Radiation Science and Engineering Center (RSEC)

Final Report

for

DE-FG07-05ID14702

Ion Uptake Determination of Dendrochronologically-Dated Trees Using Neutron Activation Analysis

**K. Ünlü^{1*} (PI), P. I. Kuniholm² ,
D. K. H. Schwarz¹, N. Ö. Cetiner¹, J. J. Chiment³**

¹Radiation Science and Engineering Center, The Pennsylvania State University, University Park, PA 16802

²The Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology, Cornell University, Ithaca, NY 14853

³ Cornell Institute for Biology Teachers, Cornell University, Ithaca, NY 14853

Ion Uptake Determination of Dendrochronologically-Dated Trees Using Neutron Activation Analysis

K. Ünlü^{1*}(PI), P. I. Kuniholm², D. K. H. Schwarz¹, N. Ö. Cetiner¹, J. J. Chiment³

¹Radiation Science and Engineering Center, The Pennsylvania State University, University Park, PA 16802

²The Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology, Cornell University, Ithaca, NY 14853

³Cornell Institute for Biology Teachers, Cornell University, Ithaca, NY 14853

Abstract

Uptake of metal ions by plant roots is a function of the type and concentration of metal in the soil, the nutrient biochemistry of the plant, and the immediate environment of the root. Uptake of gold (Au) is known to be sensitive to soil pH for many species. Soil acidification due to acid precipitation following volcanic eruptions can dramatically increase Au uptake by trees. Identification of high Au content in tree rings in dendrochronologically-dated, overlapping sequences of trees allows the identification of temporally-conscripted, volcanically-influenced periods of environmental change. Ion uptake, specifically determination of trace amounts of gold, was performed for dendrochronologically-dated tree samples utilizing Neutron Activation Analysis (NAA) technique. The concentration of gold was correlated with known environmental changes, e.g. volcanic activities, during historic periods. Several thousand wood samples were scanned initially for gold. After this initial measurement, samples containing elevated levels of gold were analyzed again for short and long half-life elements, e.g. silver, copper, etc., to investigate other elemental signatures of environmental change using a Compton suppressed NAA system. The samples are activated at 1 MW Breazeale Nuclear Reactor and are counted at newly established NAA laboratory at Penn State. The Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University has archived over 40,000 individually-dated wood samples with 4.5 million rings. These samples span the period from 7000 BC to the present. Most of the dendrochronologically-dated samples present at the Wiener Laboratory were available for this project. Using samples already collected and dated and the NAA technique we planned to define periods of global environmental stress during the past six thousand years and deduce environmental and climatic history from the measured data. This will provide modelers with a much-needed extended timeline. This project was the first coordinated dendrochemical study of a period longer than one hundred years and the first study in the archaeologically important eastern Mediterranean.

Four graduate students worked on this project. One already completed her Master of Science degree and passed the candidacy and comprehensive exam and completed her PhD thesis on May 2008. The other student is completed her Master of Science degree and graduated May 2008. Two other graduate students are currently working on this project. One already completed his Master of Science degree the other one expected to complete her Master of Science degree during Fall 2009. Several manuscripts are published and/or submitted for publication in refereed journals and conference proceedings. A no cost extension was granted for this proposal until December 2008. This report is a compilation of tree progress reports submitted for each project year. Results and Discussions related to each year of activities are given in the text and conclusions as well as MSc and PhD programs related to this project is listed. A full listing of publications related to this project is also given at the end of this report.

Progress Report

(July 01, 2007 – June 30, 2008)

Abstract

Dendrochemistry, or the study of tree-ring composition, is a promising new technique for reconstructing climate history with annual resolution. In particular, dendrochemistry may be useful for identifying periods of volcanic activity. Increased environmental acidity caused by sulfur released from volcanoes can cause greater availability of metals in the soil solution and increased uptake by trees. Neutron Activation Analysis is one of the preferred analysis methods for studying the composition of tree-rings. However, easily activated constituents such as Mn and Al may make it difficult to identify trace elements in the tree-rings with relatively small cross-sections for neutron capture. Dendrochemistry work already performed at the Radiation Science and Engineering Center at the Pennsylvania State University in conjunction with the Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University will be reviewed. The results obtained during this reporting period using a variety of irradiation schedules will be discussed with an emphasis on the applicability of the identified isotopes to environmental monitoring. Focus will be placed on elements such as Ag, Au and some rare earth element which currently appear to be promising indicators of environmental events. Recommended procedures for using NAA to determine the composition of tree-rings will be outlined. This discussion will also include the advantages and disadvantages of each irradiation schedule and the necessary steps in the experimental work itself. The advantages of using a Compton Suppression System (CSS) will be discussed for each irradiation scenario and some examples of the features of CSS are demonstrated.

Introduction

The suitability of Neutron Activation Analysis (NAA) for dendrochemical analysis depends not only on the accuracy of the results but also on the efficient quantification of isotopes or elements that are good recorders of environmental events in tree-rings. Although no unique volcanic signal has been identified in tree-rings, certain isotopes or elements have been deemed promising by some researchers as environmental markers. For instance, Pearson et al. (2006) found a correlation between an increase in Mn concentration and the eruption of Tambora in 1815. There has also been an indication that Au may be environmentally significant.

The results obtained during this reporting period using a variety of irradiation schedules will be discussed with an emphasis on the applicability of the identified isotopes to environmental

monitoring. This discussion will also include the advantages and disadvantages of each irradiation schedule and the necessary steps in the experimental work itself.

Tree-ring analysis with NAA: Irradiation Schemes, Results and Discussions

Three major irradiation and counting schemes have been employed for analyzing tree-rings with NAA. Each scheme is designed for identifying isotopes with a different range of half-lives. Certain isotopes or elements are observed in order to identify promising environmental markers. The results obtained using a variety of irradiation schedules will be discussed with an emphasis on the applicability of the identified isotopes to environmental monitoring. This discussion will also include the advantages and disadvantages of each irradiation schedule and the necessary steps in the experimental work itself. Irradiation schemes utilizing the Dry Irradiation Tubes (DIT) will be described first followed by short irradiations with the Pneumatic Transfer System (PTS). A summary of results obtained from each irradiation schemes will briefly be discussed.

Irradiation in the Dry Irradiation Tubes

Much of the work completed for the dendrochemistry project has focused on quantifying gold in tree-rings with irradiations suited to identify the ^{198}Au isotope which has a 2.7 day half-life. Following this goal, four sets of tree-ring samples each over 300 years in length have been analyzed for the dendrochemistry project according to the following method. Tree samples were cut into individual rings (after having been dated to the year by conventional dendrochronological methods) and were irradiated in batches of 40 tree-rings for 4 Megawatt hours in the Breazeale Nuclear Reactor (BNR) core. The thermal and epithermal fluxes in the BNR core are approximately $1.7 \times 10^{13} \text{ n/cm}^2/\text{s}$ and $6 \times 10^{11} \text{ n/cm}^2/\text{s}$, respectively. Each batch was allowed to decay overnight and then each tree-ring was counted for one hour. This procedure allowed for the identification of ^{24}Na , ^{42}K , ^{56}Mn , ^{82}Br , ^{69}Zn , ^{140}La , and ^{198}Au . In one tree La was not detected consistently because it was present at or below the detection limits and Au was near the detection limits in all trees. Mn was detected but has a short enough half-life (2.6 hrs) that it had decayed away before the counting of each batch of samples was completed. All other elements (Na, K, Br and Zn) were quantified well above the detection limits. The tree-ring samples analyzed in this way and the average concentration results are provided in Table 1.

