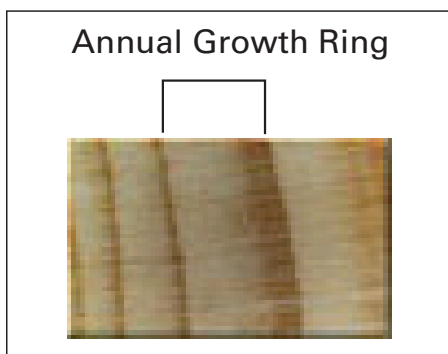


Innovative Research Methods for Environmental Studies

Laser Ablation ICP-Mass Spectrometry— A New Tool for Analyzing Metals in Tree Rings

The USGS laser-ablation inductively coupled plasma-mass spectrometer (LA-ICP-MS) is being used as a tool to analyze mining-related activities that impact element levels in mine drainage. Historical metal-release events potentially may be determined by using tree rings as the sample medium (each ring representing a fixed point in time) and the LA-ICP-MS as the analytical tool. This approach has been used successfully by the USGS at the abandoned Waldorf Mine, Colorado, (Witte and others¹). Tree cores from ponderosa pine and gray pine (*Pinus ponderosa* and *P. sabiniana*, respectively) also are being collected at selected abandoned mining sites in California and analyzed for the total concentration of the stable isotopes of Cd, Cu, Cr, Fe, Mg, Mn, Pb, Sr, and Zn. The purpose of the studies is to assess the utility of tree ring xylem (wood) analyses for measuring mining-related episodic events



Thin section view of a ponderosa pine stem cross section showing the annual rings. Growth from “left to right” in the photo and the initial cells (earlywood) are large and light in color; the darker area (latewood) is made up of smaller, denser cells. (Photo © H.D. Grissino-Mayer)

¹ Witte, K.M., Wanty, R.B., and Ridley, W.I., Engelmann spruce (*Picea engelmannii*) as a biological monitor of changes in soil metal loadings related to past mining activity: Applied Geochemistry (in press).

such as temporal changes in ground- and surface-water element loadings. The premise is that elements available for absorption by trees are “fixed” in the xylem tissue (tree ring) produced in that particular year. Theoretically, therefore, it should be possible to “date” changes in the uptake of elements. The LA-ICP-MS is a particularly powerful tool in this regard because it is capable of analyzing for a variety of elements over very small (100 μm , 1×10^{-4} m, or less) areas within the tree ring. This capability is unlike older analytical methods that consume large volumes of sample material and that usually require compositing the tissue from numerous rings. Preliminary results indicate that LA-ICP-MS provides a repeatable, minimally destructive, sensitive method for determining many elements in wood tissue, with relatively high spatial resolution.

Field and Laboratory Procedures

Cores were extracted from opposite sides of the tree, 30 cm above ground level, and were stored in rigid paper “soda” straws until dry. Following



Cores were extracted from ponderosa pine using an increment borer (inset). Usually more than one core was extracted from each tree in order to measure the chemical variability between cores within a tree.

age-dating, one surface of the core was sanded flat, sectioned, and mounted for insertion into the LA-ICP-MS instrument. Analysis of the core followed the method described in the cartoon (next page). The laser is set so that seven analyses (spots), each 100 μm in diameter, are made equidistant from each other across an annual ring—the broader the ring, the further apart the spots. The seven spots integrate any differences in the ring that may be the result of earlywood versus latewood—an issue found to



Increment core extracted from a ponderosa pine, Nevada County, California. The core is a sample of the annual growth rings—in this case encompassing about 60 years.

be important in some of our earlier studies. Integration yields one average value for the seven spots. Analysis then is made of the variability in the element concentrations among analyses within a ring, among rings within a core, and between cores taken within a tree.

Data reduction

Intensity (counts per second) is converted to concentrations by using a commercially available package, GeoPro™ (CETAC Technologies, Omaha, Nebr.). The area of the peak of interest is selected, and the blank for that peak is subtracted. Based on the analysis of a standard (usually run 3–5 times before and after each block of analyses), a calibration curve is constructed and the intensity of the sample is converted to concentration. This concentration then is normalized against a known element in the sample, in this case C. The robustness of the analysis relies on the degree of confidence and the homogeneity of the standard.

