomycorrhizal inoculation potential [*Bidartondo et al.*, 2001] (for White Mountain *Pinus longaeva* in particular) should promote elemental uptake through the bark and needles rather than the roots. Where uptake through the roots dominates there is potential for a time lag as environmental deposition interacts in the soil chemical environment. Elemental incorporation in the wood can also be less immediate as pathways from the roots disperse through many of the xylem vessels. Uptake through the bark [*Lepp and Dollard*, 1974] and foliage [*Lin et al.*, 1995] can result in much more direct deposition of metals in the outermost xylem ring [*Baes and McLaughlin*, 1987] and thus a more accurate record of annual elemental change. It seems reasonable to hypothesize that while some uptake through the roots is inevitable, the sensitivity of these trees to record atmospheric deposition will be heightened by the shared prevalence of these other more direct uptake paths. Under similar growth conditions, various species have demonstrated particular sensitivity in recording anthropogenically induced acid deposition [*Guyette et al.*, 1992; *Bondietti et al.*, 1989], a form of environmental contamination which has direct parallels with volcanic output. While the short bristlecone growth season and timing of certain eruptions may produce issues in terms of creating a complete volcanic record, overall, bristlecone pines offer excellent potential for dendrochemical reconstructions of volcanism and other environmental elemental change [*Salzer and Hughes*, 2007].

[5] Extremely narrow tree rings (sometimes less than 40 $\mu$m) coupled with the exceptional nature of *Pinus longaeva* samples means that analysis via established dendrochemical techniques such as ICPMS [*Hall et al.*, 1990; *Watmough and Hutchinson*, 1999; *Padilla and Anderson*, 2002], NAA [*Oliveira et al.*, 1997; *Wallner*, 1998; *Ünlü et al.*, 2005] or AAS [*Ferretti et al.*, 1993; *Jonsson et al.*, 1997; *Penninckx et al.*, 1999], would be problematic, if not impossible. Such techniques would destroy whole samples and for annual resolution require dissection of individual rings, something which would be largely unfeasible given the ring size. Even high-resolution techniques such as LA-ICPMS [*Watmough et al.*, 1997; *Hoffmann et al.*, 1994; *Pearson et al.*, 2005] would result in damage to the sample and require special development for the analysis of intact cores. In contrast, Synchrotron Radiation Scanning X-Ray Fluorescence Microscopy (SXFM) is nondestructive [*Hayakawa et al.*, 1990] since subcellular radiation damage is not detrimental to the growth ring pattern or the structural integrity of the sample, requires minimal sample preparation, and can be used to collect data at micron level resolution in tree ring sequences of several hundred years in a single analytical run [*Punshon et al.*, 2005]. Moreover, SXFM delivers spatially resolved microanalysis, an essential tool for understanding the underlying physiological and anatomical distribution of the elements, providing sufficient data for robust statistical analysis, and enabling informed interpretations in an anatomical context. This capability is invaluable and sets this technique apart from those previously mentioned. In addition, simultaneous measurements of tree ring density (a well established proxy for palaeoclimate [*Briffa et al.*, 2002a, 2002b]) can be made with which to compare and calibrate the elemental data set. Variations of this technique have been used in a variety of applications for the study of wood in the last few decades, from tracing pollution [*Punshon et al.*, 2003, 2005], to innovative new approaches in tropical dendrochemistry [*Poussart et al.*, 2006].

[6] While there have been numerous studies of stable isotopes of carbon [*Grinsted et al.*, 1979; *Sonett and Suess*, 1984; *Leavitt*, 1993] and hydrogen [*Feng and Epstein*, 1994] as climatic proxies from the bristlecone pine archive, and studies of general chemistry [*Sanford et al.*, 1994], as far as we are aware, no study of spatially and temporally resolved elemental variability of these species has previously been attempted. Here we present an assessment of the feasibility and potential of SXFM analysis and *Pinus longaeva* to construct a new multielemental, annual resolution record of environmental elemental change with particular attention to the detection of volcano-specific signatures.

