

# Secondary ion mass spectroscopy and synchrotron X-ray fluorescence in the study of the qualitative variation in metal content with time in tree rings

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**Abstract:** Secondary ion mass spectroscopy and synchrotron X-ray fluorescence analysis have been used to document the changes in metal content across the ring system of trees from northern Canada. The results show a seasonal qualitative variation in the uptake of Na, Al, K, Ca, Cr, Mn, Fe, Cu, and Zn. Diffusional models show that locally elevated concentrations of selected metals are sufficiently stable within individual rings that variations in content among rings remain at detectable levels for at least a century.

**Résumé :** La spectroscopie de masse des ions secondaires et l'analyse de la fluorescence par rayonnement X synchrotron ont été utilisées pour étudier les variations dans le contenu en métaux dans les anneaux de croissance des arbres du nord du Canada. Les résultats montrent une variation qualitative saisonnière dans l'absorption de Na, Al, K, Ca, Cr, Mn, Fe, Cu et Zn. Des modèles de diffusion indiquent que les concentrations localement élevées des métaux échantillonnés sont suffisamment stables à l'intérieur des cernes individuels pour que les variations quantitatives entre les cernes demeurent à des niveaux détectables pendant au moins un siècle.

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## Introduction

The study of tree ring patterns, dendrochronology, is a well-established discipline that has been used as a measure of climate variation and other environmental events (Amato 1988). Cross-dated tree rings provide ideal sources for radio-carbon calibration (Becker 1993). Ring patterns have even been used to study the prehistoric transportation of construction beams (Dean 1978). Analysis of the metal content of tree rings (dendroanalysis or dendrochemistry) has the potential both for identifying pollution events, such as metal contamination from mining operations (Guyette et al. 1991), and for providing a long-term chronology of the kinetics of metal deposition and uptake (Gough et al. 1995).

Dendroanalysis must be interpreted with caution. Lepp (1975) has been careful to point out that the mechanism of metal deposition in tree rings is poorly understood. Hage-

meyer (1993) has presented a critical review of the subject and has shown both that the literature contains conflicting results and that such questions as the mode and kinetics of metal accumulation in trees as well as the possibility of lateral migration of metals within wood have yet to be satisfactorily addressed. Contradictory results continue to appear in the literature. Trueby (1995) concludes, after an exhaustive study of several species in the Black Forest, Germany, that "There is no relation between the historic heavy metal deposition and the radial distribution of tree rings." Qian et al. (1993) studied the element distribution in trees near lead and zinc mines and concluded "a time-concentration sequence could be set up on the basis of tree-ring analysis to reflect the annual variation of the relevant elements in the soil." It seems most unlikely that the questions currently posed regarding the usefulness of dendrochemistry will be answered easily. Apparent contradictions will almost certainly be found to depend on such questions as whether or not selected elements are mobile in the soil, air, or the wood itself or if mobility when detected is concentration dependent. Studies to explore these questions will have to include analytical techniques that have better spatial resolution than solution techniques, such as inductively coupled plasma optical emission spectroscopy (ICP-OES) (Bondiette et al. 1990), which require the dissection and digestion of relatively large wood samples. Several instrumental techniques have been developed over the last several years that are capable of measuring variations in element concentrations within individual tree rings; these include laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) (Hoffman et al. 1994) and proton-induced X-ray emission

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(PIXE) (Harju et al. 1996). These studies show seasonal variations of trace element concentrations within individual tree rings, which would have been integrated in any analysis requiring dissolution of the wood.

Secondary ion mass spectroscopy (SIMS) has the potential of analysing for all elements and their isotopes in solid samples with a spatial resolution that may be in the range of 1–20  $\mu\text{m}$  (Martin et al. 1997a). In this work we have used SIMS in a surface-scanning mode to examine the trace element distribution within individual tree rings by scanning the primary ion beam across the surface of the wood obtained from a standard core sample. The information obtained has been used to demonstrate seasonal variations in metal uptake, to examine the question of element mobility, and to identify a specific suite of elements whose distribution within the wood appears to differ from that of elements generally considered to be required for healthy growth. The results are interpreted with a view to addressing the differing opinions regarding the usefulness of dendroanalysis prevalent in the existing literature.

