

## Secondary ion mass spectroscopy (SIMS) in the analysis of elemental micropatterns in tree rings

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Received May 30, 1994

Accepted October 14, 1994

MARTIN, R.R., SYLVESTER, T., and BIESINGER, M.C. 1994. Secondary ion mass spectroscopy (SIMS) in the analysis of elemental micropatterns in tree rings. *Can. J. For. Res.* **24**: 2312–2313.

Secondary ion mass spectroscopy (SIMS) has been used to examine elemental micropatterns in tree rings. Elevated potassium was detected in discrete rings, suggesting that this technique may have a wide application in dendrochronology.

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La distribution fine des éléments dans les cernes annuels a été étudiée à l'aide de la spectroscopie de masse par ion secondaire. Une concentration élevée de potassium a été détectée à l'intérieur de cernes annuels suggérant que cette technique est largement applicable en dendrochronologie.

[Traduit par la Rédaction]

### Introduction

Considerable research effort has been expended using tree rings as evidence for such events as climate variation, solar flares, and forest fires (Amato 1988). The elemental composition in tree rings is also being used to monitor environmental events, thus neutron activation analysis has been used to follow the long-term relationship between molybdenum and sulphur in western red cedar (*Thuja plicata* Donn) (Guyette et al. 1989), inductively coupled plasma – atomic emission spectroscopy has been used to assess the impact of atmospheric deposition on forests (Bondietti et al. 1989), and proton-induced X-ray emission has been used to examine the effects of altered soil chemistry (McClenahan et al. 1989). In addition, inductively coupled plasma – mass spectroscopy gives multielement analysis at exceptionally low concentrations in tree rings (Hall et al. 1990).

Secondary ion mass spectroscopy (SIMS) has not been used for tree-ring studies, yet it can add to and complement existing methods. It utilizes solid samples, thus eliminating much wet chemical preparation, and can detect virtually all elements and their isotopes with detection limits in the low parts per million range (and for some elements the parts per billion range). In principle, areas as small as 1  $\mu\text{m}$  on edge can be examined. Finally, for all practical purposes, the technique is nondestructive.

In SIMS, a focused beam of energetic ions is used to bombard a solid sample, causing ions characteristic of the sample surface composition to be ejected. These secondary ions are separated according to their charge to mass ratio using conventional mass spectroscopic methods. Unfortunately, the sample matrix and instrumental variables have a significant effect on secondary ion yields, and as a result, SIMS cannot be used as a reliable quantitative tool without calibration using recognized standards.

Since this work was undertaken as a feasibility study, we have examined only qualitative differences between the

elemental concentrations between individual rings in a single tree.

### Materials and methods

The SIMS used in this study was a Cameca IMS-3f instrument with a 100 nA  $\text{O}^+$  primary ion beam with a net energy of 7.5 keV. The sample holder was maintained at a bias voltage of –400 V to suppress molecular secondary ions. The primary ion beam was rastered over a square area 250  $\mu\text{m}$  on edge, while secondary ions were collected from a central spot 125  $\mu\text{m}$  in diameter to avoid edge effects.

The tree used was a sugar maple (*Acer saccharum* Marsh.) that had been planted in well-drained calcareous soil on the campus of the University of Western Ontario in 1907 and felled in 1990. Sample blocks (1  $\text{cm}^2$ , 0.5 cm thick) were cut to fit the SIMS sample holder. The blocks were polished with 100-mesh diamond grit on a silk wheel, sonicated in triple-distilled water followed by methanol, then maintained overnight at 105°C before gold coating to prevent surface charging during subsequent SIMS analysis.

A preliminary survey of the rings was carried out to establish which elements were present and to determine whether any given year was likely to provide anomalous results. Selected years were then examined at three different sites within the corresponding ring, and the results were averaged.

### Results and discussion

No pollutant metals such as Pb or Cu were found (more likely the pollutants, if present, were below the detection limits of the instrument). This is not surprising since the tree was in rich, well-drained soil in a relatively clean environment. Anomalously high levels of potassium were found in rings corresponding to the nominal<sup>2</sup> years 1931 and 1954. Table 1 compares the results obtained in these years, with an

<sup>2</sup>We have used the term “nominal” for the years 1931 and 1954. These dates were chosen by counting back from the bark to the appropriate dates. However, only a single transverse sample from bark to heartwood was supplied. The term nominal is used in case one or more false rings (due to frost or damage to the tree) have been included.

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TABLE 1. Secondary ions counted per half-second counting interval

Year (ring)	No. of measurements	Average K counts	SD
1920–1960	30	441	274
1954	3	3 079	404
1931	3	18 539	5074

rigorous sample preparation can serve to explain our results, since the potassium signal at each sample site showed little change with depth when the ion beam was allowed to ablate the surface for long periods (10–20 min).

On the basis of these results we conclude that SIMS provides a useful means of examining the elemental distribution of potassium in tree rings. The elevated potassium levels in individual rings merit further study.

#### Acknowledgements

We thank Dr. B. Luckman and Dr. A. Maun of the Departments of Geography and Plant Sciences, respectively, as well as Surface Science Western at the University of Western Ontario for their assistance, without which this interdisciplinary work would not have been possible.

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average value for between 1920 and 1960. Plans are underway to probe rings with SIMS and proton-induced X-ray emission as well as bulk sampling with inductively coupled plasma – mass spectroscopy. These results will be correlated with SIMS data. High mass resolution confirms that these values correspond to potassium rather than to a molecular ion of the same mass such as  $C_3H_3$ . Other elements, including C, H, O, S, P, Ca, were detected with certainty. No significant variations between rings were observed for these species. In other cases the isotope ratios suggested significant contaminations of the secondary ion signal by molecular ions. In these cases the yield was too low for high mass resolution. These species will be examined in future experiments when optimal SIMS conditions have been established. A Student's *t*-test shows the observed differences in potassium ion yields to be at a level of confidence better than 99.9%. Though the high potassium levels correspond to ground disturbance events in the immediate vicinity of the sample tree, no conclusions can be drawn from this single sample. In any event, neither surface contamination nor solubilization of potassium during the