## 2. Methods

[7] Core samples of *Pinus longaeva* from the upper tree line of California's White Mountains were collected by the Laboratory of Tree-Ring Research at the University of Arizona, where they were mounted, surfaced, and measured according to standard dendrochronological procedures [*Stokes and Smiley*, 1968]. Samples were taken from trees of similar age (400–800 years old) within a 1.5 km area, growing between 3445 and 3513 m on a dolomitic substrate with a sparse rock strewn sandy loam. The relative wetness of the position of each tree was calculated on a Topographic Convergence Index (TCI) [*Bunn et al.*, 2004] ranging from 5 to 8.5 TCI. Temperature is thought to be the main control on tree ring growth at such altitudes, but moisture may have an impact on the chemistry of the tree rings. For comparison two additional cores were taken from a tree 200 m below the upper tree line where moisture has more potential to affect ring width, and thus possibly have a heightened effect on chemistry. Prior to analysis, the cores were resurfaced with a sledge microtome to produce a flat, uncontaminated sampling surface. Intensity variations of a suite of elements were measured via SXFM at the F3 bending-magnet beamline at the Cornell High Energy Synchrotron Source (CHESS). Following experimentation with incident X-ray energy to maximize the fluorescence of specific elements, a 17 KeV, 0.3% band-pass monochromatic X-ray beam was selected using a 15Å d-spacing $Mo/B_4C$ multilayer double-bounce monochromator. This beam was collimated to 1 mm and then focused to 30 $\mu$m using a single-bounce capillary focusing optic [*Bilderback et al.*, 2007]. The dwell time was 5 s per spectrum. Incident intensity was monitored using an ion chamber located just upstream of the sample. In order to allow for examination of the data on a sample by sample basis relative to the surface of the wood, a digital image was recorded at each sampling position. In order to preserve the integrity of the X-ray fluorescence spectra, shields of molybdenum metal were placed on either side of the core in a specially designed jig to attenuate fluorescence from the core mount or mounting glue. The energy spectra were recorded using a Vortex-90EX single-element energy-

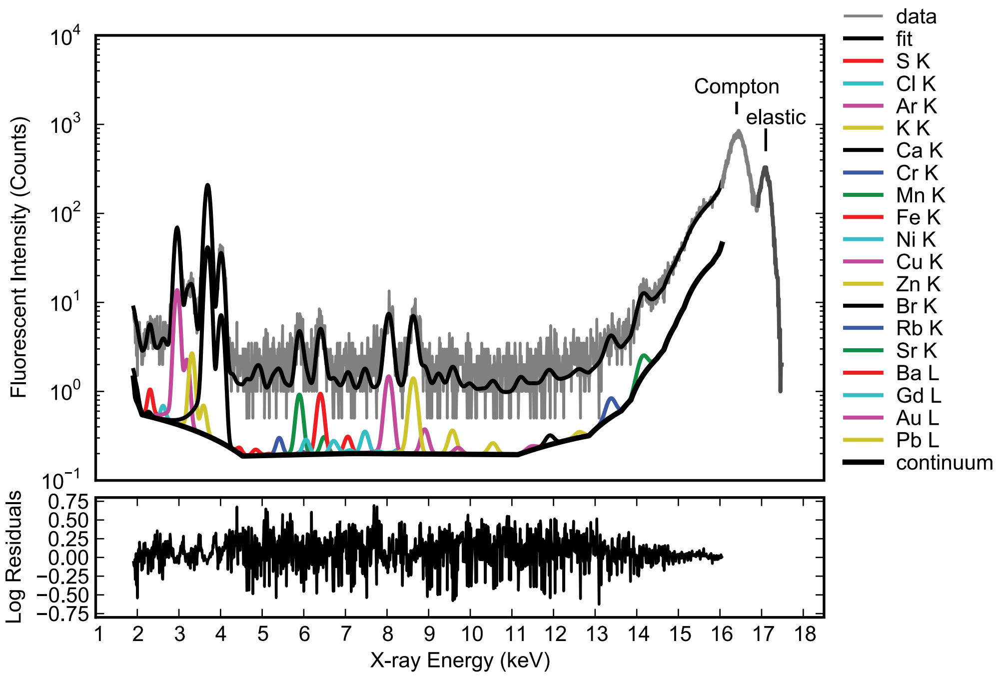


**Figure 1.** A typical energy spectrum from a bristlecone pine sample. Individual contributions to the spectrum are offset by a division of 5.