The concentration values are in parts-per-million except where specified otherwise. The values in parenthesis are the number of rings that had been identified for each element and were used as part of the calculation of the average.

Gold behaved in a unique manner compared to the other elements listed in Table 1. Au showed no anomaly at the heartwood boundary (HWB) and has large peaks in single tree-rings. In most cases the other identified elements had either peaks or increases in the continuum level at the HWB. Au concentrations observed are shown in Fig. 1 for four different samples analyzed.

Table 1. Average Isotopic Concentration in four Conifer Samples Irradiated in the DITs.

Tree Sample	C-GR-PPG4A	C-TU-KLK10B	C-TU-CAT14C	P-SW-SEQ2*
Years Analyzed	1411-1979	1628-1999	1500-1979	1446-1948
Country	Greece	Turkey	Turkey	USA (CA)
Au**	8 ppb (467)	7 ppb (314)	4 ppb (445)	8 ppb (360)
Br	.08 (470)	.07 (355)	.06 (459)	.4 (368)
K	10 (548)	22 (369)	18 (459)	37 (370)
La	.003 (42)	.006 (203)	.02 (428)	.2 (369)
Mn***	7.4 (47)	11 (67)	21 (237)	14 (200)
Na	69 (557)	60 (369)	37 (459)	86 (374)
Zn	.67 (197)	1.6 (331)	1.5 (456)	1 (307)

* PPG4A is *Pinus leukodermis* from Grevena, Greece; KLK10B is *Pinus nigra* from Kalkım, Çanakkale, Turkey; CAT14C is *Pinus nigra* from Çatacık, Eskişehir, Turkey; and SEQ2 is *Sequoia sempervirens* from the Humboldt Grove, California.

** Rows 4-10 contain the average isotopic concentrations in ppm units. The values in parenthesis are the number of concentration values used for calculating the average.

*** The Mn concentration was measured in a small percentage of the tree-ring samples due to its short half-life.

The next step in the dendrochemistry project was the analysis of four small tree samples (30-60 years in length) from the Çatacık forest in Turkey. The period of analysis, which covered at least the years 1980-2002. The four Çatacık tree samples (C-TU-CAT32, C-TU-CAT21, C-TU-CAT16 and C-TU-CAT28) were analyzed according to the procedure above except for the

following changes. It was found that the isotope with the most interesting chronologies, Au, was being detected at or near the minimum detectable concentration (MDC). Accordingly, the batch sizes were reduced to approximately 30 samples and each tree-ring was counted for 2 hours. This was sufficient for reliably recovering gold in most tree-rings and with better statistical accuracy. Doing so also decreased the La detection limits so that it could be more reliably identified. Mn-56 has a short enough half-life that it had decayed away before the samples were done being counted. To make up for this, all samples were counted for 15 minutes each prior to starting the 2-hour counts.

The four tree samples that were analyzed from the Çatacık forest are listed in Table 2. A typical gamma spectrum for two sample analyzed is shown in Fig. 2. The first tree sample analyzed was C-TU-CAT32 without the new irradiation procedure standards and the initial results of this tree sample led to the implementation of the new procedure.

Fig. 1. Gold concentrations in 4 different tree samples. Observed gold peaks at the date of tree rings are marked.

Table 2. Average Isotopic Concentrations obtained in four Tree Samples from the Çatacık Forest using Irradiation in the DITs.

Tree Sample	C-TU-CAT32	C-TU-CAT21	C-TU-CAT16	C-TU-CAT28
Years Analyzed	1940-2002	1969-2002	1972-2002	1971-2002
Au	1.3 (61)	.19 ppb (30)	.42 ppb (30)	.14 ppb (16)
Br	27 ppb (62)	18 ppb (33)	18 ppb (30)	43 ppb (31)
K	41 (62)	20 (33)	19 (30)	30 (31)
La	27 ppb (62)	15 ppb (33)	19 ppb (30)	16 ppb (31)
Mn	51 (62)	44 (33)	42 (30)	29 (30)
Na	3.1 (62)	5.1 (33)	6.2 (30)	2.5 (31)
Zn	.78 (62)	.81 (33)	.36 (30)	.86 (31)

Fig. 2. Typical gamma spectrum from C-TU-CAT32C (1995) and C-CY-RVA5 (1993) Tree ring samples for long irradiation and 1 hr count after 24 hours of decay.

Large peaks in Au concentration were observed and each ring was reanalyzed with the new procedure to check the reproducibility of the gold peaks. The remaining three samples were analyzed with the new procedure described above. Tree Sample C-TU-CAT16 was divided in half lengthwise and each piece was cut into individual rings and analyzed separately. The results in Table 2 for C-TU-CAT16 are the average of the results from the two sections and the results for C-TU-CAT32C represent the average of the results from the first and second irradiations.

At a later time, each of the tree-rings from C-TU-CAT32 and C-TU-CAT21 was recounted for one day each. Although this process was extremely time consuming (7 samples per week versus 40-60 per week with the 2-hour count time), a wealth of isotopic data was obtained. It resulted in the identification of 7 additional metals including ^{46}Sc , ^{59}Fe , ^{60}Co , ^{65}Zn , $^{110\text{m}}\text{Ag}$, ^{124}Sb and ^{134}Cs . The concentrations of these long-lived isotopes in C-TU-CAT32 and C-TU-CAT21 are presented in Table 3. The Ag and Au concentrations in C-TU-CAT32 were correlated with each other. 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 of environmental effects such as volcanic activity and/or Mediterranean dust storms, another candidate for such an effect on a tree.

Table 3. Average Concentrations of Long-lived Isotopes in two Tree Samples

	C-TU-CAT32	C-TU-CAT21
Years Analyzed	1962-2000	1969-2000
^{46}Sc	1.6 ppb (39)	2.6 ppb (33)
^{59}Fe	16 ppb (33)	26 ppb (33)
^{60}Co	78 ppb (39)	32 ppb (33)
^{65}Zn	1.8 ppm (39)	1.7 ppm (33)
$^{110\text{m}}\text{Ag}$	6.7 ppb (37)	4.3 ppb (33)
^{124}Sb	2.8 ppb (38)	1.8 ppb (29)
^{134}Cs	1.9 ppb (34)	2.0 ppb (30)

* Rows 3-9 contain the average isotopic concentrations. The values in parenthesis are the number of concentration values used for calculating the average.

Ag has a short lived isotope (^{108}Ag) which might be identified with short irradiations of tree rings. This study was pursued 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.

Irradiation in the Pneumatic Transfer System (PTS)

A sample of *Pinus brutia* from the Roudhias Valley, Arodafna, Cyprus, C-CY-RVA5 (S.W. Manning 2007, pers. comm.) was chosen for analysis in the PTS and obtained from the Malcolm and Carolyn Wiener Laboratory at Cornell. An activity prediction indicated that 1-minute irradiations at 900 kW (the maximum allowed power while using the PTS) may make it possible to quantify the amount of Ag in each tree-ring. The empty vials were labeled with a permanent marker and weighed. Individual tree-rings were then cut from the sample using a stainless steel knife or chisel, cleaned with alcohol, and placed in the vials which were heat-sealed and re-weighed. Shortly before each run, sample vials were loaded into the rabbits for irradiation in groups of 25-35 at a time. Each sample was irradiated for 1 minute and counted for a live time of 200 seconds. The decay time was minimized as much as possible for each sample and was typically 40-60 seconds. After counting, each spectrum file was saved in the Genie-2000 for analysis at a later time.

