

Chapter 19

Synchrotron Applications in Wood Preservation and Deterioration

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Several non-intrusive synchrotron techniques are being used to detect and study wood decay. The techniques use high intensity synchrotron-generated X-rays to determine the atomic structure of materials with imaging, diffraction, and absorption. Some of the techniques are X-ray absorption near edge structure (XANES), X-ray fluorescence spectroscopy (XFS), X-ray absorption fine structure (EXAFS), and X-ray computed microtomography (XCMT). Micro-fluorescence spectroscopy was used to map the accumulation and spatial distribution of elements around hyphae at the site of decay. MicroXANES determined the valence states of metals, such as manganese and iron, during fungal colonization of wood. Microtomography was used to characterize loss of wood structural integrity. The techniques are providing information about molecular structures and compositions in the heterogeneous matrix of wood.

Nondestructive methods are needed to analyze the chemistry and internal structures of wood without disturbing spatial integrity or producing structural artifacts (1). The methods are needed to study wood during attack by decay fungi and wood treatment with preservatives. To meet this need, we have successfully studied several systems using the X-ray facilities at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton, NY. Chemical mechanisms of fungal wood decay are dependent on transition metal redox reactions producing free radicals (2-4). Synchrotron methods are uniquely suited to detect and image metal oxidation states as probes of the decay process. The same methods have been applied to study metal-based preservatives that undergo redox reactions during fixation of wood. These methods include X-ray absorption near edge structure (XANES), X-ray fluorescence spectroscopy (XFS), extended X-ray absorption fine structure (EXAFS), and X-ray computed microtomography (XCMT). In addition to decay and preservation studies, the XCMT method has also proven to be invaluable as a tool to analyze insects and fungi that cause major diseases of forests worldwide (5). Microtomography was employed to study beetle structure and function, to locate fungal spores on or in beetles, to assist in identification of fungi, and to provide images depicting spatial relationships of tree-insect-fungus (6,7).

Synchrotrons

Synchrotrons are large scientific instruments that generate high intensity electromagnetic radiation that range from the infrared through the x-ray spectrum. They are particle accelerators consisting of an electron source; a circular storage ring and connecting beamlines that end in experimental work stations. Electrons are introduced into the vacuum storage ring, driven to velocities near the speed of light, guided by magnets to travel around the ring where the charged particles tangentially lose energy, emitting electromagnetic radiation known as synchrotron light. At NSLS, a third generation synchrotron, bending and insertion device magnets, wigglers and undulators control electrons in the storage ring, enhancing the intensity of the light (Figure 1). The emitted radiation is directed down a path known as a beam port, which is split into two to four beamlines (8). Light from the storage ring is a mixture of many wavelengths. Each beamline has a collection of lenses, special mirrors and filters to select specific wavelengths that direct and focus the synchrotron light to a specially designed experimental station. The station is outfitted for particular

types of experiments with radiation detectors, recorders, computers, and other specialized equipment. Computer software, unique to each beamline, interprets data from the detector and images the results on a video screen in the form of graphs, element-specific spectra, or molecular models. Synchrotron radiation is used to determine the atomic structure of materials by diffraction, absorption, and imaging techniques at the beamline.

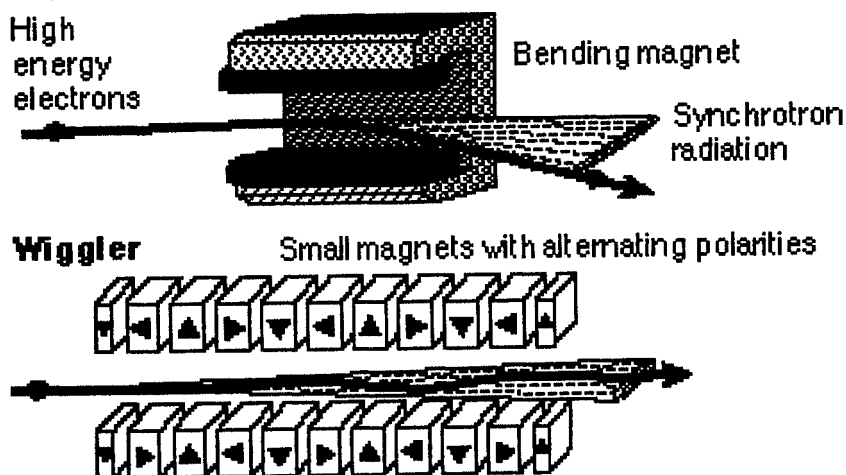


Figure 1. Schematic of synchrotron radiation created from high-energy electrons and radiation path in bending magnet and wiggler insertion devices.

The NSLS has an ultraviolet and an X-ray ring, which provide intense focused light at infrared and hard X-ray energies in excess of 100 keV and gamma rays at 200-400 MeV. The X-ray ring operates at 2.5 GeV to optimize radiation between 1 keV and 20 keV (9). The X-ray ring has over 30 beamlines extending from the ring to end at ports with multiple workstations. The beamlines are named from X1 to X30 with stations designated as letters. Wood deterioration and preservation experiments were conducted at beamlines X26A and X27A.