Accuracy, Precision, and Detection Limits

Evaluation of the absolute accuracy and precision of the LA-ICP-MS technique relies on carefully characterized standards. In the case of whole-sample techniques, the standards need to be homogeneous at a scale finer than the resolution of the analyses. For quantitative measurements, ^{13}C is used as an internal standard (pressed pellets of purified cellulose doped with major and trace elements are used for calibration), and National Institute of Standards and

Technology standard reference materials were used as secondary standards.

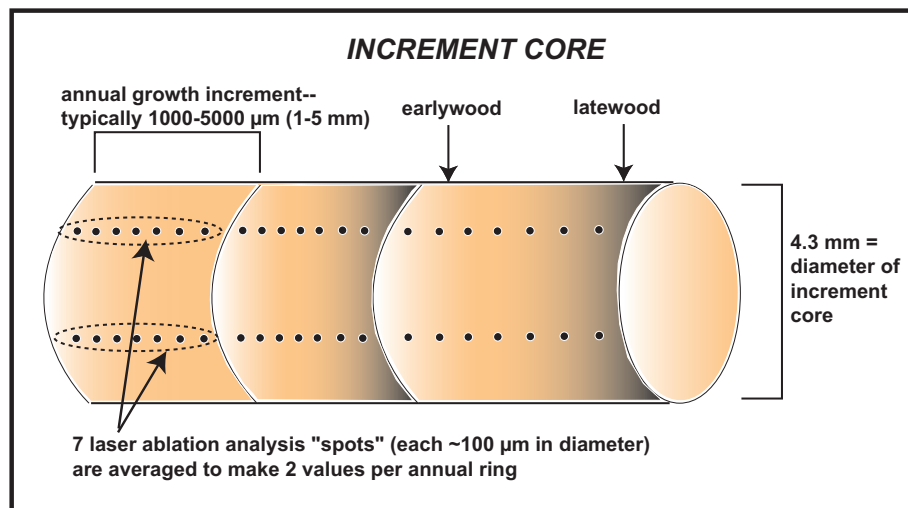
Example of Results

With this new laser ablation technique it now is possible to determine the variability in the analytical data within and between cores (and within and between trees). This type of information is critical to know before conclusions can be made regarding the use of the data to date element contamination episodes. For example, if duplicate analyses within a tree ring indicate excessively large differences in results within a given year (see the error bars for the analyses of Cd in gray pine on last page), possible differences between years (rings) cannot be assessed.

In contrast, the variability in the data for Cr in gray pine for a particular year is very small, which makes possible the interpretation of trends between years. The example of Cd in gray pine also is good for demonstrating how different the chemistry of two cores can be that are taken from the same tree. The data for Cd in gray pine could never be used to assess element uptake trends over time; there is simply too much variability in the data within and between rings and cores.

