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Application of Laser Ablation ICP-MS for the Analysis of the Relative Distribution of Trace Elements between the Bark Pockets and Annual Rings of a Beech (*Fagus sylvatica* L.) Tree

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Abstract

Laser ablation ICP-MS analysis of bark included within the trunk of a beech (*Fagus sylvatica* L.) tree collected in Derbyshire, UK recorded the local distribution of trace elements between the bark pockets and neighbouring annual rings. V, Co, Ni, Cu, Zn, As, Cd, Sb, Hg and Pb showed sharp peaks in the outer bark of the bark pocket, indicating atmospheric deposition to the bark surface at the time it was exposed to the atmosphere. Coincident peaks in Al, Sc, Ti and Fe indicated deposition of airborne particles. Zn and Hg were also accumulated at the boundary of the inner bark and annual rings, suggesting accumulation in the cambium layer.

Key words: annual rings, bark pockets, beech, dendrochemistry, laser ablation, ICP-MS, trace elements, pollution.

Introduction

Inclusions of bark within the tree trunk, or bark pockets, are well known in the forestry industry as a point of weakness deleterious to the economic value of wood. They may be formed following damage to the trunk, at the joint of two branches, by inclusion of a broken branch or between opposing lobes of irregularly shaped trunks (Satake 2001). Recently, bark pockets included over different time periods have been employed as records of historical change in lead and arsenic pollution (Satake *et al.* 1996, Bellis *et al.* 2002, Bellis *et al.* 2003). Bark accumulates trace metals from the atmosphere through wet and dry deposition (Hammp and Höll 1974), which may be preserved in the bark pocket following inclusion. In contrast, annual rings accumulate trace metals indirectly either from the soil via the roots or following deposition to the bark or leaves (Lepp 1974).

Typically, bark pockets and annual rings are separated for analysis by cutting with a knife or razor, limiting the spatial resolution that may be achieved. The objective of this study was to investigate the application of a laser ablation microprobe coupled to inductively plasma mass spectrometry (ICP-MS) (Hoffmann *et al.* 1994, Idegawa *et al.* 2001), for measuring the relative distribution of trace elements on a local-scale between bark pockets and neighbouring annual rings. Laser ablation microprobes employ a Nd:YAG (Neodymium, Yttrium, Silver) laser to directly ablate solid samples. The resulting aerosol is introduced directly to an elemental analyser such as ICP-MS. The potential advantages include minimal sample preparation, spatial resolution in the μm range and low limits of detection.

Materials and Methods

Trunk sections containing bark pockets were obtained in 1998 from a 150 year-old beech (*Fagus sylvatica* L.) tree located in the Longshaw Estate near Hathersage in the Peak District National Park, Derbyshire, UK. Slices of 1 cm thickness were prepared using band saws, cut in the radial plane (Fig. 1). The series was formed due to the converging directions of growth of either flank of the asymmetrically shaped trunk (Satake 2001). Bark from either flank was preserved, orientated in the radial plane. The bark pockets were dated using the annual rings intersecting the bark pockets. The bark pockets (Fig. 1) consisted of a central region of outer bark, comprising the two compressed surfaces, flanked by inner bark.

The section was cut into cubes containing the bark pockets, no greater than $3 \times 3 \text{ cm}^2$ in area for placement in the laser ablation chamber. Multi-element analysis was performed by a laser ablation microprobe (LSX2000, Cetac Technologies) coupled to ICP-MS (HP4500, Agilent Technologies). A continuously firing (20 Hz) laser beam of 100 μm diameter was employed to scan across the sample at a speed of 40 $\mu\text{m s}^{-1}$. The laser was initiated in the wood tissue and directed to describe a linear track through the bark pocket, orientated tangentially to the radius of the trunk (Fig. 1). Measurement of each element was performed every 2.5 seconds providing a spatial resolution of 100 μm .