Irradiation in the PTS allowed for the analysis of 14 isotopes including ^{18}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 . The concentration of each isotope in the wood was calculated using Instrumental NAA and assuming a constant efficiency calibration performed for the bottom of the sample vial. The average concentration of each isotope and the number of rings used for the calculation are given in Table 4.

Ag was considered the most promising element that could be identified using short irradiations. ^{108}Ag has a convenient half-life (2.37 m) and based on previous results appears to be climatically significant. Ag was identified in tree sample C-CY-RVA5 although there are many missing values (evidently due to decreasing concentration towards the center of the tree) at years earlier than about 1965.

Table 4. Average Concentrations of Short-lived Isotopes in Tree Sample C-CY-RVA5

Isotope	Concentration	Isotope	Concentration
^{17}O	632 (138)	^{41}K	12 (138)
^{23}Na	10 (138)	^{48}Ca	1.0 (138)
^{26}Mg	9.0 (138)	^{51}V	4 ppb (130)
^{27}Al	2.0 (138)	^{55}Mn	4.8 (138)
^{36}S	7 ppb (102)	^{65}Cu	.067 (119)
^{37}Cl	5.0 (138)	^{107}Ag	64 (56)
^{39}Ar	46 (138)	^{127}I	.068 (129)

Fig. 3 shows the silver concentrations from tree samples C-TU-CAT32 and C-CY-RVA5 plotted together. It is evident that the chronologies are similar with large peaks within one year of each other in 1984-5, 1988-9 and 1996-7. 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. Fig. 3 loosely shows an apparent correlation between one tree in Cyprus and one tree in Turkey.

Fig. 3. Comparison of Ag Concentration in C-TU-CAT32 and C-CY-RVA5

Most of the identified elements are relatively constant between 1865 and the bark, neglecting variability. The heaviest isotope identified was ^{128}I , which exhibited larger ring-to-ring variability than the other isotopes and is lacking the strong 1929 anomaly evident in many of the other elements.

It was also possible to measure the concentration of S which may be available to trees in greater amounts during acidic events. If the S concentration in tree-rings is found to reliably record the availability of S to the tree, it may be possible to differentiate between types of environmental events. The data would be similar to that obtained by from the S composition analysis of ice cores. Volcanic eruptions tend to release large amount of S gases and aerosols which are washed out of the atmosphere as acid rain. This may cause high solubility of metals and therefore greater availability to the tree. Extended acidification may also cause leaching and depletion of these metals in the soil. The dry deposition of dust may result in a greater availability of metals due to direct fallout with less of a S signal than for a volcanic eruption. Correlation studies may be important for comparing the S concentration or S buildup in the tree to concentrations of other elements.

In some tree-rings the amount of S in the wood was only slightly higher than the total amount of S in the polyethylene vial and the tree-ring sample. The variation of S in the blank vials contributed errors to the S concentration in the tree-rings. It may be possible to create better reliability in detecting S by reducing the vials' size or extending the counting time.

Comparison of Irradiation Schemes

A comparison of each of the irradiation schemes used, their time requirements and isotopic data obtained is provided in Table 5. Due to the smaller time constraints, flexible scheduling and wealth of data obtained, short irradiations in the PTS were selected as the preferred irradiation scheme. It is not necessary to allow for time to count 20-30 samples between irradiations, thereby making it easier to schedule reactor time. Another advantage of the short irradiations is the lower amount of radioactivity created. The longer irradiations in the DITs (discussed below) activated long-lived isotopes such as ^{60}Co in the wood. The activity of the samples was small but

easily measurable after several months. However, the longest-lived isotopes activated in the PTS were K and Na (14 and 13 hours respectively). This made the samples suitable for non-controlled storage within a couple of days.

Table 5. A Comparison of Three Different Tree-Ring Irradiation Procedures

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

* PTS = Pneumatic Transfer System, DIT = Dry Irradiation Tube

[†] Ag and La were only occasionally identified.

If all of the irradiation schemes are to be completed to achieve the full range of isotopic data available with NAA, it is advisable to begin analysis of samples with the short irradiations. Radio-chemical changes may be taking place during the long irradiations. For instance, Al-28 goes through more than 100 half-lives during a 4 hour irradiation. In addition, samples are less radioactive after the short irradiations and easier to prepare for subsequent irradiations.

The major problem seen with the short irradiations is the variability in the data. For most isotopes the concentration errors are expected to be about 25% at one standard deviation. This is slightly worse than the errors in the longer irradiations which were within 15-20% for most isotopes. It is believed that some of these errors come from changes in sample height and therefore changes in the γ -ray detection efficiency. The height of each sample in its vial is dependent on the mass of the tree-ring sample and the size of the wood shavings.

If each wood sample had the same height in the vial, the concentrations would be off by a constant factor since an efficiency calibration for the bottom of the vial was used. However, variations in the height of the wood will introduce relative errors between samples. Error due to the efficiency variations could be eliminated by considering the ratio of elements in each tree ring. O concentration may serve as an appropriate comparison element for calculating ratios. Measuring the height of each sample and adjusting the efficiency calibration appropriately may eliminate some errors.

The minimum detectable concentration (MDC) would be greatly reduced by decreasing the heights of the Compton shoulders in the background. The presence of the isotopes ^{49}Ca , ^{56}Mn , ^{28}Al and ^{41}Ar all contribute significantly to the background under the smaller peaks such as Ag and I. Reducing the excess air in the vials would reduce the ^{41}Ar continuum. Ashing or digesting the samples so that they have a consistent geometry would make this easier. The presence of ^{56}Mn which is easily activated and has a long half-life compared to the other identified isotopes contributes a great deal of background. Any radiochemical separation that removed the Mn would be highly beneficial to detecting isotopes present in lesser amounts. Due to the presence of Mn it is very difficult to design a better scheme for short irradiations to identify Ag, making it a good candidate for use of a Compton Suppression System, also available at the RSEC.

Measurements with Penn State Compton Suppression System

The Penn State Compton suppression spectrometer (CSS) system consists of a high-purity germanium detector used as the primary detector, i.e. the central detector, NaI(Tl) detectors as the secondary detectors, i.e. the guard and the plug detectors, lead shield, measurement electronics, data acquisition device, a personal computer and the spectroscopy software Genie-2000 from Canberra Technologies, Inc. Compton Suppression Systems are used to reduce the contribution of scattered gamma rays that originate within the HPGe detector to the gamma ray spectrum. The HPGe detector is surrounded by an assembly of guard detectors, usually NaI(Tl). The HPGe and NaI(Tl) detectors are operated in anti-coincidence mode. The NaI(Tl) guard detector detects the photons that Compton scatter within, and subsequently escape from the

HPGe detector. Since these photons are correlated with the partial energy deposition within the detector, much of the resulting Compton continuum can be subtracted from the spectrum reducing the unwanted background in gamma ray spectra. A commercially available Compton Suppression Spectrometer (CSS) was purchased from Canberra Industries and tested at the Radiation Science and Engineering Center at Penn State University. The PSU-CSS includes a reverse bias HPGe detector, four annulus NaI(Tl) detectors, a NaI(Tl) plug detector, detector shields, data acquisition electronics, and a data processing computer with Genie-2000 Gamma Spectrum Analysis software. The HPGe detector is n-type with 54 % efficiency. The guard detectors are on an annulus with 9-inch diameter and 9-inch height, plug detector that goes into/out of the annulus with the help of a special lift apparatus to raise/lower. The detector assembly is placed in a shielding cave. State-of-the-art electronics and software are used. Fig. 4 shows a picture of the Penn State Compton suppression spectrometer with the measurement electronics.