resolving silicon-drift detector and multichannel analyzer. Each energy spectrum was analyzed using the PyMca [*Solé et al.*, 2007] open-source software package which is capable of deconvolving overlapping peaks and determining peak areas and mass fractions for individual elements. Line scans were converted from a linear micron scale to annual resolution data sets via normalization to dendrochronological ring width measurements.

[8] Area scans were made to investigate the physiological distribution of elements within the wood structure and the spatial/temporal distribution of elements around the time of two major volcanic events. Sequences covering the eruptions of Tambora (AD1815) and Huaynaputina (AD1600) were selected, both events known to have caused significant, short term perturbations to Northern Hemisphere climate [*Pyle*, 1998]. While AD1816 has become known as the year without a summer [*Hoyt*, 1958; *Oppenheimer*, 2003], bristlecone pine tree rings show only a general decrease in width following this eruption, not sufficiently significant to be used as a ring width minima proxy for volcanism [*Salzer and Hughes*, 2007]. This event was mapped to see if it is possible to find an elemental marker (caused by volcanogenic elemental deposition) in the years around AD1815, even though there is no morphological reason to suspect an eruption at this time. AD1600 was selected as AD1601 was the year of the most severe short-term Northern Hemisphere cooling event of the past 600 years [*Briffa et al.*, 1998]. It is marked by a frost ring, a well established anatomical proxy for volcanism, where anomalously low temperatures during the growth season promote extracellular ice formation resulting in dehydration and deformation of the weakest outermost cells [*LaMarche and Hirschboeck*, 1984]. The scan of this anatomical feature was made to see if any additional independent elemental proxy, or ideally, volcano-specific signature could be derived.

[9] To replicate area scan findings and provide an extended record of temporally resolved elemental change for the White Mountains (including numerous eruptions of known and approximate date), line scans were made covering the last 500 years of growth from five different trees. Two cores were analyzed from one tree so that variation both within a single tree and between different trees could be examined. These data sets were evaluated in the context of elemental/anatomical associations recorded from the area scans using point by point checking of the scan data against simultaneously collected images of the sample surface. In addition, attempts were made to remove short-term oscillations resulting as the beam tracked across anatomical features (e.g., resin ducts) using low-pass filters and moving averages to leave longer-term trends (sustained sudden or gradual increases/decreases). To remove additional oscillations from relative fluctuations in density (as manifest in the intensity of the Compton scattering) the data were normalized to the sum of counts of the Compton peak (Figure 1).

## 3. Results

### 3.1. Elemental, Anatomical, and Physiological Associations

[10] Energy spectra (Figure 1) were analyzed for fluorescence lines from 18 elements (sulfur (S), chlorine (Cl), argon (Ar), potassium (K), calcium (Ca), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), bromine (Br), rubidium (Rb), strontium (Sr), barium (Ba), gadolinium (Gd), gold (Au), and lead (Pb). In 168 hours of analysis over 30,000 spot samples were measured. Of the fluorescence lines analyzed K, Ca, Mn, Fe, Cu, Zn, Br, Rb, and Sr were most reliably resolved for all samples. Several elemental/anatomical associations were replicated in both area and line scans. An example is provided in