Synchrotron X-ray fluorescence analysis (SXFRA) uses synchrotron radiation to excite X-ray fluorescence from the elements in the sample. The resultant X-ray emission is representative of the sample composition. SXFRA is becoming an important tool for analysis of environmental samples (Jones et al. 1994). This technique is capable of examining areas as small as 10  $\mu\text{m}$  on edge and operates at atmospheric pressure thus eliminating possible changes in the sample induced by high-vacuum conditions. The technique has low detection limits and a greater sampling depth than SIMS. In this study, SXFRA was used to probe the same areas interrogated by the SIMS instrument. The SXFRA had the twofold aim of assessing the usefulness of this technique in dendroanalysis and providing confirmation of the SIMS findings.

## Materials and methods

Three trees were selected for SIMS analysis from specimens of black spruce trees (*Picea mariana* (Mill.) BSP) growing in peat in the Hudson Bay Lowlands. These samples were selected because good data exists on the local soil chemistry (Cowell et al. 1978) and the tree rings are very narrow, of the order of 0.16 mm, because of harsh growing conditions in the form of a short season and low nutrient availability. The narrow rings are ideal for analysis by SIMS in the scanning mode, since many rings can be included in each scan. Samples for SIMS analysis were cut from stem sections prior to mounting in metal-free epoxy resin. The sample surfaces were polished using 1200-grit  $\text{SiO}_2$  sandpaper with no lubricant and sputter coated with gold using a Hummer VI Sputter Coater to reduce surface charging during SIMS analysis. The SIMS was a Cameca IMS 4f instrument located in Surface Science Western at the University of Western Ontario. Analysis was carried out in the step-scanning mode. The sample was moved past the primary ion beam in discrete 20- $\mu\text{m}$  steps. After each individual step the sample was scanned for C, O, Na, Al, K, Ca, Cr, Mn, Fe, Cu, and Zn using a 2-nA  $\text{O}^-$  primary ion beam with a 4500-V accelerating voltage. The primary ion beam was rastered over a 50  $\times$  50  $\mu\text{m}$  area while collecting secondary ions from a central circular spot 10  $\mu\text{m}$  in diameter to avoid edge effects. A 2-nA primary ion beam was used both because the low current helps to minimize sample charging and to reduce sputtering during analysis to an acceptable level. Preanalysis sputtering ensured removal of any surface contamination that may have been introduced

during sample preparation. The estimated ablation rate under these conditions is 0.02  $\mu\text{m}/\text{min}$ . No sample offset was used for C, but a 200-V offset was used for all other elements. This offset was judged to be adequate to suppress molecular secondary ions to the point where they would make a negligible contribution to the secondary ion yield. Since metals served as the focus for this study, only positive secondary ions were collected. Differential analysis times were used for each element to allow in part for differences in secondary ion yield. Each analysis cycle took the following form: 55-s preanalysis sputter to remove surface contamination followed by individual element analysis times: C, 1 s; O, 1 s; Na, 2 s; Al, 5 s; K, 5 s; Ca, 5 s; Cr, 20 s; Mn, 20 s; Fe, 20 s; Cu, 20 s; and Zn, 20 s. A set of data was collected for  $^{54}\text{Fe}$ . The secondary ion yield, while low, showed the same patterns as  $^{56}\text{Fe}$ . This observation is consistent with effective suppression of molecular ions (such as  $\text{CaO}^+$ ) by the 200-V offset applied to the sample holder. Only the  $^{56}\text{Fe}$  results are presented. The resulting analysis provides data from a line of contiguous circular sites 10  $\mu\text{m}$  in diameter separated by 10- $\mu\text{m}$  spaces. This scanning sequence should allow determination of the general spatial arrangement of elements across individual rings. Clearly, some detail is lost, and small features may be missed.

The  $\text{O}^+$  secondary ion yield was used as an internal reference since the  $\text{O}^-$  primary ion beam guarantees a uniform oxygen surface coverage. The  $\text{O}^+$  secondary ion yield was adjusted in each case to yield  $1 \times 10^6$  ions/s, and the appropriate correction factor was applied to all other elements. No attempt was made to obtain quantitative results both because seasonal variations in the ring make this difficult (Martin et al. 1997b) and relative changes provide an adequate insight into possible chronological changes and metal mobility. Five step scans were carried out in total, one on each of the first two specimens. Three were obtained from the third tree, and one of this set, taken to be representative of the form of the results, is reported here.