Fig. 4. A picture of Penn State Compton Suppression System

Four photomultiplier tubes that are connected to the NaI(Tl) crystals that form an annulus detection volume around the HPGe detector as well as the plug detector –also NaI(Tl) can be seen in Fig. 5, which shows the interior of the spectrometer. The cylindrical enclosure has lead shields with copper lining.

Fig. 5. Interior picture of the Penn State Compton Suppression Spectrometer.

The measurement electronics is shown in Fig. 6. Two high-voltage power supplies are used to power the HPGe and NaI(Tl) detectors. The unit includes spectroscopy amplifiers and the coincidence unit. The output of the coincidence unit is sent to Canberra Multiport II multichannel analyzer (MCA).

Figure 6: Picture of the NIM BIN that has the spectroscopy electronics

Elemental analysis of a wood sample (C-TU-POR-3) from Porsuk, central Anatolian region of Turkey with 819 Relative Gordion Year was performed by using the PSU CSS. The CTUPOR-819 wood sample was activated at 1 MW in the PSU Breazeale Nuclear Reactor and then counted in the CSS. Fig. 7 shows the comparison of suppressed and unsuppressed spectra with determined gamma peaks. As demonstrated in Fig. 8, the 411.8 keV gold peak was buried in the Compton continuum without the suppression, whereas with the CSS, it was possible to resolve the gold peak.

Fig. 7. Comparison of CTUPOR3-819 wood sample gamma-ray spectrum with and without Compton suppression

Fig. 8. Expanded region of the CTUPOR3 spectrum showing the gold (Au) peak is visible under suppression.

Progress Report

(July 01, 2006 – June 30, 2007)

Abstract

Dendrochemistry, or the study of tree-ring composition, is a promising new technique for reconstructing climate history with annual resolution. In particular, dendrochemistry may be useful for identifying periods of volcanic activity. Increased environmental acidity caused by sulfur released from volcanoes can cause greater availability of metals in the soil solution and increased uptake by trees. Neutron Activation Analysis is one of the preferred analysis methods for studying the composition of tree-rings. However, easily activated constituents such as Mn and Al may make it difficult to identify trace elements in the tree-rings with relatively small cross-sections for neutron capture. Dendrochemistry work already performed at the Radiation Science and Engineering Center at the Pennsylvania State University in conjunction with the Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University will be reviewed. This progress report then considers the potential advantages of using long or short irradiations to perform analysis on tree-rings and extract as much useful information as possible. Focus will be placed on elements such as Ag, Au and some rare earth elements (REE) which currently appear to be promising indicators of environmental events. The advantages of using a Compton Suppression System will be discussed for each irradiation scenario and the possibility of using combustion or separation techniques to isolate elements of interest will be considered. Recommended procedures for using NAA to determine the composition of tree-rings will be outlined.

Introduction

The suitability of Neutron Activation Analysis (NAA) for dendrochemical analysis depends not only on the accuracy of the results but on the efficient quantification of isotopes or elements that are good recorders of environmental events in tree-rings. Although no unique volcanic signal has been identified in tree-rings, certain isotopes or elements have been deemed promising by some researchers as environmental markers. For instance, Pearson et al. (2006) found a correlation between an increase in Mn concentration and the eruption of Tambora in 1815.¹ There has also been an indication that Au may be environmentally significant.²

The results obtained using a variety of irradiation schedules will be discussed with an emphasis on the applicability of the identified isotopes to environmental monitoring. This discussion will

also include the advantages and disadvantages of each irradiation schedule and the necessary steps in the experimental work itself.

Experimental

The dendrochemistry project at The Pennsylvania State University is an ongoing collaboration between the Radiation Science and Engineering Center (RSEC) and the Malcolm and Carolyn Wiener Laboratory for Near-Eastern and Aegean Dendrochronology at Cornell University. The project began when some preliminary experimental work using NAA of a tree sample divided into groups of 15 tree-rings indicated increased concentrations of gold in the sample corresponding to the eruption of Krakatoa.³ Much of the work since then has focused on quantifying gold in tree-rings with irradiations suited to identify the ¹⁹⁸Au isotope which has a 2.7 day half-life.⁴ Following this goal, four tree samples each over 300 years in length have been analyzed for the dendrochemistry project according to the following method. Tree samples were cut into individual rings and were irradiated in batches of 40 tree-rings for 4 MegaWatt hours in the Breazeale Nuclear Reactor (BNR) core. The thermal and epithermal fluxes in the BNR core are approximately 1.7×10^{13} n/cm²/s and 6×10^{11} n/cm²/s, respectively.⁵ Each batch was allowed to decay over night and then each tree-ring was counted for one hour. This procedure allowed for the identification of ²⁴Na, ⁴²K, ⁵⁶Mn, ⁶⁹Zn, ⁸²Br, ¹⁴⁰La, and ¹⁹⁸Au. In one tree ¹⁴⁰La was not detected consistently because it was present at or below the detection limits and Au was near the detection limits in all trees. Mn was detected but has a short enough half-life (2.6 hrs) that it had decayed away before the counting of each batch of samples was completed. All other elements were quantified well above the detection limits (Na, K, Br and Zn). The tree samples analyzed in this way and the average concentration results are provided in Table 1.

Gold behaved uniquely compared to the other elements listed in Table 1. Au showed no anomaly at the heartwood boundary (HWB) and has large peaks in single tree-rings². The next step in the study was the analysis of four short lived tree samples (30-60 years in length) from the Catacik forest in Turkey.⁶ The period of analysis which covered at least 1980-2002 corresponded to the availability of data from the Total Ozone Mapping Spectrometer (TOMS) including the dust aerosol index. These tree samples were analyzed according to the procedure above except for

the following changes. Tree-rings were irradiated in batches of 20-30 rings and each ring was counted for two hours instead of one hour each. This decreased the Au detection limits so that it could reliably be identified even at the lower continuum values. Doing so also decreased the La detection limits so that it 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. The four tree samples that were analyzed from the Catacik forest are listed in Table 2. The first tree sample analyzed was C-TU-CAT32 with out the new irradiation procedure standards and analysis of this tree sample lead to the implementation of the new procedure. Large peaks in Au concentration were observed and each ring was reanalyzed with the new procedure to check the reproducibility of the gold peaks. The remaining three samples were analyzed with the new procedure described above. Tree Sample C-TU-CAT16 was divided in half lengthwise and each piece was cut into individual rings and analyzed separately. The results in Table 2 for C-TU-CAT16 are the average of the results from the two sections and C-TU-CAT32C.