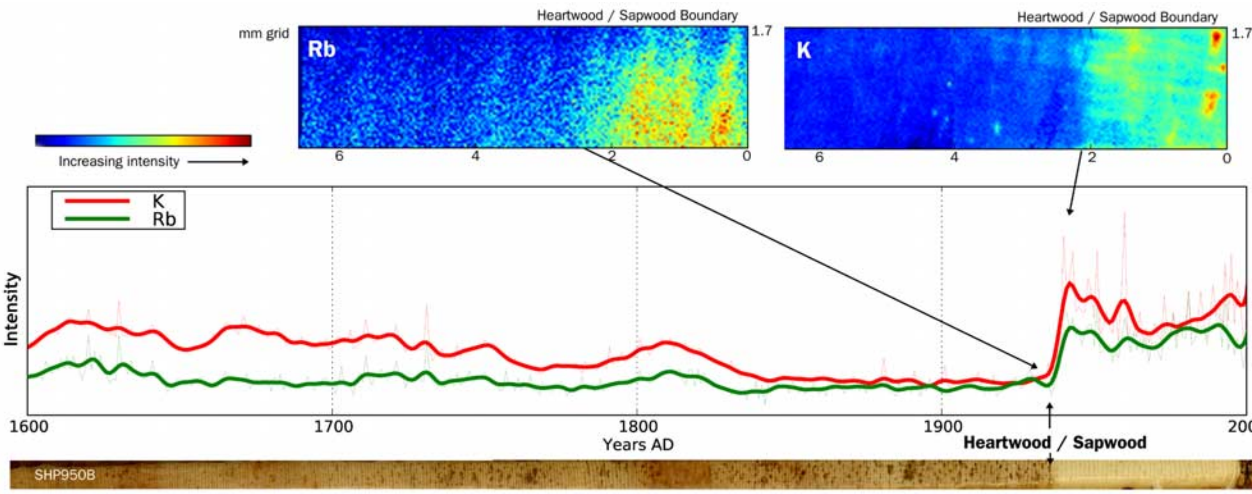


**Figure 2.** Area and line scans for K and Rb showing changes in chemistry at the heartwood/sapwood boundary. Bold lines represent normalized intensity values with an 11-year polynomial smooth. Fine lines represent unsmoothed data.

Figure 2 for K and Rb. Intensities for both elements increase at the heartwood/sapwood boundary. Br, Zn, and Fe show a similar, less distinct response. Ca, Zn, and Sr are higher in the heartwood than the sapwood, with Gd decreasing from the heartwood/sapwood boundary. K, Ca, and Zn show higher concentrations in the resin ducts (Figure 3), and along with Sr are higher in the latewood than the early wood, though this is not consistant for every latewood band, possibly indicating a response to something at seasonal resolution. Ca, Mn, and Zn are higher in the tracheid walls, with Ca declining from pith to bark. Fe occurs as random concentrated patches and as contamination spikes where

