Neutron Activation Analysis of Absolutely-Dated Tree Rings

D. K. Schwarz,[1,2] N. O. Centiner,[1,2] D. Sahin,[1,2] T. H. Daubenspeck,[1] K. Ünlü,[1,2]

Service Provided: Penn State Breazeale Reactor, Neutron Activation Analysis, Radionuclear Applications Laboratory

Sponsors: National Science Foundation, Department of Energy Nuclear Engineering Education Research grant, Cornell University's Malcolm and Carolyn Wiener Laboratory for Aegean and Near-Eastern Dendrochronology, and the Pennsylvania State University Radiation Science and Engineering Center

Introduction

Neutron Activation Analysis (NAA) is the preferred analysis method for studying the composition of tree-rings. It was hypothesized when the project began that gold would be well suited as an environmental marker in tree-rings. Much of the work since then has focused on irradiations suited to identify ^{198}Au, which has a 2.7-day half-life. Following this goal, four tree samples each over 300 years in length have been analyzed at the Radiation Science and Engineering Center during recent years. Each tree sample was cut into individual rings and was irradiated in batches of 40 for 4 MW hours. This procedure allowed for the identification of ^{24}Na, ^{42}K, ^{56}Mn, ^{69}Zn, ^{82}Br, ^{140}La, and ^{198}Au.

Next, four short-lived tree samples (30-60 years in length) were analyzed for a period corresponding to the availability of dust aerosol index data from the Total Ozone Mapping Spectrometer (TOMS) database. Tree-rings were irradiated in batches of 20-30 rings and each ring was counted for two hours instead of one. This decreased the Au and La detection limits so that they could be more reliably identified. In addition, the rings in each batch of samples were counted for 15 minutes each prior to beginning the 2-hour counts to allow for the identification of Mn in every sample.

Later, the tree-rings from two tree samples was recounted for one day each. This additional procedure resulted in the identification of ^{46}Sc, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{110m}Ag, ^{124}Sb, and ^{134}Cs (Table 1 identifies typical isotopic concentrations found in tree rings). The Ag and Au concentrations in tree number C-TU-CAT32 were correlated with each other and appeared to be correlated with the TOMS aerosol index over the forest in Turkey where the tree grew (Figure 1). Ag and Au are the only elements that had the sharp peaks above the level of their continua. It was hypothesized that the unique noble metal characteristics of these elements made them suitable for documenting events in the life of the tree. In particular, the Ag and Au compositions may have been documenting the severity and frequency of Mediterranean dust storms.

Experimental

Ag has a short-lived isotope (^{108}Ag), which might be identified with short irradiations of tree rings. Work was performed to determine if environmentally significant data, especially the concentration of Ag in tree rings, could be determined in a more efficient manner through short irradiations. The Pneumatic Transfer System (PTS) allows samples to be sent from the NAA laboratory directly into the reactor core through a pneumatic tube and with a transfer time of about 5 seconds.

A sample of *Pinus brutia* identified as C-CY-RVA5 from Cyprus was analyzed using one-minute irradiations in the PTS. The empty vials were first labeled with a permanent marker and weighed. Individual tree-rings were then cut from the sample using a stainless steel knife chisel cleaned with alcohol and placed in the vials, which were then heat-sealed and re-weighed. Shortly before each run, sample vials were loaded into the PTS tubes for irradiation in groups of 25-35 at a time. With each batch of samples, one blank vial and the same sample of a NIST standard reference material, SRM-1568, Rice Flour, were irradiated.

Results and Discussion

For the Rice Flour standard that was analyzed with each batch, the percent differences at one standard deviation ranged between 16-26% for most elements. Preliminary results from a recent control study indicate that much of the variability is due to the position-sensitive flux profile within the rabbit capsule and shifting of the flux profile in day-to-day operations. Further work is being carried out to eliminate the errors as much as possible.

Irradiation in the PTS allowed for the analysis of 14 isotopes including ^{19}O, ^{24}Na, ^{27}Mg, ^{28}Al, ^{37}S, ^{38}Cl, ^{42}K, ^{49}Ca, ^{52}V, ^{56}Mn, ^{64}Cu, ^{108}Ag, ^{128}I and ^{41}Ar. A comparison of the time requirement and data obtained for each irradiation scheme is provided in Table 2. The concentration of each isotope in the wood was calculated using Instrumental NAA and assumed a

[1] Radiation Science and Engineering Center, The Pennsylvania State University, University Park, PA 16802
[2] Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802