Table 1. Average Isotopic Concentrations in four Tree Samples

Tree Sample	C-GR-PPG4A	C-TU-KLK10B	C-TU-CAT14C	P-SW-SEQ2
Years Analyzed	1411-1979	1628-1999	1500-1979	1446-1948
Country	Greece	Turkey	Turkey	USA (CA)
¹⁹⁸ Au	8 ppb (467)	7 ppb (314)	4 ppb (445)	8 ppb (360)
⁸¹ Br	.08 (470)	.07 (355)	.06 (459)	.4 (368)
⁴¹ K	10 (548)	22 (369)	18 (459)	37 (370)
¹³⁹ La	.003 (42)	.006 (203)	.02 (428)	.2 (369)
⁵⁵ Mn*	7.4 (47)	11 (67)	21 (237)	14 (200)
²³ Na	69 (557)	60 (369)	37 (459)	86 (374)
⁶⁸ Zn	.67 (197)	1.6 (331)	1.5 (456)	1 (307)

* The Mn concentration was measured in a small percentage of tree-ring samples due to the short half-life of ⁵⁶Mn

Table 2. Average Concentrations of Tree Samples from the Catacik forest, Turkey

Tree Sample	C-TU-CAT32	C-TU-CAT21	C-TU-CAT16	C-TU-CAT28
Years Analyzed	1940-2002	1969-2002	1972-2002	1971-2002
¹⁹⁸ Au	1.3 ppb (61)	.19 ppb (30)	.42 ppb (30)	.14 ppb (16)
⁸¹ Br	27 ppb (62)	18 ppb (33)	18 ppb (30)	43 ppb (31)
⁴¹ K	41 (62)	20 (33)	19 (30)	30 (31)
¹³⁹ La	27 ppb (62)	15 ppb (33)	19 ppb (30)	16 ppb (31)
⁵⁵ Mn	51 (62)	44 (33)	42 (30)	29 (30)
²³ Na	3.1 (62)	5.1 (33)	6.2 (30)	2.5 (31)
⁶⁸ Zn	.78 (62)	.81 (33)	.36 (30)	.86 (31)

Later, each of the tree-rings from C-TU-CAT32 and C-TU-CAT21 were recounted for one day each. This additional procedure, although time consuming, was rewarding since it resulted in the identification of 7 additional metals including ⁴⁶Sc, ⁵⁹Fe, ⁶⁰Co, ⁶⁵Zn, ^{110m}Ag ¹²⁴Sb and ¹³⁴Cs. The concentrations of these long-lived isotopes in C-TU-CAT32 and C-TU-CAT21 are presented in Table 3. The Ag and Au concentrations in 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 grew⁶. Ag and Au are the only elements that had the sharp peaks above the level of their continuums. 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.

Table 3. Average Concentrations of Long-lived Isotopes in two Tree Samples

Tree Sample	C-TU-CAT32	C-TU-CAT21
Years Analyzed	1962-2000	1969-2000
⁴⁵ Sc	1.6 (39)	2.6 (33)
⁵⁸ Fe	16 (33)	26 (33)
⁵⁹ Co	78 (39)	32 (33)
⁶⁴ Zn	1.8 ppb (39)	1.7 ppb (33)
¹⁰⁹ Ag	6.7 ppb (37)	4.3 ppb (33)
¹²³ Sb	2.8 (38)	1.8 (29)
¹³³ Cs	1.9 (34)	2.0 (30)

Ag has a short lived isotope (^{108}Ag) which might be identified with short irradiations of tree rings. This study was pursued 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 timer system provided by the reactor is set to the required irradiation time plus the 5 second travel time. At the end of the irradiation the sample is automatically returned to the hood in the NAA laboratory. With practice, it is possible to begin counting the sample 40-50 seconds after the sample leaves the core. The time between irradiation and counting is measured by hand with a stopwatch.

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 heat-sealed and re-weighed. Shortly before each run, sample vials were loaded into the rabbits for irradiation in groups of 25-35 at a time. With each batch of samples, one blank vial and the same sample of NIST standard Rice Flour were irradiated.

Results

The content of the blank vials were calculated using Instrumental NAA and the efficiency calibration at the bottom of the vial. The blanks, which were different each time, showed errors of about 20% for most isotopes at 1σ . However, the errors in the Ar content were only about 13%. Polyethylene is notorious for its inconsistent composition and the other elements could be explained by actual differences in trace elements. In addition, each blank and sample vial was irradiated with a permanent marker label and the inconsistencies in the blank vials should include any errors introduced by the marker ink. For all elements except S, the errors introduced by the vials are minimal since the activity was much lower than that for the wood.

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. Three isotopes had errors outside of this range. S and Cu (29% and 39%, respectively) had small peak areas contributing to random counting errors. O (31%) has a relatively small half-life (26.7 seconds) making it highly sensitive to timing errors.

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 . The concentration of each isotope in the wood was calculated using Instrumental NAA and assuming a 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 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.

The average concentration of each isotope in tree sample C-CY-RVA5 is given in Table 4. The concentration shown was very similar to the radial concentration trend obtained for K and both have a peak in concentration in 1883. The Ag concentration in C-CY-RVA5 is plotted with the Ag concentration in C-TU-CAT32 to show the similarities between the chronologies.

Table 4. Average Concentrations of Short-lived Isotopes in Tree Sample C-CY-RVA5

Isotope	Concentration	Isotope	Concentration
^{17}O	632 (138)	^{41}K	12 (138)
^{23}Na	10 (138)	^{48}Ca	1.0 (138)
^{26}Mg	9.0 (138)	^{51}V	4 ppb (130)
^{27}Al	2.0 (138)	^{55}Mn	4.8 (138)
^{36}S	7 ppb (102)	^{65}Cu	.067 (119)
^{37}Cl	5.0 (138)	^{107}Ag	64 (56)
^{39}Ar	46 (138)	^{127}I	.068 (129)

Discussion

Ag was considered the most promising element that might have been identified using short irradiations. ^{108}Ag has a convenient half-life (2.37 m) and based on previous results appears to be climatically significant. Ag was identified in tree sample C-CY-RVA5 although there are many missing values (evidently due to decreasing concentration towards the center of the tree) at years less than about 1965. It is evident that the chronologies are similar with large peaks within one year of each other in 1984-5, 1988-9 and 1996-7. 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.

The minimum detectable concentration (MDC) would be greatly reduced by decreasing the heights of the Compton shoulders in the background. The presence of the isotopes ^{49}Ca , ^{56}Mn , ^{28}Al and ^{41}Ar all contribute significantly to the background under the Ag peaks. Due to the easily-activated Mn it is very difficult to design a better short irradiation scheme for identifying the Ag, making it a good candidate for use of a Compton Suppression System, also available at the RSEC. An example of a tree sample analyzed in the DITs and counted with and without Compton suppression is shown in Figure 1.

Figure 1. Gamma Spectrum of tree-ring irradiated in the DITs and counted with and without Compton Suppression.

In Figure 2, the Cl concentration data have been fit with an exponential curve and the residuals have been normalized so that their standard deviation is equal to unity. The result clearly shows a peak in 1883 outside of the 3σ regime. This is also the year of the large Krakatoa eruption in Indonesia.