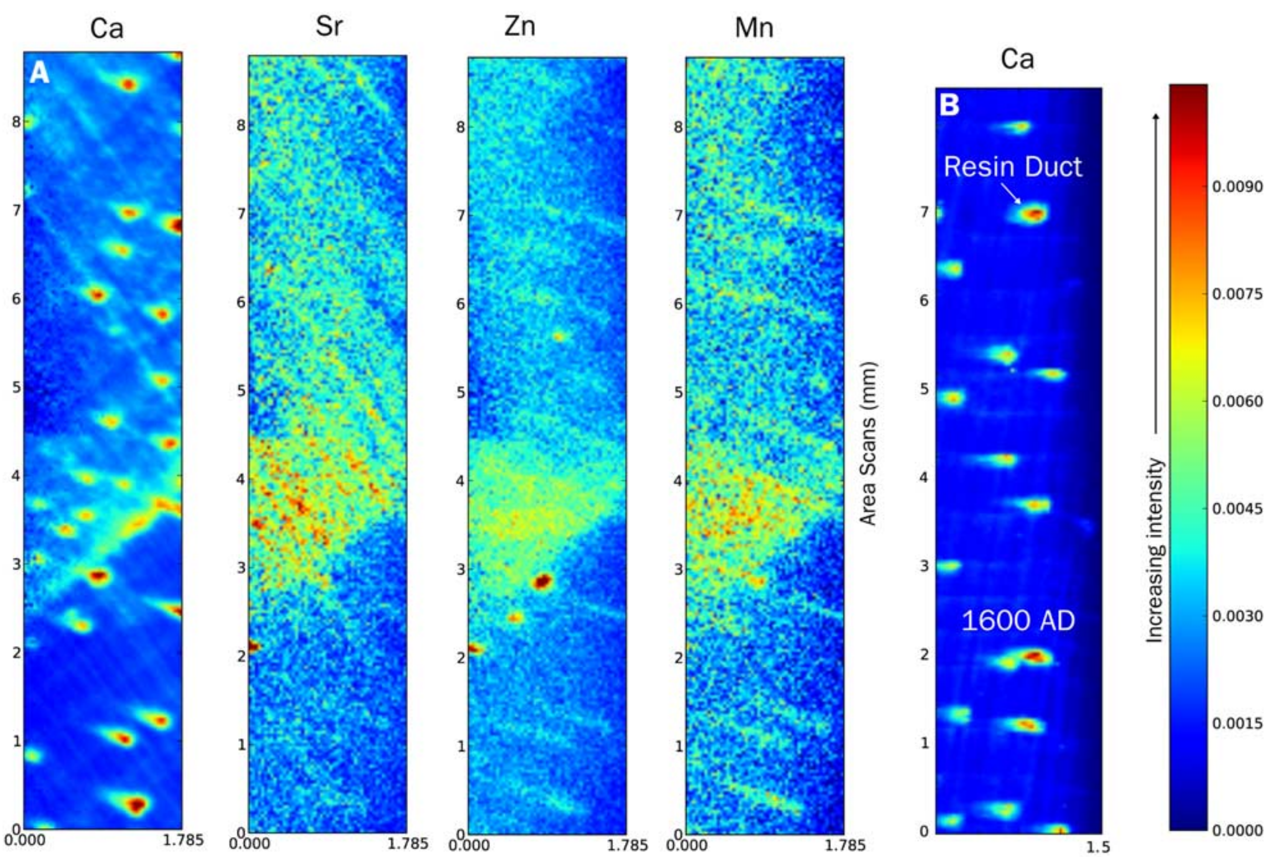


**Figure 3.** (a) Area scans for Ca, Mn, Zn, and Sr covering the AD1601 frost ring in sample SHP910A. The ring for 1602 was missing from this sample. (b) Area scan showing Ca in Sample SHP926A for the period AD1595–1610.