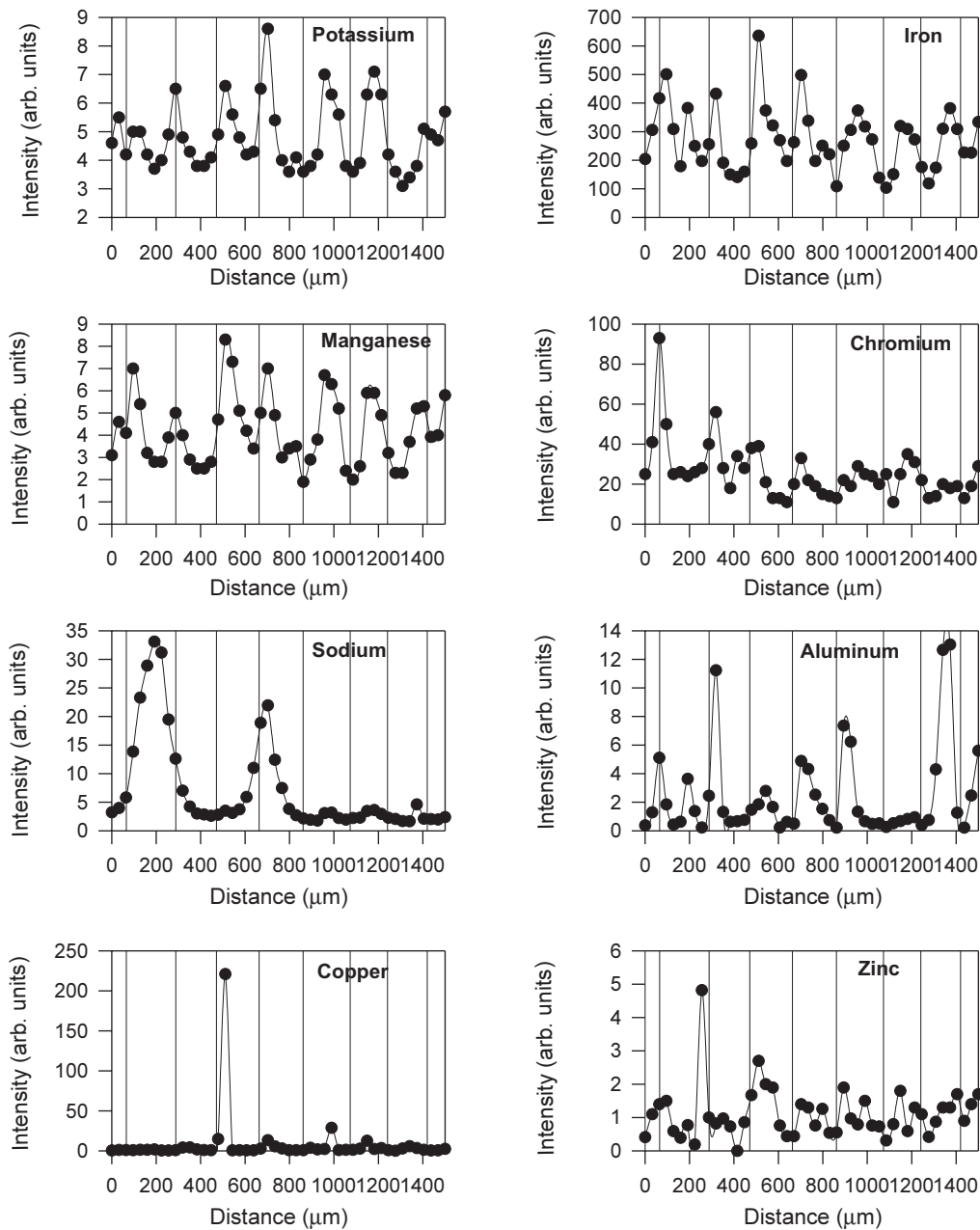
The SXFRA measurements were carried out using the X-ray microprobe installed at the X-26C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory in the ion trench left on the sample surface by SIMS analysis. This approach ensured that the areas scanned by the synchrotron radiation and SIMS were closely matched and that, since passage of the SIMS ion beam had sputter cleaned the surface, there was no surface contamination. The storage ring was operated at 2.5 GeV with a 200-mA injection current. The scans reported here were carried out with a 10- $\mu\text{m}$  beam.