Another interesting isotope identified was ^{18}O . The ratio of ^{18}O to ^{16}O in the atmosphere is a function of its temperature and has been measured in tree-rings as a proxy for temperature during the tree's growth. The concentration of ^{18}O is relatively constant except for the year to year variations which were mostly within the 1σ errors indicated by the NIST Rice Flour results. It is impossible to judge the ratio of ^{18}O to ^{16}O since changes in ^{18}O may be due to actual changes in the amount of oxygen. However, as a main constituent of wood it may prove useful in calculating isotope ratios by serving as the denominator. It is technically possible to measure the ^{16}O concentration with the $^{16}\text{O}(n,p)^{16}\text{N}$ fast reaction. However this would be extremely difficult due to the small gamma abundances and short half-life of ^{16}N .

Most of the identified elements are relatively constant between 1865 and the bark, neglecting variability. The heaviest isotope identified was ^{128}I , which exhibited larger ring-to-ring variability than the other isotopes and is lacking the strong 1929 anomaly evident in many of the other elements. There are peaks in I concentration in 1889 and 1974.

The major problem seen with the short irradiations is the variability in the data. For most isotopes the concentration errors are expected to be about 25% at one standard deviation. This is slightly worse than the errors in the longer irradiations which was within 15-20% for most isotopes. It is believed that the majority of these errors come from errors in the measurement of the irradiation and decay times and from changes in sample height and therefore efficiency. It may be possible to reduce the errors considerably by addressing these issues.

For instance, measuring the height of each sample within the sample vial and adjusting the efficiency calibration appropriately may eliminate some errors. If each wood sample had the same height in the vial, the concentrations would be off by a constant factor. However, variations in the height of the wood will introduce relative errors above and beyond the errors in the NIST Rice Flour content. Error due to the efficiency calibration would be eliminated by considering the ratio of elements in each tree ring. Since oxygen plays an integral role in the organic structure of wood it may be appropriate to use this element as the denominator in any elemental ratios. Ashing or digesting may allow for a more consistent geometry between ring samples.

The possible reason for the errors in the NIST Rice Flour results includes actual changes in neutron flux at the position of the PTS vial in the core. This would most likely be due to changes in control rod position as a function of xenon concentration in the core. Another possible source of errors is in the measurements of the irradiation and decay time.

If all irradiation schemes are to be completed in sequence on a tree sample in order to achieve the full range of isotopic data available with NAA, it is advisable to begin analysis of samples with the short irradiations. 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.

Figure 2. Chlorine Concentration in Tree Sample C-CY-RVA5

One advantage of the short irradiations is the lower amount of radioactivity created making them easier to prepare for subsequent irradiations. The 4-hour irradiations activated long-lived isotopes such as ^{60}Co in the wood. The activity of the samples was small but easily measurable after several months. However, the longest lived isotopes activated in the PTS were K and Na with 12 hour and 15 hour half-lives, respectively. This made the samples suitable for non-controlled storage within a couple of days. A comparison of the time requirement and data obtained for each irradiation scheme is provided in Table 5.

Table 5. A Comparison of Three Different Tree-Ring Irradiation Procedures

	Short Irradiations in the PTS*	Long Irradiations in the DITs* (short count time)	Long Irradiations in the DITs (long count time)
Irradiation time	1 min	4 hours	4 hours
Count time	4 min	2 hours	1 day
Reactor time per sample	6 min	8 min	8 min
Samples per 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

* PTS = Pneumatic Transfer System, DIT = Dry Irradiation Tube

[†] Ag and La were only occasionally identified.

[§] The Mn was actually identified by counting all of the samples for 15 minutes each prior to counting them for 2 hours.

References

1. C. L. Pearson, S. W. Manning, M. Coleman, K. Jarvis, *Appl Geochem* 21 (2006) 1681
2. K. Ünlü, P. I. Kuniholm, J. J. Chiment and D. K. Hauck, *J. of Radioanal Nucl Ch*, 264 (2005) 21
3. J. J. Chiment, The Detection of Unique, Biologically Important Events in Prehistory: A report to the Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University. Internal Report (1998).
4. M. D. Glascock, *Tables for Neutron Activation Analysis*. The University of Missouri, Columbia (1991)
6. 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.
7. N. O. Cetiner, NAA of Tree-Rings, Masters Thesis, The Pennsylvania State University, In Progress.

Progress Report

(July 01, 2005 – June 30, 2006)

Abstract

The dendrochemistry project at the Radiation Science and Engineering Center (RSEC) is part of an on-going study of ancient and historic trees from the Near-East and other places around the globe. In recent years dendrochemistry, or the compositional analysis of tree rings, has become a promising tool for recovering records of major climate change. In particular, dendrochemistry is especially promising as a method for dating past volcanic activities. Since trees grow one ring per year they record conditions of the soil and atmosphere in the corresponding ring. Volcanic eruptions are both interesting and important to document because of their large climatic and archaeological repercussions and the narrow time span over which they occur. The dendrochemical method employed for analysis at is Neutron Activation Analysis (NAA). This is a multi-elemental isotope-specific nuclear technique with up to parts-per-billion sensitivity. It is non-destructive so that tree-rings may be analyzed multiple times with different experimental parameters thus increasing the number of elements that may be identified in a single sample. At RSEC we are using Instrumental Neutron Activation Analysis (INAA) to achieve accurate and replicable quantitative results. Because of all these advantages, NAA is considered arguably the best analysis method available for the study of dendrochemistry.

Introduction

Trees in temperate zones grow one ring per year, forming an annual record or ring pattern that reflects climatic conditions. The widths of these rings are dependent on the quality of the yearly growing season. Wood samples are dated by creating a time line series of tree-ring widths, called a chronology. Often, climatically significant years are readily apparent on a chronology as having anomalously large or small ring widths or similarly varying wood densities. Trees which grew in the vicinity of each other will exhibit similar ring width patterns which may be matched against each other, a method called cross-dating. Environmental events which are large may affect trees worldwide, providing a global dating marker. By creating chronologies for trees which died in a known year, it is then possible to match chronologies for undated samples to major patterns in the dated tree. By overlapping chronologies, dendrochronologists at the Malcolm and Carolyn Wiener Laboratory at Cornell University have successfully dated wood

samples dating back to 7000 BC and in the process of doing so have dated many important events in human history. Dendrochemistry, or the study of tree-ring constituents, supposes that the concentrations of key elements in tree-rings are also indicative of environmental change. In particular, spikes, dips, or major changes in trace element concentration may be an indication of changes in soil or atmospheric chemistry.

As part of the dendrochemistry project at RSEC, three tree samples from Turkey and Greece each covering a time period of at least 350 years have been analyzed. In the past year, an additional Sequoia tree from California covering the years 1285 to 1945 was also analyzed. A fifth tree sample from Turkey also covering over 400 years is currently being studied. In addition, several tree samples from the Catacik forest in Turkey which cover the years 1970-2000 are being studied in depth to determine the compositional changes in tree rings caused by the eruptions of El Chichon (1982) and Pinatubo (1991). This report presents data from the Sequoia tree (tree sample PSWSEQ2) and four Catacik trees (tree samples CTUCAT16, CTUCAT32, CTUCAT21 and CTUCAT28).

In the past year a student in Nuclear Engineering finished a Masters degree titled “Neutron Activation Analysis of Dated Tree Rings” in which she evaluates the possibility of using dendrochemical data for dating volcanic activity. The hypothesis of her thesis, and other dendrochemistry work at the reactor, is that increased levels of environmental acidity caused by volcanic activity can result in greater solubility of metals in groundwater and subsequent uptake by trees. In particular, increased levels of gold in a tree-ring may indicate a period of volcanic activity. This student has continued with the dendrochemistry project and is currently working on her doctoral thesis along related lines.