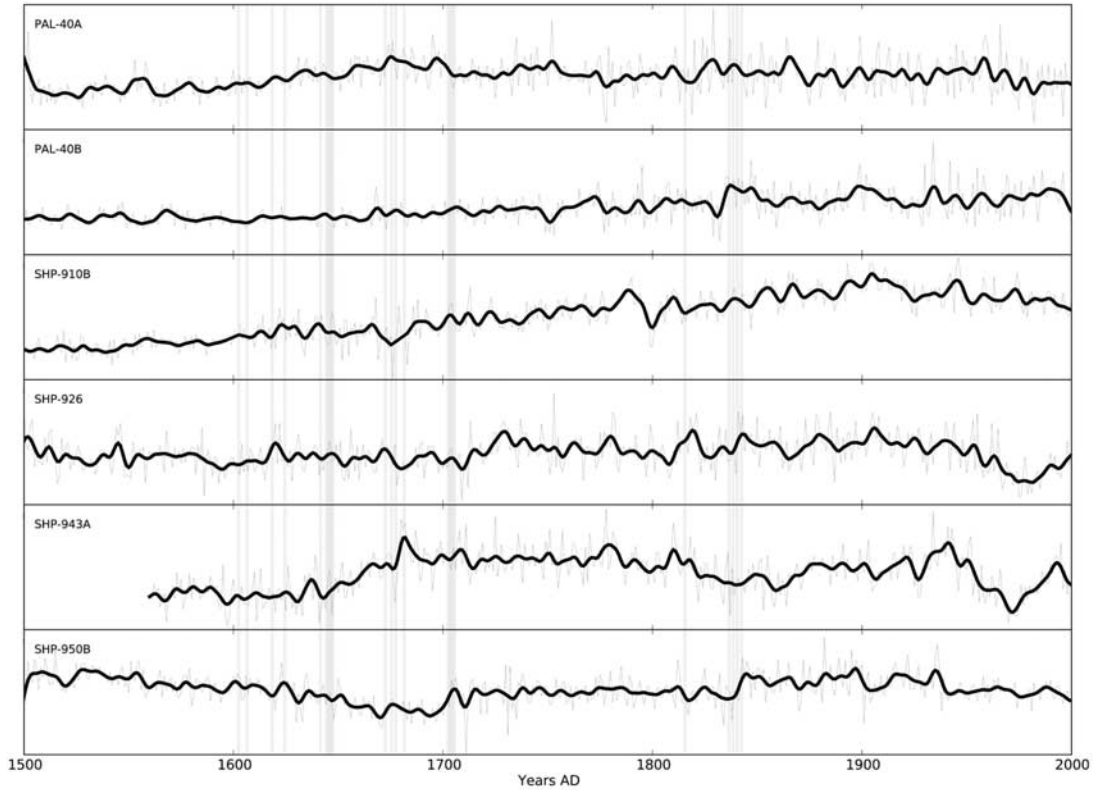


**Figure 4.** Au intensity line scans for six samples including two from the same tree (PAL40) showing variability between trees over 500 years. Bold lines represent normalized intensity values with an 11-year polynomial smooth. Fine lines represent unsmoothed data. Vertical lines mark years of probable volcanic activity (ice core acidity, ring width minima, frost rings compiled from *Salzer and Hughes* [2007]). Au uptake has been linked with the impact of volcanogenic sulphate [*Ünlü et al.*, 2005]; however, no response or replication could be found in this study. The degree of variability shown by this element is typical of that for other elements between trees.

there are pinholes in the samples. Ca, Rb, and Sr show a positive relationship with denser areas of the wood structure. Mn shows a negative relationship.

### 3.2. Volcanic Area Scans

[11] Figure 3a shows a distinct elemental response associated with the AD1601 frost ring. The cells of this feature are highlighted by higher-intensity Ca, partly in relation to a difference in the density of the deformed cells. Ca also highlights traumatic resin ducts in the years immediately following the ring, with a background increase in Ca incorporated in the tracheids. Mn, Zn, and most markedly Sr, show an increased intensity in the tracheid walls for several years following the frost ring and do not return to prefrost ring levels for the rest of the scan. Similar increases of these elements were observed in other trees with the AD1601 frost ring. A scan of the same time period in a different tree from the same site which had escaped frost damage (Figure 3b) failed to show any elemental increases following AD1601. Area scans for the period AD1780–1845 showed no changes in elemental chemistry following the eruption of Tambora in AD1815.

### 3.3. Five Hundred–Year Line Scans

[12] Line scans for Pb, Au, Fe, Br, and Cu show no correlation within the same tree or between different trees. La, Gd, and Ba showed some degree of correlation in two radii from the same tree but did not replicate between trees. The data for Mn, Zn, Rb, Ca and Sr show correlations with one another in the same tree, but little correlation in terms of annual, decadal, or centennial trends between different trees. Figure 4 provides an example of typical variability for the same element between different trees.

## 4. Discussion

[13] Trees do not passively record the external environment [*Smith and Shortle*, 1996], and the various internal physiological controls on element mobility in the xylem of *Pinus longaeva* are not fully understood. Many of the elemental/anatomical associations observed in this study were, however, similar to those reported for other species in a range of studies [*Wardell and Hart*, 1973; *Saka and Goring*, 1983; *Bailey and Reeve*, 1996; *Wimmer and McLaughlin*, 1996; *Penninckx et al.*, 2001]. Increases in K and Rb at the heartwood/sapwood boundary, indicative of the function of the live sapwood zone, have similarly been observed by [*Okada et al.*, 1993]. Increased levels of elements (in this case K, Ca, Zn, and Sr) associated with resin ducts and latewood have likewise been observed for Ca, Mn, K, and Cu in Picea species [*Sunden et al.*, 2000]. The elevated presence of elements in the resin ducts reflects