Neither the SXFRA nor the SIMS results were used to estimate the absolute concentrations of elements within the wood samples. The results presented here are used solely to assess the relative changes in signal while scanning laterally across the ring system.

## Results and discussion

The first SIMS scan shows a typical result for the relative potassium secondary ion yield (Fig. 1). There is clear evidence for seasonal variation with the maximum potassium yield generally occurring in the early part of the growing period. The trend to a maximum in the later part on the season, evident in only one ring, is probably due to some uncertainty in establishing the position of the primary ion beam, since in the step-scanning mode only, a continuous ion trench is visible rather than the distinct localized craters obtained during depth profiling. This small uncertainty in assigning the position of the ion beam during the scan is still sufficient that the exact seasonal variation should be regarded as tentative. Similar seasonal variations have been observed in eastern white pine (*Pinus strobus* L.) (Martin et al. 1997b), although

**Fig. 1.** Intensity (arbitrary units) of the secondary ion yield for various elements of interest during a typical step scan across seven complete rings. Vertical lines indicate earlywood–latewood boundaries; the rings are dated to the years 1920–1927.

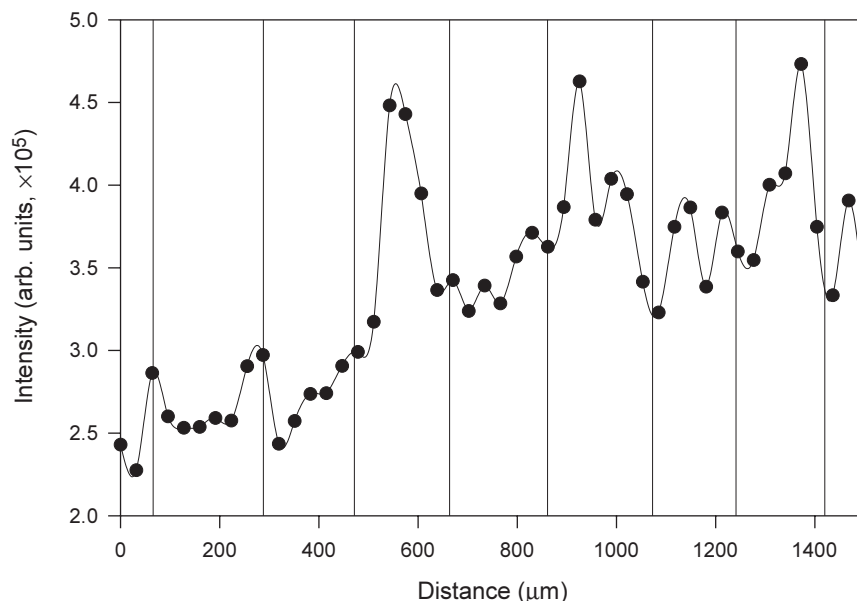


the maxima were later in the season. Other authors (Harju et al. 1996) have observed seasonal maxima in the earlywood. This difference may be species specific or result from variation between sites; the white pine studies were carried out in southwestern Ontario, and it is possible that the behaviour of northern samples may reflect changes in the depth of the permafrost during the growing season. The seasonal changes reported here do not reflect changes in secondary ion yield resulting from changes in wood chemistry or density through the growing season since virtually identical results were obtained when carbon rather than oxygen was used as the internal standard. This suggests that a real concentration difference was observed rather than an artifact resulting ei-

ther from increased wood density (with enhanced  $^{12}\text{C}$  yield) or a change in the distribution of oxygen functional groups (with enhanced  $^{16}\text{O}$  yield). The distribution patterns obtained for  $^{56}\text{Fe}$ ,  $^{55}\text{Mn}$ , and  $^{52}\text{Cr}$  are also shown. The Fe and Mn patterns are essentially identical to  $^{39}\text{K}$  and  $^{40}\text{Ca}$  (not shown), while that observed for Cr was similar (Fig. 1).  $^{54}\text{Fe}$  was also monitored to ensure that the pattern ascribed to  $^{56}\text{Fe}$  was not the molecular ion  $^{40}\text{Ca}^{16}\text{O}$ . The pattern was essentially identical to that obtained for  $^{56}\text{Fe}$ .