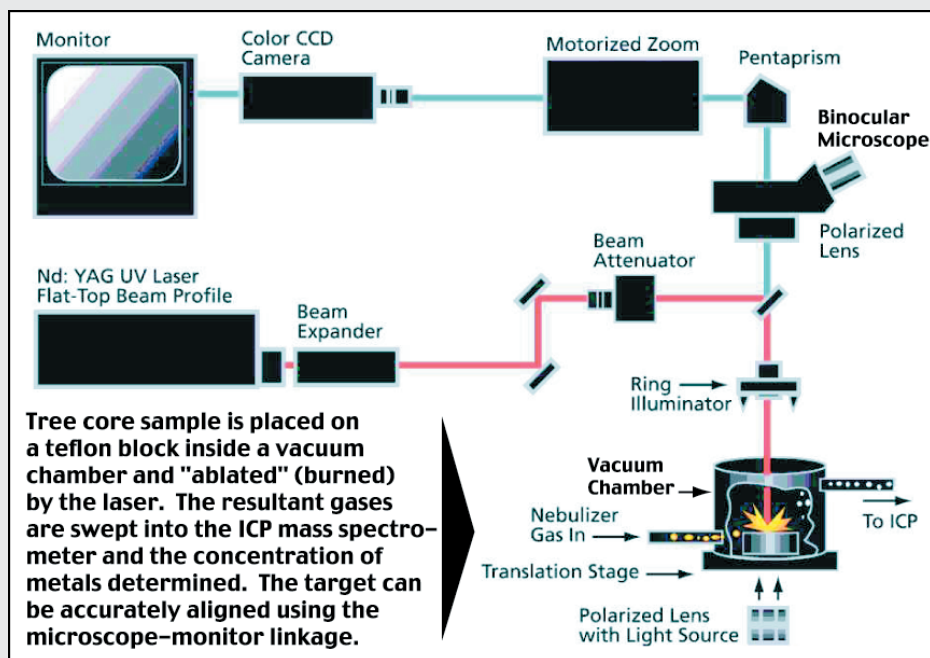
In contrast, a number of different conclusions can be drawn from the plots for the element concentrations in ponderosa pine. First, except for perhaps Cr, the concentrations are much less than those in the gray pine (the left-hand vertical scales in the figures above are the same for both trees). (One reason for this is probably because the gray pine had its roots in mine tailings [shown last page] that were rich in available elements, whereas the ponderosa pine did not.) The variability shown between analyses within a ponderosa pine ring is small (small error bars), making comparisons between rings possible; the comparison of the data between cores also is quite good (the r^2 values are significant for all tree elements shown). For this tree species at this site it should be possible to assess yearly trends in element uptake.

A further complication is the possibility that metals may migrate between individual rings and thus are not “fixed” within the tissue of a specific ring. This condition would complicate the interpre-



This cartoon of a tree ring core shows the relative size and position of the laser-ablation analysis spots or craters. Each spot is an individual multielement analysis. The coupling of a laser with a mass spectrometer is a powerful tool and in this case enables precise within-ring and between-ring element-concentration data analysis.

The LA-ICP-MS Technique



USGS Laser ICP-MS Specifications:

MASS SPECTROMETER: Perkin Elmer 6000 ICP-MS

Laser System (and settings used in this study)—CETAC LSX 200+

Frequency quadrupled Q-switched Nd:YAG laser, 266 nm

Real-time imaging in transmitted and reflected light

Flow-controlled Ar+He carrier gas

Variable laser pulse repetition rate (pulse rate used: 20 Hz)

Adjustable spot size (spot size used: 100 μm)

Computer controlled ablation methods of spots, lines, scanning areas, and raster of spots (single-line raster used)

Each analysis represents the integration of data from seven 100 μm -diameter "spots" (craters) equally spaced across the ring (laser pulse rate: 20 pulses/sec.)

Element isotopes measured: ^{13}C , ^{111}Cd , ^{65}Cu , ^{52}Cr , ^{57}Fe , ^{24}Mg , ^{55}Mn , ^{208}Pb , ^{88}Sr , and ^{66}Zn .

tation of differences between tree rings tremendously. For example, some plants are known to physiologically transport excess metals (or potentially toxic metals) from the roots to leaves and are not "fixed" in the woody tissue. With the shedding of leaves during fall leaf-drop, the metals also are shed, thus protecting the plant from a buildup of potentially harmful metals (elements).