TABLE 1: Typical isotopic concentrations in tree rings

Element	Concentration	Element	Concentration	Element	Concentration	Element	Concentration
^{17}O	600 ppm	^{41}K	10 ppm	^{59}Co	1 ppb	^{109}Ag	10 ppb
^{23}Na	10 ppm	^{45}Sc	1 ppm	^{64}Zn	1 ppb	^{123}Sb	1 ppm
^{26}Mg	10 ppm	^{48}Ca	1 ppm	^{65}Cu	0.01 ppm	^{127}I	0.1 ppm
^{27}Al	1 ppm	^{51}V	1 ppb	^{68}Zn	1 ppm	^{133}Cs	1 ppm
^{36}S	10 ppb	^{55}Mn	10 ppm	^{81}Br	0.1 ppm	^{139}La	10 ppb
^{37}Cl	10 ppm	^{58}Fe	10 ppm	^{107}Ag	10 ppm	^{198}Au	1 ppb

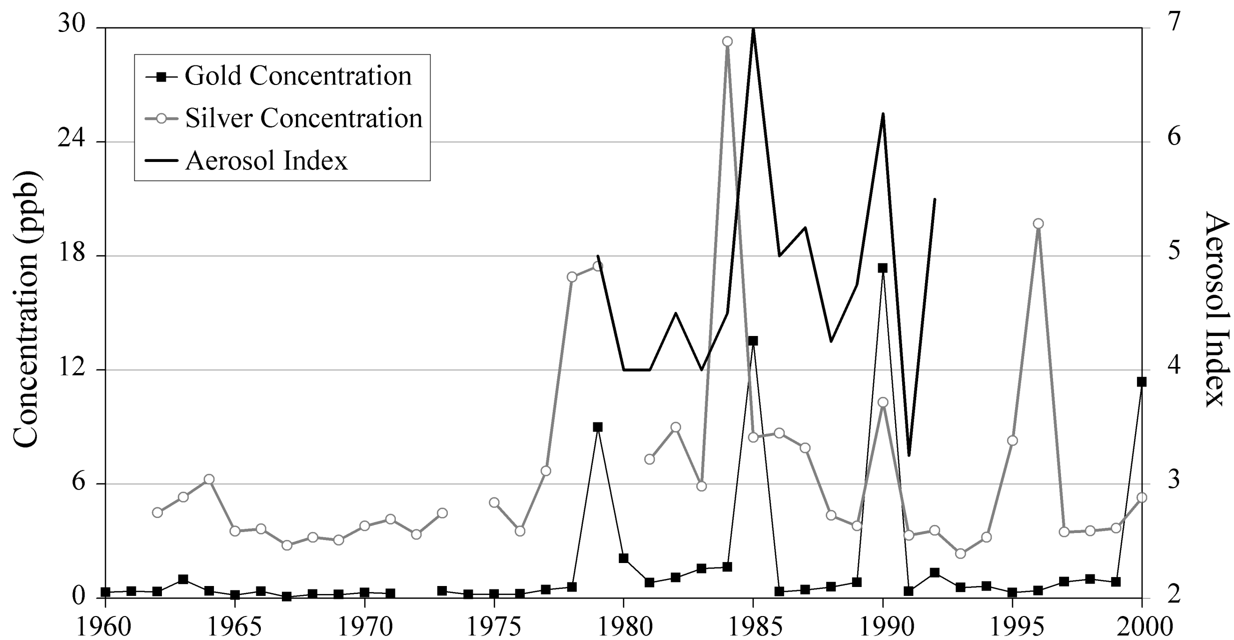

FIGURE 1: Silver and gold concentrations in tree number C-TU-CAT32, as compared to the TOMS aerosol index for the tree's region of origin

TABLE 2: Three different tree ring irradiation procedures used at the RSEC

	Short Irradiations in the PTS	Long Irradiations (short count time)	Long Irradiations (long count time)
Irradiation time	1 min	4 hours	4 hours
Count time	4 min	2 hours	1 day
Reactor time/sample	6 min	8 min	8 min
Samples / week	90	60	7
Elements Identified	O, Na, Mg, Al, S, Cl, K, Ca, V, Mn, Cu, Ag, I	Na, K, Mn, Br, Zn, La, Au	Sc, Fe, Co, Zn, Ag, Sb, Cs

constant efficiency calibration performed for the bottom of the sample vial. A large fraction of the ^{41}Ar activity is created from the air in the empty portion of each irradiated vial. Similar concentrations of ^{41}Ar calculated for the blank vials and sample vials indicate the concentration of Ar in wood is similar to the concentration in air.