X-ray Fluorescence Spectroscopy

X-ray fluorescence spectroscopy (XFS) is a powerful and flexible technique that has long been available for the analysis and characterization of materials (10). The high intensity and brightness of synchrotron-generated X-rays make it possible to detect and quantify trace element distribution *in situ*. Beamline configuration of the X-ray microprobe at NSLS beamline X26A for white light has a spot size ranging from 10 square microns to 150-micron height x 350 microns vertical with an energy range from 3-30 keV. We have used XFS to scan for transition metal accumulation in decayed wood, tree rings of boreal forest spruce trees, brown-stained hemlock wood and hemlock tree rings for element distribution, especially for chromium, cadmium, and brown stain caused by manganese and iron oxides (Illman et al, unpublished data). We determined element location and distribution with XFS before obtaining spectroscopy spectra of trace elements in decayed wood or metal treated wood.

X-Ray Absorption Spectroscopy

Synchrotron-based XAS allows the study of elements at subatomic resolution. Synchrotron XAS techniques do not require a vacuum at the experimental station outside the storage ring, a distinct advantage over more established absorption techniques such as X-ray Photoelectron Spectroscopy (XPS). The XAS technique is based on element-specific absorption of electromagnetic radiation at distinct energies and, therefore it is highly dependent on an optical subassembly, a monochromator that accepts the polychromatic input radiation and outputs selectable monochromatic energy. An XAS experiment consists of irradiating a sample with a monochromatic beam of X-rays that is in the energy range above, and then below, the absorption edge of an element in question. The X-ray absorption coefficient is recorded as a function of energy. Two complimentary synchrotron XAS techniques are XANES and EXAFS. The XANES K-edge absorption spectrum for a representative transition metal, such as Mn, can be interpreted as follows. At low energies, the energy of the incoming radiation is not high enough to be absorbed by Mn in the sample, detected as the pre-absorption edge region of the spectrum. At sufficiently high energies, radiation is absorbed. The K-shell electron is ejected from the atom, released as photoelectron, giving rise to the absolute absorption edge of the spectrum. The absorption edge also contains a substructure of small peaks or shoulders. The EXAFS region of the spectrum is the result of outgoing photoelectron reflection by the atoms in the environment of the metal. Interference of outgoing and reflected parts results in oscillation modulation of the absorption coefficient at energies above the edge. Differences between the

XANES and EXAFS portions of a representative absorption spectrum are illustrated in Figure 2.

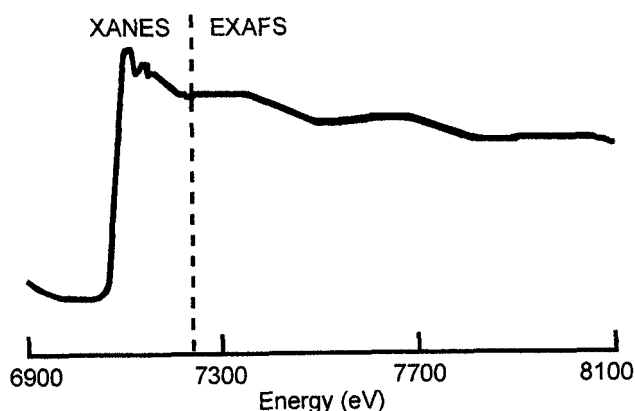


Figure 2. Representative XANES and EXAFS spectra

X-ray absorption near edge structure (XANES)

XANES spectroscopy is used to detect and determine oxidation states of metals that are provided by the absolute position of the absorption edge. The near edge absorption region, up to 40 keV above the edge, contains information about vacant orbitals, electronic configuration and site symmetry of the absorbing atom.

The microprobe beamline at NSLS X26A pioneered *in situ* detection of transition metal redox states in biological, environmental, and geological samples. The current X26A XANES sensitivity for trace element analyses is 10-100 ppm. The beamline is ideally suited for detection of metal oxidation states used to probe changes in chemical degradation of wood lignocellulose by decay fungi (1,6,7). Representative microXANES spectra of and Mn^{4+} in Southern yellow pine wood during decay by the white-rot fungus *Phanaerochaete chrysosporium* are illustrated in Figure 3. Peaks and shoulders in the rising edge can provide information about electronic configuration, ligand bonds, and atomic symmetry.

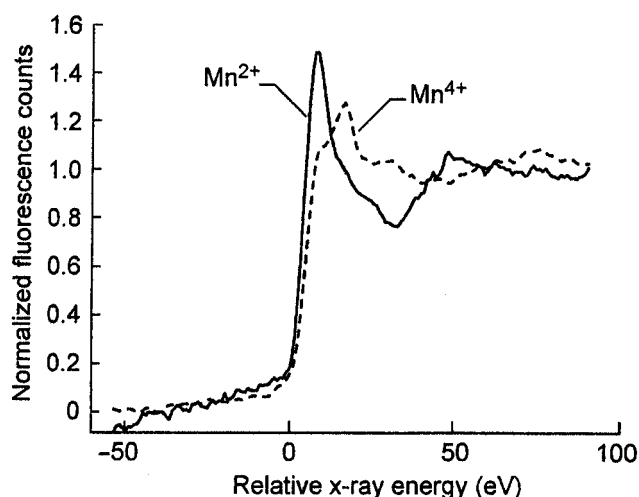


Figure 3. MicroXANES spectra of manganese oxidation in Southern yellow pine wood. Solid line is control wood: dashed line is wood inoculated with *Phanaerochaete chrysosporium*.