Conclusions

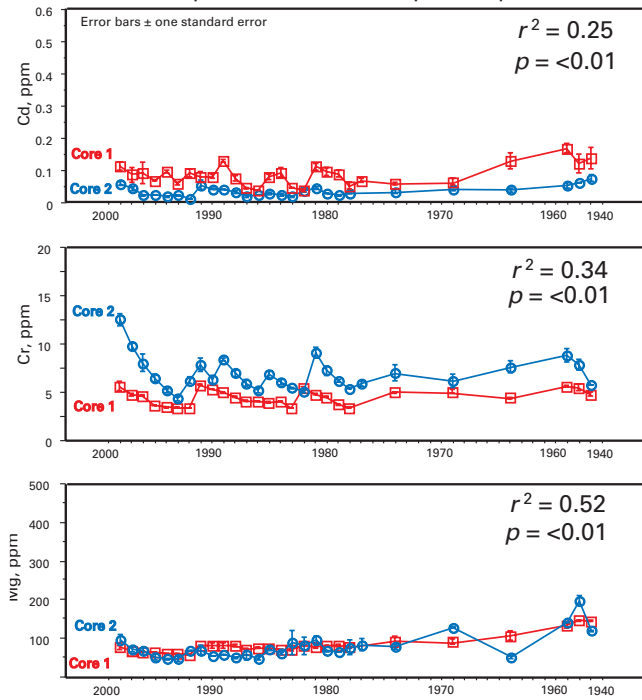
• LA-ICP-MS provides a highly sensitive, precise, and quantitative whole-tissue method of tree-ring analysis and allows for:

- Within-ring, multiple-spot integration

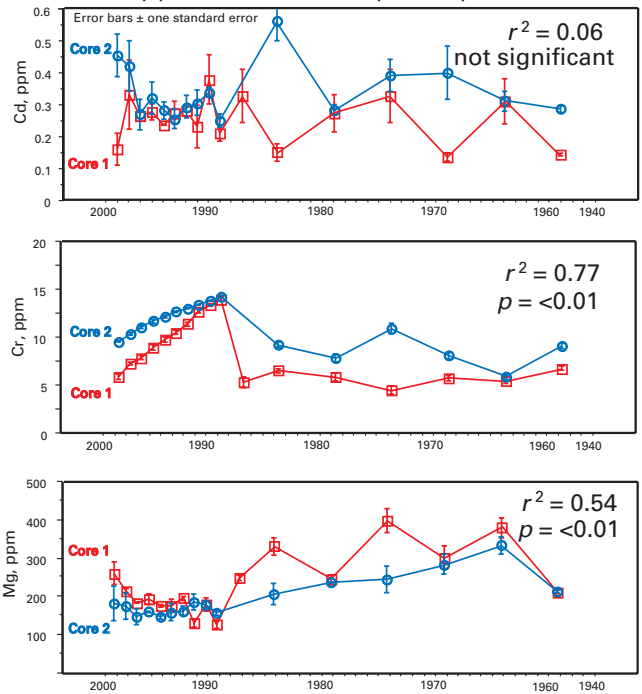
- Reuse of sample material (the method is minimally destructive of the sample)
- Nearly simultaneous multielement analysis
- Element uptake can be very different between tree species.
- Within-ring variability appears low, which means that the integration of analysis "spots" (i.e., progressing as a traverse between earlywood and latewood) is sufficient for this study.
- The variability in element concentration between analyses within a core is different for different elements but in general is low. This low variability allows for the comparison of element levels between years within a core.

- Within-tree, between-core element-concentration variability is low; however, this trend needs to be carefully examined before conclusions regarding element level trends over time can be adequately interpreted.
- Trees growing in, or adjacent to, mine tailings generally have higher levels of elements in their ring tissue compared to trees growing in nonimpacted (native soil) sites.
- Work is needed on the possible migration of elements between tree rings in these tree species.

Ponderosa pine (number of comparison points = 27)



Gray pine (number of comparison points = 16)



These figures show the change in the concentration (in parts per million, ppm) of cadmium, chromium, and magnesium over about 50 years in two species of pine found in California. The plots are used to assess the variability between duplicate analyses within a core and between duplicate cores taken from a single tree. The latter are collected at the same height above ground but from different sides of the tree trunk. The degree of similarity (correlation) between the cores is given by the r^2 value. The larger the number (as it approaches 1) the better the correlation. The p value simply indicates whether the correlation is significant in a statistical sense. Any number less than 0.05 (a 1 in 20 chance that this could happen randomly) is considered significant.



Transported tailings material is fine- to coarse-sand in texture, composed of quartz, limonite, carbonate, chlorite, and sulfides (mostly pyrite and arsenopyrite), and is rich in available metals.

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