These results show that the seasonal uptake is similar for all the metals in this set. In addition, different maximum yields are observed for the individual elements in different years, strongly suggesting that there are annual differences

**Fig. 2.** Original intensity (arbitrary units) of the secondary ion yield for oxygen during a typical step scan across seven complete rings. Vertical lines indicate earlywood–latewood boundaries, rings are dated to the years 1920–1927.



in their concentrations. This finding is consistent with the view that dendroanalysis provides an effective means of monitoring chronological changes in element availability.

There is also a notable fine structure to the scans that is a consequence of the size of the spot being interrogated by the primary ion beam at each step in the scanning process. In this case a spot 10  $\mu\text{m}$  in diameter is used; thus, metal aggregates having areal distributions smaller than the spot size will appear as metal-rich regions. Structured peaks in the secondary ion spectra will be observed when metal-rich regions consisting of collections of discrete sites are scanned. Flat-topped peaks will occur if the feature, or collection of features, is larger than the size of the spot interrogated. Only the last of these possibilities is not observed. We conclude that the variations in metal concentrations recorded for this element set are confined to areas with lateral distributions of 10  $\mu\text{m}$  or less. The fine detail of the results helps to underscore the need for analytical techniques that investigate small areas. Such results both complement and expand those obtained by bulk analytical techniques.

The patterns obtained for this suite of elements (Ca, K, Fe, Mn, and Cr) is of interest for another reason. It reflects on the continuing debate about the mobility of individual metals in tree rings (Symeonides 1979; Kennedy and Bergeron 1991). Consider K as a representative element in the set. There is an essentially constant background of  $35 \times 10^4 - 40 \times 10^4$  counts with well-defined peaks ranging as high as  $88 \times 10^4$ . These maxima represent a 100% increase in the K concentration within annual rings approximately 70 years old. The inevitable conclusion is that some fraction of the K is bound for periods close to a century. These maxima may provide a long-term record of K uptake. It is possible that some of the element is mobile resulting in a nearly constant background.

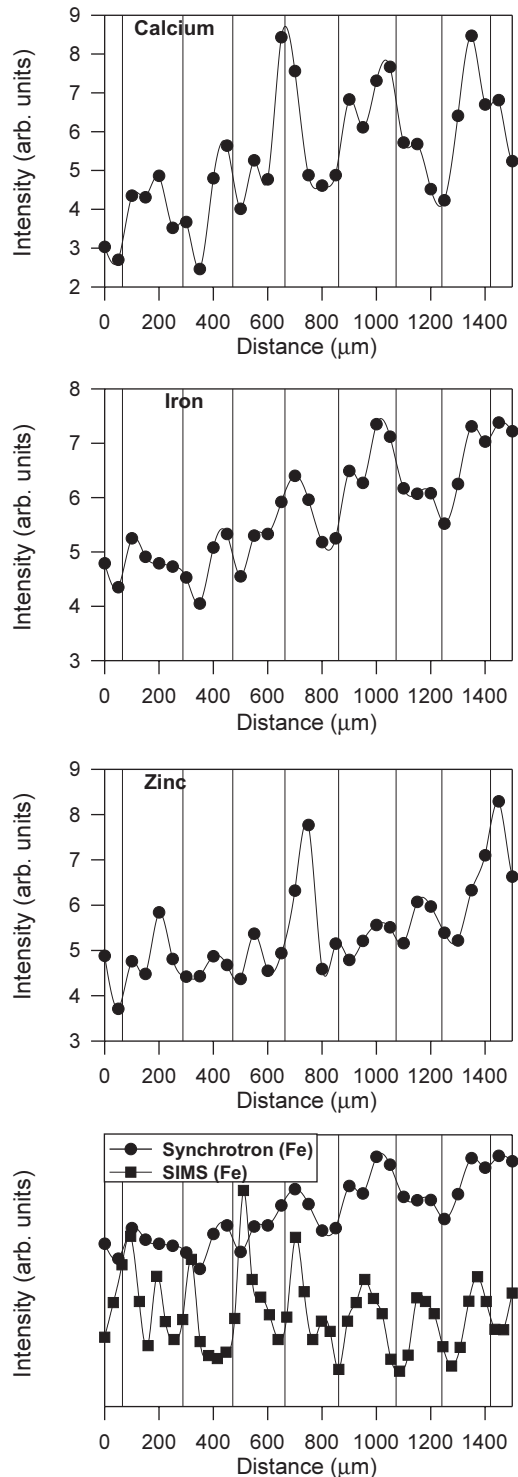
It is important that the most conservative interpretation consistent with the results be employed. Other species may well display a different behaviour. Vroblesky et al. (1992)