the use of metal ions in these features as they function as live metabolic pathways in the xylem. It is interesting to note that the resin itself is not always enriched with the same elements as the resin ducts. For example, increased Zn is shown in the resin but not in the epithelial cell walls of the duct. The positive relationship with density shown by Ca, Rb, and Sr is associated with both the presence of resin and denser cell structure. The distribution of Fe in random 'hot spots' [*McClenahen et al.*, 1989; *Lövestam et al.*, 1990; *Sunden et al.*, 2000] adds to the overall picture of elemental heterogeneity for these tree rings.

[14] Tree ring heterogeneity is an increasingly well documented problem for dendrochemical analysis [*Brabander et al.*, 1999; *Pearson*, 2006] and clearly explains many of the difficulties in replicating trends based on line scans through different trees. The line scans are, in some respects, too high a resolution for the material being sampled. It was hypothesized, however, that for those elements that make up the tracheid structure it should be possible to discern longer-term background trends over time. For example, in terms of identifying volcanic signatures, undulations over two or more years in essential elements such as Ca, Mn, Sr, or Zn might register a response to changes in environmental acidity over time. This hypothesis is based on a large number of studies of the impact of acidic, anthropogenically induced deposition. Such deposition has been shown to mobilize elements in a variety of soil environments [*Bondietti et al.*, 1989; *DeWalle et al.*, 1991; *Shortle and Bondietti*, 1992; *Watmough et al.*, 1999; *Penninckx et al.*, 2001], and, critically, to increase uptake through the needles and bark [*Huttunen et al.*, 1983; *Percy and Baker*, 1988; *Lin et al.*, 1995]. Mobilization can typically result in an increase in availability for uptake with the onset of deposition. However, if the deposition is especially concentrated/prolonged (particularly in combination with an impoverished soil), elements may be depleted in the xylem as they are leached out of the soil, or blocked as mobilized aluminum binds to the fine root tips [*Shortle et al.*, 1997]. As it is likely that more direct uptake through the bark and leaves dominates for the trees used in this study, an increase in elemental concentrations is the more likely scenario. While increases in certain essential elements could therefore be hypothetically linked with the impact of volcanogenic acid deposition, detection of S, Cl or other elements (e.g., Selenium (Se) [*Greenland and Aruscavage*, 1986]) which could be directly used to fingerprint a specific volcanic source is the ultimate goal.

[15] In this study, in order to maximize the count rate for S and Cl (which fluoresce at lower energy) elements which fluoresce at higher energy (such as Se) were not detected. Unfortunately sensitivity for S and Cl, even at these lower levels, was not sufficient for reliable resolution; however, numerous increases/decreases in essential elements could be observed in all five trees. Many of these coincided with eruptions of known or approximate date, and some with key changes in climatic variables such as temperature, precipitation and in the case of Mn, possibly solar activity. Yet none of these trends replicated sufficiently over the same temporal period for multiple trees, or even within different radii from the same tree. As a result it must be concluded that although there was an indication of real potential for a multielemental record in certain trees, in certain years, for certain events, it is as yet impossible to access that potential due to a tree-specific combination of highly localized environmental variables and physiological controls.

[16] The tree which showed the most potential for replicable, responsive elemental patterns was from a slightly higher, more exposed growth location, but no clear relationship with altitude was demonstrated between the other samples. Replication of this observation in a larger number of individuals from various heights would be required for substantiation, but it may be that in terms of the elemental record, even slight variations in height/exposure can be significant. No relationship was found between pattern replicability/responsiveness and TCI, nor the overall age of the tree. While the samples used in this study were selected from sites with a very similar substrate, it is possible that subtle, highly localized variations in loam chemistry and depth may also be influential. Future studies should focus on an increased number of samples and replicate analyses, from the most marginal locations possible, and include detailed characterization (including geochemical analysis and pH) of tree/site specific loam/bedrock rubble.