Metal-based wood preservatives have also been detected with the X26A microprobe. When lumber is pressure treated with chromated copper arsenate (CCA), the desired outcome is complete conversion of the toxic, more mobile Cr^{6+} species to the less toxic, less mobile Cr^{3+} species. Preliminary microXANES data of the ratio of Cr^{6+} to Cr^{3+} detected Cr^{3+} and not Cr^{6+} in wood stored for two years after CCA pressure treatment (11).

Extended X-Ray absorption fine structure (EXAFS)

EXAFS probes the local atomic and chemical environment of a selected element. By analyzing the modulations in the X-ray absorption coefficient at energies just above the X-ray absorption edge threshold, EXAFS measurements give quantitative information about coordination species, number, and distance. Extended X-ray absorption refers to the sinusoidal variation of the X-ray absorption coefficient as a function of X-ray photon energy, which occurs on a spectrum after each absorption edge of an element and extends for up to 1500 keV (Figure 2).

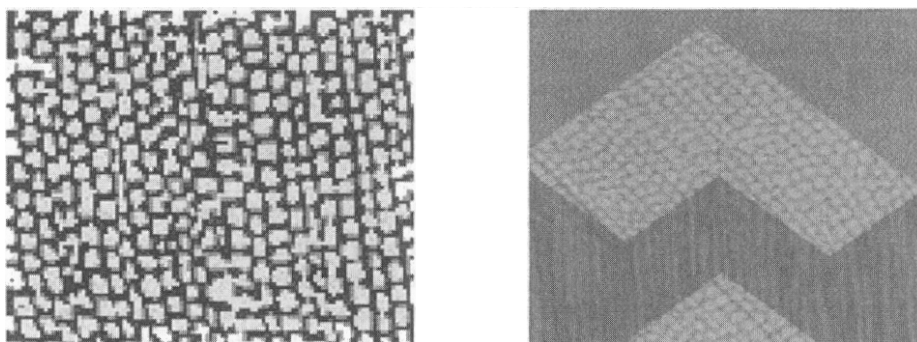
Bull et al. (12) measured copper and arsenic K-edge EXAFS of CCA-treated pine wood (*Pinus radiata*). They report that the data are consistent with arsenate

anions bound to copper and chromium ions isolated from other heavy elements at all depths into the wood.

X-Ray Computed Microtomography

The XCMT instrumentation at NSLS beamline X27A has been described previously (13,14). Briefly, the facility is equipped with a single-crystal YAG:Ce scintillator with peak emission at 540 MM for converting X-ray an attenuation map to a visible image. The scintillator is coupled to a cooled charge-coupled device (CCD) by a mirror/lens combination. The CCD detector, with 1317 x 1035 pixels, can record data to reconstruct up to 1035 horizontal slices simultaneously. The beamline instrumentation can be illuminated by a filtered 'white' X-ray beam with energy of around 18 keV or by a monochromatized beam with a 1% bandpass and energy tunable between 4 and 14 keV. The monochromator is comprised of a highly efficient pair of W-B₄C multilayers deposited on Silicon substrates with properties well matched to the synchrotron source beam. Data for wood decay was collected with the monochromator tuned at 8.5 keV, which is in the range of the biologically important transition metals iron and manganese. A Si-III channel cut monochromator which replaced the multilayer monochromator on X274 was used to verify results reported here. Microtomograms are obtained with resolutions down to 3-micrometer voxels and fields of view of over 5 millimeters.

A specimen is mounted in a vertical position on a motorized x-y stage for centering in the optical field of view. The specimen stage in turn is mounted to a rotational stage attached to a tilt and translational stage for prealignment of the rotational stage to the CCD. During data acquisition, the specimen is rotated over a full 180 degrees, producing angle-dependent views of the attenuation map digitally recorded by the CCD camera. The recorded views of the specimen are processed using a Fourier-based Fast Filtered Back Transform algorithm to generate transverse images or slices through the sample for every row of the CCD. The reconstructed slices are stacked to produce a volume representation of the specimen. The IBM Data Explorer software was used for volume rendering. Representative tomographic images of Southern pine wood are given in Figure 4. A reconstructed, smoothed and segmented slice of control wood is given in Figure 4a and a reconstructed volume in Figure 4b. Density differences were observed in the reconstructed images, reflecting differences in chemical composition of structures within the wood.



Slice

Volume

Figure 4, Microtomographic images of control Southern yellowpine wood

Summary

Non-intrusive synchrotron methods have been successfully applied to detect and follow chemical mechanisms of fungal wood decay and metal-based wood treatments.

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