have shown increased K in the heartwood of tulip-trees (*Liriodendron tulipifera* L.) in response to groundwater contamination, with increased K in the sapwood of trees not exposed to pollution. They attribute this result to a tendency of tulip-trees to store K in heartwood when the element is available in high concentration. Our suggestions should, accordingly, be taken as applying only to black spruce under harsh growing conditions with both a short growing season and low nutrient input similar to those experienced by our samples.

This observation makes the data obtained for Na all the more remarkable. Two localized high concentrations of Na are evident in or spanning localized areas corresponding to rings approximately 70 years old. While the argument that suggested that these features must result from long-term localization of the element still applies, the peaks are sufficiently well defined that an attempt was made to fit the distributions observed to standard diffusion models. Diffusion coefficients were calculated assuming the Na distribution to be Gaussian with the full width at half-maximum (whh) given by the equation:  $\text{whh} = 4[(\ln 2)Dt]^{0.5}$  (Crank 1983) where  $D$  is the diffusion coefficient and  $t$  is the time in years. This yielded diffusion coefficients for both peaks having values of  $5.0 \times 10^{-3} \text{ cm}^2/\text{year}$  and  $2.1 \times 10^{-3} \text{ cm}^2/\text{year}$ , respectively. There are good reasons to doubt the efficacy of using a simple diffusion model here. The results do, however, suggest that lateral motion of Na is slow enough that discrete features would be preserved for long periods. Similar localized concentrations of salts have been reported in tree rings using both SIMS and SEM (Martin et al. 1997b). In addition, while some of the effect may be produced by drying the sample and subjecting it to high vacuum, the effect observed could only occur if the parent event was localization of the element in the first instance.

Additional SIMS step scans carried out parallel to that shown in Fig. 1 do not show matching Na inclusions, while the other recurring patterns are substantially maintained.

**Fig. 3.** Intensity (arbitrary units) of the SXFRA signal for various elements of interest taken from the same region as Fig. 1. The last image compares SIMS and SXFRA.



These scans were within 0.5 mm of that shown in Fig. 1. Local contamination is highly unlikely both because of the precautions taken during sample preparation and analysis and the absence of a comparable increase in K. Small inclusions of this type might be expected if a single pathway from an individual root or branch is analysed. Localized

metal concentrations within individual tree rings in response to exposure of a limited portion of a tree's root mass have been noted using SIMS imaging techniques (Goldsmith et al. 1993).

The pattern obtained for Al, while it is substantially similar to those obtained for K, Fe, Mn, and Cr, shows marked excursions from the general pattern. It is premature to speculate on the reasons for these events, although they appear to be indicative of unique environmental events. The distributions shown for Cu and Zn are remarkable. Other results obtained using SIMS and scanning electron microscopy have shown both of these elements to be confined to small regions in tree samples (of the order of 10  $\mu\text{m}$ ) and essentially randomly distributed with respect to the relatively small areas interrogated by the primary ion beam. This pattern is observed in all scans. The results here support earlier suggestions that these elements occupy relatively small regions associated with enzyme activity or are otherwise localized (possibly in resin ducts) (Martin et al. 1997b).