A second master’s student has been hired for the purpose of installing and evaluating a Compton Suppression System (CSS) for use of the dendrochemistry project. In the past year this system has been validated through comparison with NIST standards and other NAA systems already active at the facility.

Analysis

Dendrochemistry has been useful in the past for demonstrating the period and spatial extent of pollution events. Despite this promising work, the mechanism(s) which lead to correlation between uptake and element deposition/acidification have not yet been pinpointed. Many studies have shown that increased environmental acidity causes trees to increase uptake of some elements, especially metals, through the root system. Another major uptake path is through the leaves which would result from the direct deposition of material onto the tree. Both uptake mechanisms may be important when considering the effect of volcanic eruptions on tree uptake. This is because dust from volcanic eruptions often travels long distances before settling out of the atmosphere and sulfur particulates interact with water vapor to cause acid rain.

The mechanism for explaining the observed correlation between trace element uptake and changes in environmental chemistry is not known. For this reason, a good starting place for study is determining elements which appear to be important, or indicative of changes in environmental chemistry. Table 1 lists the isotopes that are commonly identified in tree-rings, their biological role and their typical concentrations. Isotopes which are important for biology of the tree (nutrients) are believed to be poor indicators of environmental change external to the tree. Often they have high mobility in the tree and therefore are not suitable for yearly resolution. However, nutrients may be important for identifying biological changes internal to the tree (such as the heart wood/sap wood boundary) that would otherwise be mistaken as an environmental event. It may be that information on environmental change will come from a comparison between nutrient and non-nutrient chronologies.

Originally, the RSEC dendrochemistry project focused on studying the concentration of gold in tree rings. This is because gold is uniquely suitable for NAA and because it is chemically similar to the plant nutrient copper. However, there may be other reasons why gold was a good choice for dendrochemical studies. Figure 1 shows the gold concentration plotted per year for four different long chronologies from trees across the globe. Three tree samples, CGRPPG4 (Greece), CTUKLK10 (Turkey) and CTUCAT14 (Turkey) were analyzed in previous years. Tree sample PSWSEQ2 was taken from a Sequoia tree in California and was analyzed in 2005-

2006. Some critics of dendrochemistry have proposed that the width of the sapwood would limit the time resolution of the data. Sapwood refers to the part of the tree that is still transporting nutrients, which usually corresponds to the outer five to twenty tree-rings. It is thought that even relatively immobile elements are transported across the width of the sapwood and this would smear any annual increase in element uptake. However, Figure 1 clearly shows large peaks in gold concentration that occur in single tree rings. This behavior is limited (for the most part) to concentrations of gold. In fact, gold is often called a “noble metal” because it is un-reactive under most circumstances. The fact that gold only becomes soluble under very specific conditions may explain the presence of yearly peaks in concentration. And, for this reason gold may provide an important key to understanding element uptake in trees.

In addition to the long tree chronologies shown in Figure 1, four shorter tree samples from a single forest near Catacik, Turkey were analyzed. Figure 2 shows the isotope chronologies in tree samples CTUCAT16 and CTUCAT28. Because of the low concentrations of gold in these tree samples, the data have relatively poor statistics. The other isotopes that were identified have lower relative detectable concentrations and better statistics. However, many of these isotopes are plant nutrients and not of great interest by themselves. For this reason, tree-rings in the following two tree samples, CTUCAT32 (Figure 3) and CTUCAT21 (Figure 4) were counted three times each. In other words, following irradiation, each tree ring was counted initially for 15 minutes (to accurately measure the Mn concentration), counted again for 2 hours (to measure the usual isotopes included in Figure 2) and again for 1 day to measure the concentrations of long-lived isotopes. Although the final procedure is lengthy, it resulted in additional information of at least 7 isotopes including Cs-133, Ag-109, Co-59, Zn-69, Fe-58, and Sc-46, Sb-125 and Cr-51.

In Figures 3 and 4 it is easy to see that in general the non-nutrient isotopes do not follow the same general pattern as the nutrients. In particular, the gold concentration in CTUCAT32C (Figure 3) shows gold concentration peaks that are more than one order-of-magnitude in size in the years 1980, 1985 and 1990. Recent analysis, which is only preliminary, indicates that these peaks may be related to the intensity and frequency of African dust storms over the Mediterranean Sea. Another interesting point is that silver, another noble metal, is the only

isotope that roughly follows the gold concentration, and certainly the only other isotope to show peaks of this magnitude. Again, the related chemistries of gold and silver may be providing an important clue about the uptake mechanisms of trees and ultimately, environmental change.

Figure 1. Gold concentrations in four long tree chronologies. The chronology that was analyzed in

Figure 6: Evolution of the concentration of the elements Br, K, Mn, La, Na, Zn and Au in the melt during the crystallization of the melt.

Figure 3. Isotope Chronologies in Tree Sample CTUCAT32. This tree sample was counted three successive times. The Mn concentration (graphed in ppm) was measured in the first count which lasted 15 minutes per sample. The concentrations of Na, K, Zn, Br and La (graphed in ppm) were measured during the second count which lasted one hour. Finally, each tree-ring sample was counted for 1 day each to analyze Sc, Fe, Co, Ag, Sb and Cs concentrations (graphed in ppb).

Isotope Chronologies in Tree Sample CTUCAT21

Table 1. Isotopes consistently identified in tree -rings, their biological role and typical concentrations. The biological role of individual isotopes probably effects the trends in their concentrations through out the tree. The major gamma -ray decay energies used to identify each isotope are also included.

Isotope	Biological Role	Concentration	Major Decay Lines
Na-23	macronutrient	5 ppm	1368.60 keV
K-41	macronutrient	20 ppm	1524.58 keV
Sc-45	cosmic element	1 ppb	889.98, 1120.55 keV
Mn-55	micronutrient	50 ppm	846.76, 1100.72 keV
Fe-58	micronutrient	1 ppb	1099.25, 1291.60 keV
Co-59	pollutant	1 ppb	1173.24, 1332.50 keV
Zn-64	micronutrient	.5 ppm	1115.55 keV
Zn-68	micronutrient	.1 ppm	438.63 keV
Zn-70	micronutrient	5 ppb	386.28, 487.34, 620.19 keV
Br-81	pollutant	20 ppb	776.52, 554.35, 619.11, keV
Ag-109	pollutant	5 ppb	657.76, 884.69 keV
Cs-133	pollutant	10 ppb	569.32, 604.70, 795.85
La-139	pollutant	20 ppb	1596.21, 487.02, 815.77 keV
Au-197	pollutant	1 ppb	411.80 keV

Conclusions

The dendrochemistry project at the Radiation Science and Engineering Center has been successfully implemented over the past several years. The experimental results and the discussions of these results are given in the progress report submitted each year for last three years. Several conclusions were drawn. The summary of some of these conclusions can be given as follow:

Four long chronology and four short chronologies have been analyzed for several isotopes and an additional long chronology is currently undergoing analysis. Recent data have allowed us to postulate ideas about tree biology and chemistry that can be tested in future years. In addition, the technique of obtaining multi-isotopic data with low detection limits and high accuracy through Neutron Activation Analysis was improved to achieve better results.