[17] The area scans of the two periods of known major volcanic eruptions demonstrated the usefulness of SXFM mapping by providing a physiological and anatomical context against which to study elemental variations. The Ca increase following AD1601 was concluded to be a physiological response as it occurs most obviously within the frost damaged cell walls and traumatic resin ducts. More generalized increases in Mn, Zn and Sr in the tracheid walls following the frost ring initially appeared to have potential to link to a volcanic response, as the duration extends well beyond the physically damaged cells. A general increase of these elements in the years following an eruption could link with the impact of volcanogenic acid deposition, known to be widespread in AD1602 from ice core records [*Zielinski et al.*, 1997; *Clausen et al.*, 1997; *Cole-Dai et al.*, 1997; *Crowley*, 2000; *Budner and Cole-Dai*, 2003; *Vinther et al.*, 2006] and sustained over a longer period of time by alteration of the chemistry of the soil environment. Similar increases due to anthropogenic acidification have been noted for Mn [*Guyette et al.*, 1992; *Guyette and Cutter*, 1994; *Lin et al.*, 1995; *Hutchinson et al.*, 1998] and Zn [*Legge et al.*, 1984; *Lin et al.*, 1995; *Hutchinson et al.*, 1998] in a variety of tree species, on a range of substrates. However, when this response was further tested by analysis of a core from a different tree which had escaped physical damage in AD1601, it did not replicate, indicating the cause was entirely physiological. Similarly no evidence for a response to volcanic fallout was derived from the AD1815 sequence.

## 5. Conclusions

[18] The developed protocol provided an effective methodology for exploration of the potential of SXFM for the production of multielemental maps and annual resolution line scan data from *Pinus longaeva*. The excellent potential of SXFM for nondestructive dendrochemical studies of long sequences of submillimeter tree rings at annual to subannual resolution was demonstrated. Area scans, with the capacity for observation of multielemental change within the context of physiological controls on the tree ring chemistry, offer the best possible approach for reconstructing elemental change

over time. Such analysis for the full length of a core would be prohibitively time consuming however, without a multipixel energy-dispersive detector to increase signal and sample throughput. Line scans may be more successfully applied to tree species with wider rings and more homogeneous chemistry, but possible improvements to protocol could improve this mode of data collection from bristlecone pines.

[19] The lack of replication between trees in this study may indicate that *Pinus longaeva* is unsuitable for temporally resolved dendrochemical reconstructions. If, however, it were possible to gain a better understanding of the range of individual physiological and microenvironmental variables affecting element uptake/distribution in each tree, it might be possible to establish a range of filters to improve replicability of future data sets. Extraction of mobile products such as resins prior to analysis may also reduce contamination to any possible common signal by removing the elemental fraction that is potentially out of temporally acquired sequence (due to mobility in the xylem). Improved detection of a wider range of elements could also yield new palaeoenvironmental information. This could be achieved by running the experiment under vacuum to minimize air attenuation of fluorescence below 4 KeV, or use of a multipixel detector to increase the incident count rate and improve the signal to noise ratio. Other synchrotron sources capable of lower incident X-ray energy could be used to improve sensitivity to elements such as S and Cl (of particular interest when attempting to elucidate volcanic signatures).

[20] Given these improvements in future studies, this paper demonstrates a feasible first step by which a new, multicentennial, annual resolution record of palaeoenvironmental chemistry may one day be derived from the North American bristlecone pines.

[21] **Acknowledgments.** Samples used in this study were supplied by the Laboratory of Tree-Ring Research, Tuscon, where we thank Thomas Swetnam. We would also like to thank Malcolm Hughes for support and insightful comments on an earlier version of this text. We are very grateful to Mary Jaye Bruce and two anonymous reviewers for their critical appraisal and improvement of the text. M. W. Salzer was supported by the National Science Foundation under grant 0551986 to Malcolm K. Hughes. This work is based upon research conducted at CHESS which is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under NSF award DMR-0225180. At CHESS we would like to thank Sol Gruner, Arthur Woll, Don Bilderback, and Sterling Cornaby.

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