Ag was identified in tree sample C-CY-RVA5 although there are many missing values due to decreasing concentration towards the center of the tree. Figure 2 shows the silver concentrations from tree samples C-TU-CAT32 and C-CY-RVA5 plotted together. It was hypothesized that Ag and Au maintain large peaks in single rings because they become soluble only under special chemical conditions and once deposited in the tree may be relatively immobile. A correlation of Ag concentration among different trees would support the hypothesis that Ag is an appropriate monitor of environmental conditions. Figure 2 loosely shows an apparent correlation between the Ag concentrations of one tree in Cyprus and one tree in Turkey.

Conclusions

Different irradiation schemes have been used to analyze tree-rings at the Radiation Science and Engineering Center at the Pennsylvania State University. A total of 24 different isotopes have been identified in 8 different tree samples. Serial use of each irradiation scheme would allow for all 24 isotopes to be identified in a single tree sample.

It is recommended that analysis of any tree sample start by using the PTS. Radio-chemical changes may be taking place during the long irradiations. For instance, ^{28}Al goes through more than 100 half-lives during a 4 hour irradiation. Any further analysis of the tree sample may then be guided by the location of peaks in ^{109}Ag concentration. One major advantage of the short irradiations is the reduced radioactivity induced in the samples, which were suitable for non-controlled storage within a few weeks. This also makes it simpler to prepare the samples for re-analysis using longer irradiations.

Publications

D. K. H. Schwarz, K. Ünlü, "Dendrochemistry of Pinus Sylvestris Trees from a Turkish Forest," in *Tree Rings, Kings & Old World Archaeology and Environment*, S. W. Manning, Ed., In Press.

D. K. H. Schwarz, K. Ünlü "Typical Elemental Concentrations in Tree-Rings and Appropriate Irradiation Parameters for Determination with NAA" The 12th International Conference on Modern Trends in Activation Analysis (MTAA-12), Hachioji, Japan, September 16-21, 2007.

D. K. H. Schwarz, K. Ünlü, "Silver and Gold: Possible evidence of Dust Storms in Tree-rings" Transactions of the American Nuclear Society.

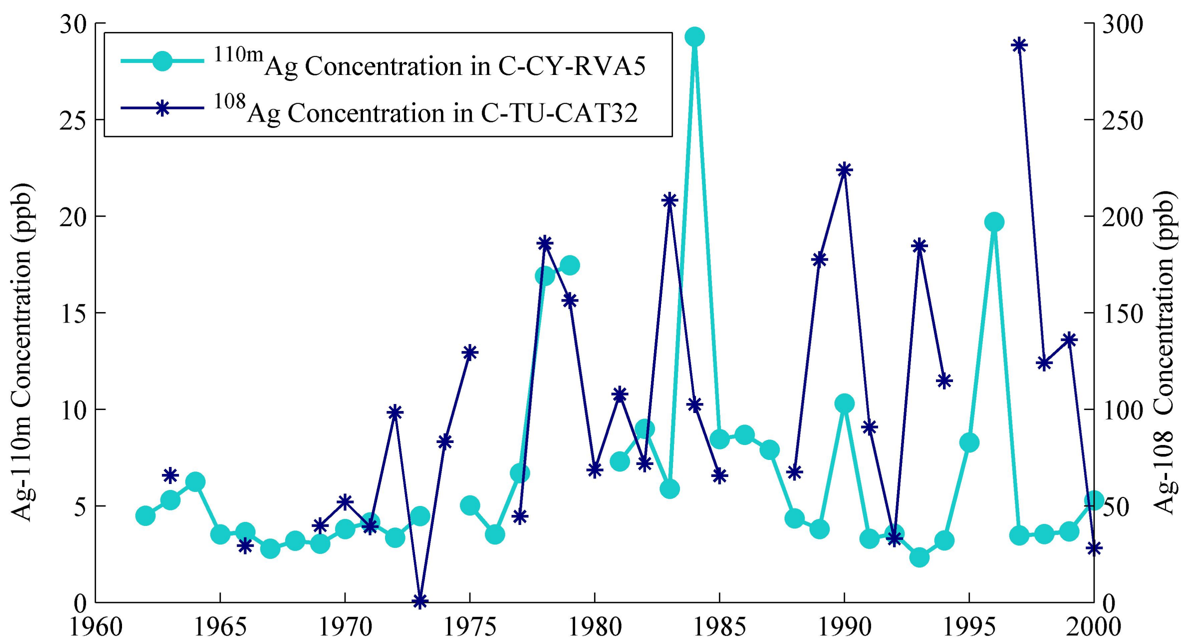

FIGURE 2: Ag concentration in tree samples C-CY-RVA5 and C-TU-CAT32