Different irradiation schemes that have been used to analyze tree-rings at the Radiation Science and Engineering Center at the Pennsylvania State University have been reviewed. The results obtained, especially including the isotopes that were identified with each scheme were given and discussed. 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.

For NAA of tree-rings, short irradiations in the Pneumatic Transfer System (PTS) were an efficient method of identifying a wide range of elements. It is recommended that analysis of any tree sample start by using the PTS. Any further analysis of the tree sample may then be guided by the isotopic information that it would provide. Due to the nature and number of short-lived isotopes identified, a schedule of short irradiations with the (PTS) has been chosen as the recommended irradiation scheme. Reducing the errors in the data would make it possible to identify small scale true variability in the tree-rings which may be relevant to environmental conditions.

Four graduate students worked on this project. One already completed her Master of Science degree and passed the candidacy and comprehensive exam and completed her PhD thesis on May 2008. The other student is completed her Master of Science degree and graduated May 2008. Two other graduate students are currently working on this project. One already completed his Master of Science degree the other one expected to complete her Master of Science degree during Fall 2009. Several manuscripts are published and/or submitted for publication in refereed journals and conference proceedings. A no cost extension was granted for this proposal until December 2008. A full listing of publications related to this project is given below.

Publications List

N. Ö. Çetiner*, K. Ünlü, J.S. Brenizer, “*Compton Suppression System at Penn State Radiation Science And Engineering Center*,” Journal of Radioanalytical and Nuclear Chemistry, Vol. 276, No. 3, 615-621, (2008) <http://dx.doi.org/10.1007/s10967-008-0609-7>

N. O. Cetiner, “*Specifications and Performance of the Compton Suppression Spectrometer at the Pennsylvania State University*”, MSc. Thesis. Pennsylvania State University, May 2008

D. K. H. Schwarz*, K. Ünlü, "Silver and Gold: Possible Evidence of Dust Storms in Tree-Rings", Trans. Am. Nucl. Soc. 97, 257, (2007).

K. Ünlü, P. I. Kuniholm, D. K. H. Schwarz*, N. Ö. Cetiner*, and J. J. Chiment, “*Neutron Activation Analysis of Dendrochronologically-dated Trees*,” (will be published in a book), Tree-rings, Kings, and Old World Archaeology and Environment: Cornell Dendrochronology-Archaeology Conference in Honour of Peter Ian Kuniholm, 3-5 November 2006

D. K. H. Schwarz*, K. Ünlü, “*Dendrochemistry of Pinus Sylvestris trees from a Turkish forest: Identifying the effects of Pinatuba*,” (will be published in a book), Tree-rings, Kings, and Old World Archaeology and Environment: Cornell Dendrochronology-Archaeology Conference in Honour of Peter Ian Kuniholm, 3-5 November 2006.

D. Sahin, K. Ünlü, Activity, “*Exposure Rate And Spectrum Prediction With Java Programming*”, Submitted to 8th International Conference on Methods and Applications of Radioanalytical Chemistry, Kailua-Kona, Hawaii, April 5-9, 2009

D. Sahin, K. Ünlü, “*Modelling A Gamma Spectroscopy System And Predicting Spectra With Geant4*”, Submitted to 8th International Conference on Methods and Applications of Radioanalytical Chemistry, Kailua-Kona, Hawaii, April 5-9, 2009

K. Ünlü, P. I. Kuniholm, J. J. Chiment, D. K. Hauck*, “*Neutron Activation Analysis of Absolutely-Dated Tree Rings*”, Journal of Radioanalytical and Nuclear Chemistry, Vol. 264, No. 1 (2005) 21-27.

D.K. Hauck*♦, K. Ünlü, P.I. Kuniholm, J.J. Chiment, “*Uses of NAA: Gold Concentrations in Dated Tree Rings*,” Trans. Am. Nucl. Soc., 90, 320 (2004).

D. K. Hauck*, N. O. Cetiner*, T. H. Daubenspeck, and K. Ünlü, “Facilities, uses and capabilities of NAA at the Radiation Science and Engineering Center at Penn State,” (invited) *Presented at the Joint Meeting of the National Organization of Test, Research, and Training Reactors and the International Group on Research Reactors, Special session honoring the Pennsylvania State University Breazeale Reactor 50th Anniversary*, September 12-16, 2005. (First Author supervised by candidate)

"Compton Suppression System (CSS) at PSU-RSEC", Penn State University, The Radiation Science and Engineering Center, 52nd Annual Progress Report, p. 54-58

Neutron Activation Analysis of Absolutely-Dated Tree Rings", Penn State University, The Radiation Science and Engineering Center, 52nd Annual Progress Report, p. 81-83

"Compton Suppression System " Penn State University, The Radiation Science and Engineering Center, 51st Annual Progress Report, p. 44-47

"Neutron Activation Analysis of Absolutely-Dated Tree Rings", Penn State University, The Radiation Science and Engineering Center, 51st Annual Progress Report, p. 66-70

"Compton Suppression System " Penn State University, The Radiation Science and Engineering Center, 50th Annual Progress Report, p. 30-33

"Neutron Activation Analysis of Absolutely-Dated Tree Rings", Penn State University, The Radiation Science and Engineering Center, 50th Annual Progress Report, p. 39-42

"Neutron Activation Analysis of Absolutely-Dated Tree Rings", Penn State University, The Radiation Science and Engineering Center, 49th Annual Progress Report, p. 69-72

"Neutron Activation Analysis of Absolutely-Dated Tree Rings: Identifying Climatically Significant Marker Events in History and Prehistory", Penn State University, The Radiation Science and Engineering Center, 48th Annual Progress Report, p. 44-56

K. Ünlü “*Typical Elemental Concentrations in Tree-Rings and Appropriate Irradiation Parameters for Determination with NAA*” presented in International Conference of Modern

Trends in Activation Analysis 12 (MTAA12), Tokyo, Japan, September 2007 (Conference Proceedings)

K. Ünlü, “*Ion Uptake Determination of Dendrochronologically-dated Trees using Neutron Activation Analysis*,” Invited talk in 8th International Conference on Nuclear Analytical Methods in the Life Sciences (NAMLS8), April 17-22, 2005, Rio de Janeiro, Brazil. (Conference Proceedings)

K. Ünlü “*Neutron Activation Analysis of Absolutely-Dated Tree Rings*”, 6th International Conference on Methods and Applications of Radioanalytical Chemistry, April 2003, Kailua-Kona, Hawaii. (Conference Proceedings)

Master of Science and PhD Thesis Related to this Project

Danielle Hauck, PhD program, “*Dendrochemistry: Seeing the Forest through the Trees*”. Penn State, May 2008

Nesrin Ozgan Cetiner, M.Sc. program, “*Neutron Activation Analysis of Dendrochronologically dated Tree Rings with Compton Suppression System*”. Penn State, May, 2008

Dagistan Sahin, M.Sc. program, “*NAA and Dendrochemisrty*” Penn State, December 2008.

Danielle Hauck, MSc program, “*Neutron Activation Analysis of Dendrochronologically dated Tree Rings*”. Penn State, May, 2005

Sarah Bender, M.Sc. program, “*Analysis of Environmental Samples with Compton Suppression System*” Penn State, will be completed in Fall 09