Trace element concentrations were estimated from laser response factors ($\mu\text{g g}^{-1} \text{ counts}^{-1}$), calculated as follows. 10 g of the 'present' outer bark was homogenised using a tungsten carbide mill. 4g was prepared into a pressed disc (as commonly employed in x-ray fluorescence spectrometry). Five 0.5 g aliquots

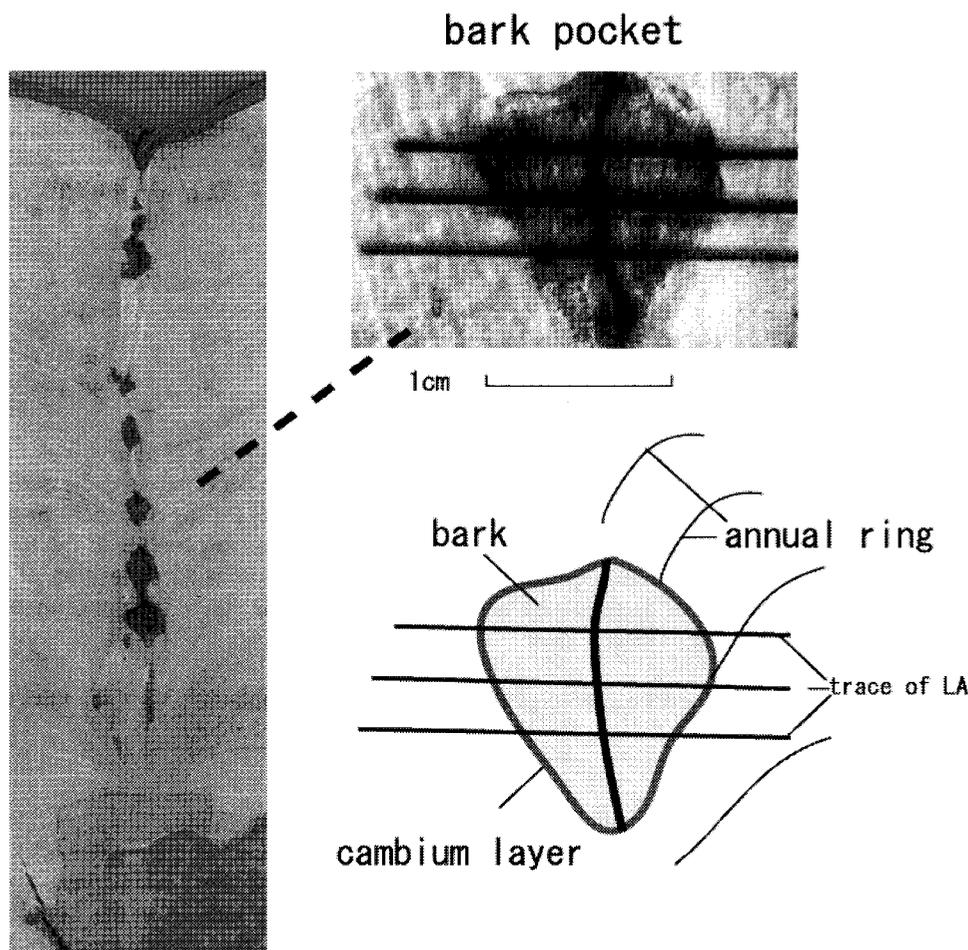


Fig. 1. Trunk section of beech containing bark pockets and laser ablation track across the bark pocket.

were digested by concentrated nitric acid using microwave digestion (Bellis *et al.* 2001), trace element concentrations ($\mu\text{g g}^{-1}$) were measured by ICP-MS. The pressed disc was analysed by laser ablation ICP-MS on the day of analysis for 100 seconds to gain average signal intensities (counts). ^{13}C was employed as an internal standard.

Results and Discussion

The analysis recorded peaks in V, Co, Ni, Cu, Zn, As, Cd, Sb, Hg and Pb (Fig. 2) in the outer bark of the bark pocket, indicating wet and/or dry deposition to the bark surface during the time it was exposed to the atmosphere. Whilst these elements occur naturally in the atmosphere at low concentrations, it is likely that their concentration is elevated by emissions from industrial or other anthropogenic activities. With the exception of Hg, which may be present in the atmosphere as volatile Hg^0 , these elements are typically associated with airborne particles or may be dissolved in precipitation. The sharp nature of the peaks suggests that the elements are relatively immobile within the bark pockets.

Coincident peaks in Al, Sc, Ti and Fe (Fig. 3), which are common constituents of airborne particles and have

limited solubility, indicated that deposition of particles was an important accumulation pathway. In contrast, the concentration of the elements in the inner bark and annual rings was relatively low indicating limited uptake from the soil via roots. Zn and Hg, which are considered to be mobile elements, also showed minor peaks in concentration located at the boundary between the annual rings and inner bark, suggesting past accumulation in the cambium. It is likely that these peaks resulted from accumulation from the soil via the roots.