Figure 2 shows the uncorrected yield for oxygen acquired during the SIMS scan. No changes that might allow an interpretation of the metal yields as a function of changes in wood chemistry are evident.

The SXFRA spectra obtained for Ca, Fe, and Zn from the ion track left by the SIMS instrument are shown in Fig. 3. These results are not expected to match those obtained by SIMS. Differences are expected because the alignment of the starting positions in the scan is imperfect. In addition, SIMS is surface sensitive, while SXFRA excites and obtains spectra from a depth of at least 10  $\mu\text{m}$ . Finally, the instrumental sensitivities for matching elements are different. The following observations can be made regarding the synchrotron results in isolation.

The signal obtained for Ca shows the same general features as the SIMS results with well-defined concentration maxima. The latter is consistent with the suggestion that some fraction at least of the Ca has either no or very low lateral transport within the ring system. The Fe signal shows the same general pattern as Ca, leading to the same conclusions. It is clear that there is no good agreement between the SIMS and the SXFRA results. The Zn signal is atypical when compared with Ca and Fe (as is the case with SIMS). This is consistent with the suggestion that the Zn in the tree is confined primarily to limited areas within the wood such as resin ducts and cell vacuoles. Figure 3 also shows a superposition of the SXFRA and SIMS results for Fe. The two different instrument scans are not well matched for the reasons previously outlined.

Five SIMS step scans were carried out in total. It is important to note that, in this context, the figures presented show only the relative changes in signal yield for single elements during the step scans presented. No direct inferences may be made between the concentrations of different elements. In short the results should be considered to be qualitative. In addition the results shown here for both the SIMS and SXFRA are from a single scan taken to represent a typical result. The SIMS step-scanning mode employed here leads to some uncertainty in assigning the exact location of the analysis spot. A low-power microscope is used to monitor the beam location to provide a general indication of the beam position, but some displacement of the analytical spot

may result from sample charging. This uncertainty is unfortunate because it makes interpretation of the SXFRA data more difficult. This instrument is aligned by observing the location of the exciting X-ray on a phosphorescent screen. Once alignment is complete the sample is inserted. Scanning is accomplished by moving the sample past the beam focus. Because of the combined uncertainties in positioning the instruments during analysis a conservative approach has been taken to the interpretation of the data. In general the results reported here are consistent with other SIMS data. Bailey and Reeve (1994) have shown selected elements to be correlated with morphological features in wood such as the torus, middle lamella, cell corners, and ray cell walls.

## Conclusions

The SIMS results show a pattern consistent with seasonal variation in uptake for elements such as K, Ca, Fe, and Mn. The patterns are of a nature that suggests that a significant fraction of each of these species is localized within individual growth rings and that, if they are diffusing at all, it is at a rate that preserves the local enhancement for at least 70 years.

In addition the SIMS results show significant local concentrations of Na that are consistent with both localized vertical transport of sodium within individual rings and local precipitation during sample preparation. Diffusion coefficients based on the width of two of these inclusions suggest that lateral movement of Na is slow and that local concentration anomalies may persist for decades. This observation is consistent with the local maxima observed for other elements. Aluminum shows anomalous behaviour, approximating K, Ca, and Fe but with sufficient differences to suggest some kind of environmental perturbation.

SIMS also shows that Cu and Zn are distributed in essentially random patterns (at least on the small analytical scale used in these measurements). This is consistent with cellular activity and (or) a mechanism that secretes these elements in resin ducts. The SXFRA spectra for Zn tend to confirm this observation.

The fact that seasonal patterns are preserved for K, Ca, Fe, Mn, and Cr means that, for these elements and in this species at least, dendroanalysis may provide an effective tool for dating environmental events. The Na anomalies also support this suggestion, as do the patterns for Al. The distributions of Zn and Cu on the other hand may be consistent with an active transport model in which the resin ducts play an important role. Such an interpretation means that dendroanalysis may be appropriate to some elements and not others.

Finally SIMS and SXFRA have been used here as complementary techniques. For some applications, SXFRA has the advantage of operating at atmospheric pressure, thus avoiding the high-vacuum step required for SIMS and possible changes in the sample structure as a result. The differences between the SIMS and SXFRA data may be explained in part by differences in instrument alignment and sampling depth.

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