Na, Mg, K, Rb and P (Fig. 4) showed accumulation in the outer bark and cambium layer. In the case of Na, Mg, and K, there was a relatively small difference in concentration between the bark pocket and annual rings, suggesting a relatively high level of accumulation from the soil via the roots. Ca, Sr and Mn showed similar distributions, being higher in the inner bark than annual rings with a double peak in the outer bark. The distribution suggests that these elements, which form +2 ions, are a structural component of bark rather than a surface deposit.

The data is consistent with previous studies of current bark that recorded elevated trace element concentrations in outer bark compared to inner bark

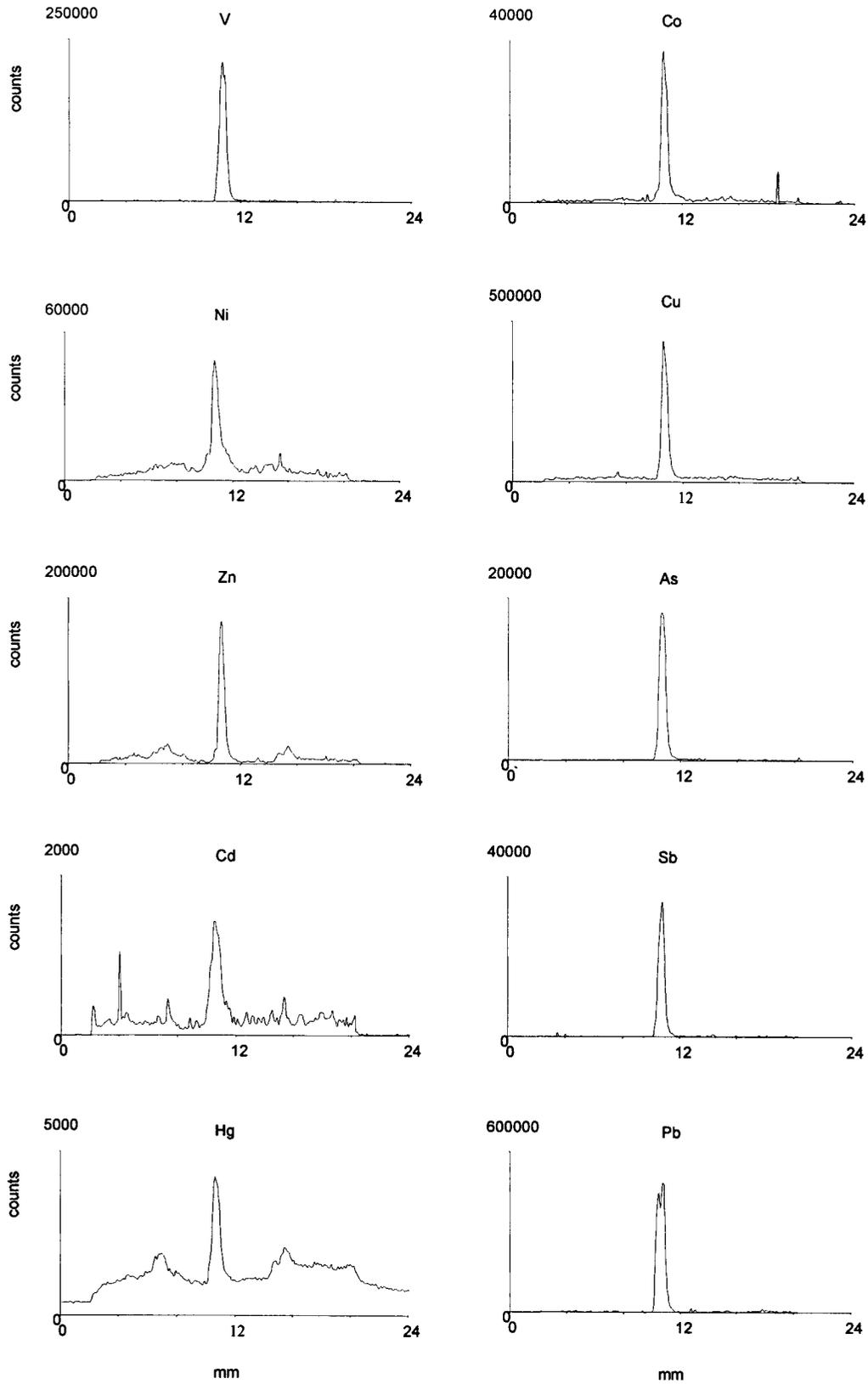


Fig. 2. Relative distribution of trace elements recorded in a bark pocket formed c.1940.

(Hampp and Höll 1974, Schulz *et al.* 1999) and accumulation of Zn in the cambium (Satake *et al.* 1993). It confirms that the concentration of trace elements in bark is higher than in annual rings and that the accumulated elements are 'preserved' following the formation of the bark pocket. Table 1 shows the mean concentration of the trace elements recorded in the bark pockets dating from 1900 to 1998. Trace element concentrations were relatively high, due to the accumulation of the element at the bark surface. There

was substantial variation between successive measurements of bark pockets of the same age and no apparent historic trend to the data. The variation most likely resulted from the small area of bark ablated and the heterogeneous distribution of trace elements on the bark surface. Whilst laser ablation ICP-MS was effective for measuring the spatial distribution of elements it proved unsuitable for measuring trends in concentration.

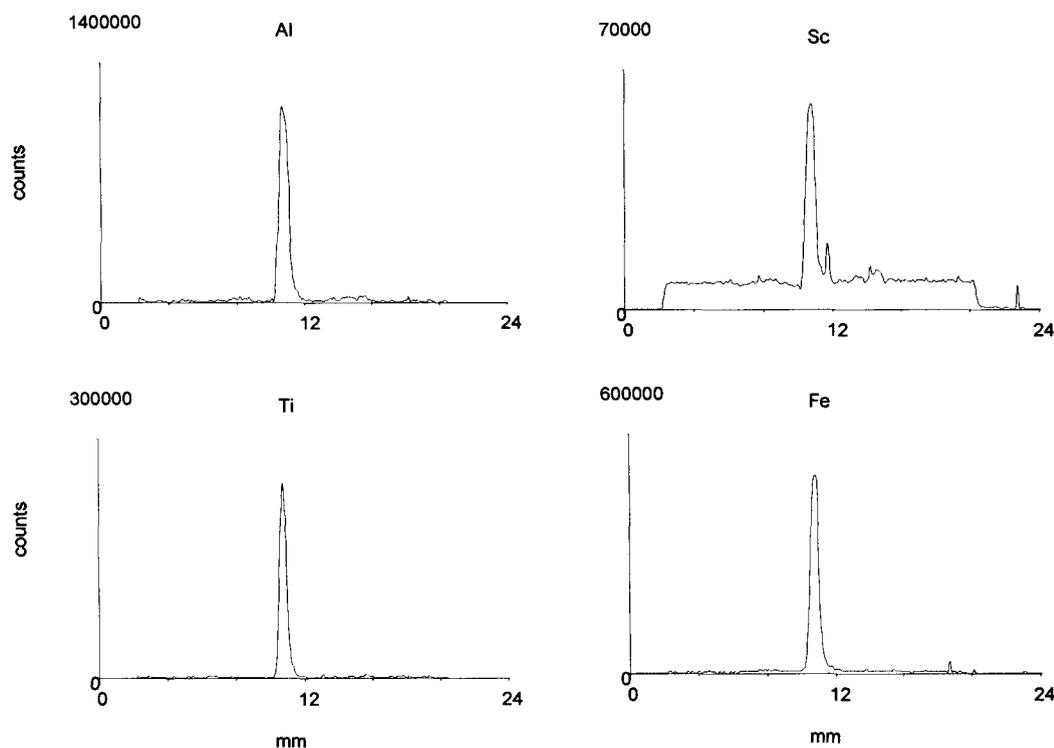


Fig. 3. Relative distribution of Al, Sc, Ti and Fe recorded in a bark pocket formed c.1940

Table 1. Mean trace element concentrations ($\mu\text{g g}^{-1}$) in the bark pockets (1900 to 1998) (nd = not determined in calibration).

| | mean $\mu\text{g g}^{-1}$ | s | | mean $\mu\text{g g}^{-1}$ | s | | mean $\mu\text{g g}^{-1}$ | s |
|----|---------------------------|-----|----|---------------------------|-----|----|---------------------------|------|
| V | 45 | 39 | As | 34 | 28 | Al | 4000 | 2200 |
| Co | 20 | 12 | Cd | 1.3 | 0.7 | Sc | 1.6 | 0.8 |
| Ni | 83 | 41 | Sb | 8.1 | 7.0 | Ti | 110 | 93 |
| Cu | 250 | 120 | Hg | nd | nd | Fe | 17000 | 9200 |
| Zn | 350 | 270 | Pb | 1100 | 780 | | | |

s = standard deviation

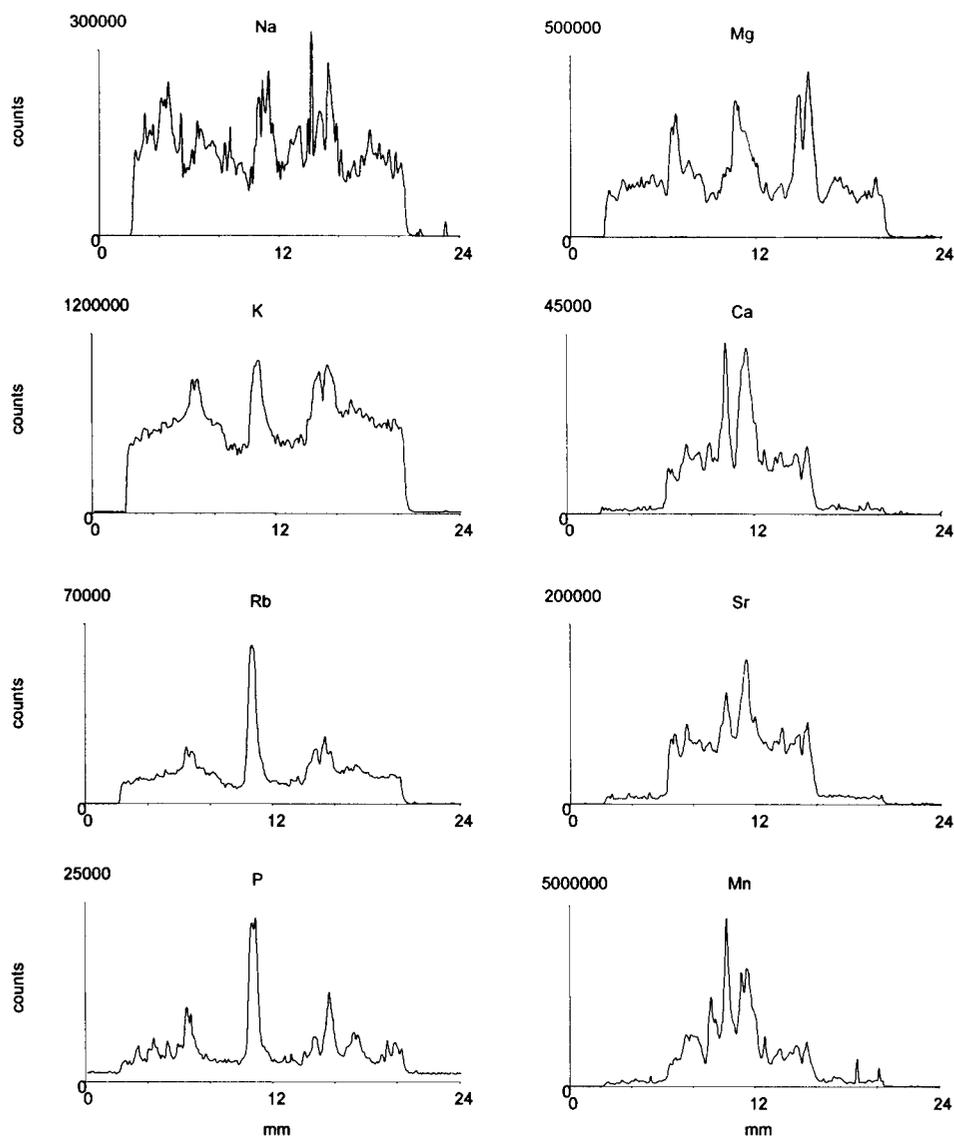


Fig. 4. Relative distribution of Na, Mg, K, Ca, Rb, Sr, P and Mn recorded in a bark pocket formed c.1940.

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