



# ForSeaDiscovery: ESR11

## Identification of potential biomarkers of wood for provenance analysis

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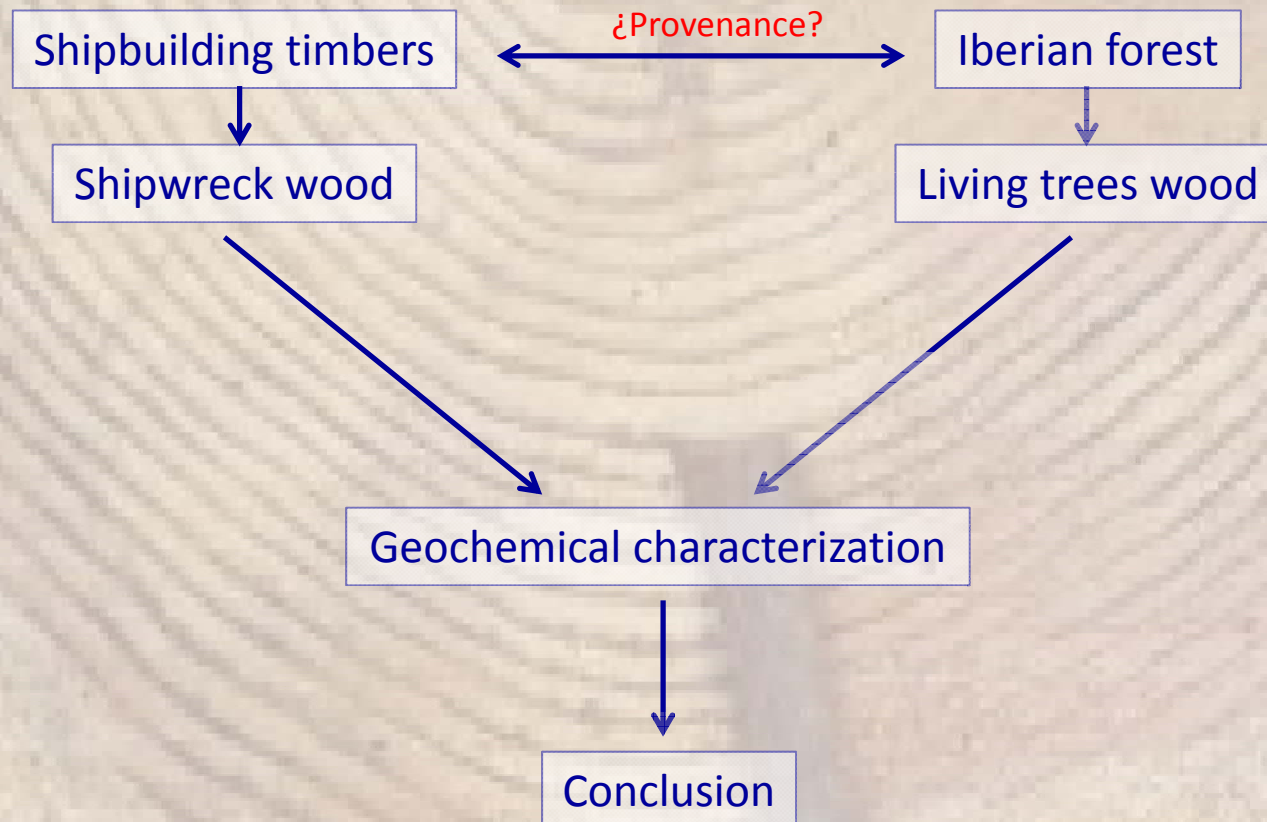
Supervised by

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## Iberian shipwreck and wood provenance

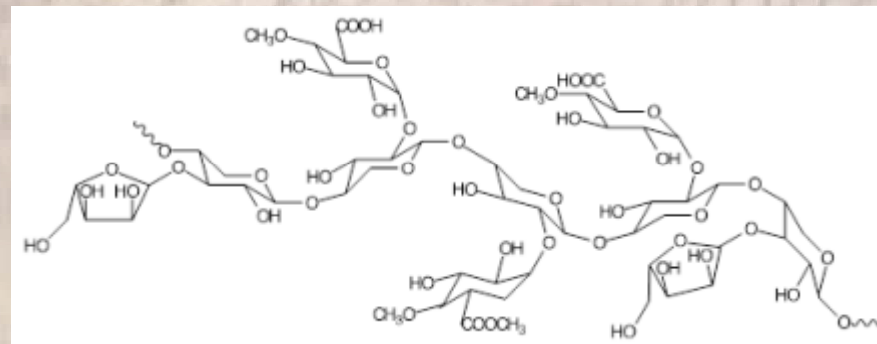
Wood, an important feedstock that influenced modern age society and economy

Contributed to shipbuilding development between the 15<sup>th</sup> and 17<sup>th</sup> century



## Wood organic components

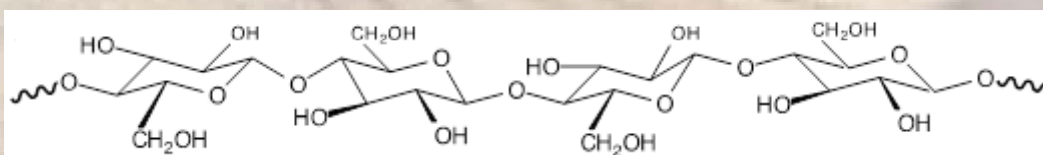
Wood is a complex material made up of hollow cells with a strong wall that consists mainly of three polymers: cellulose, lignin, and hemicelluloses.



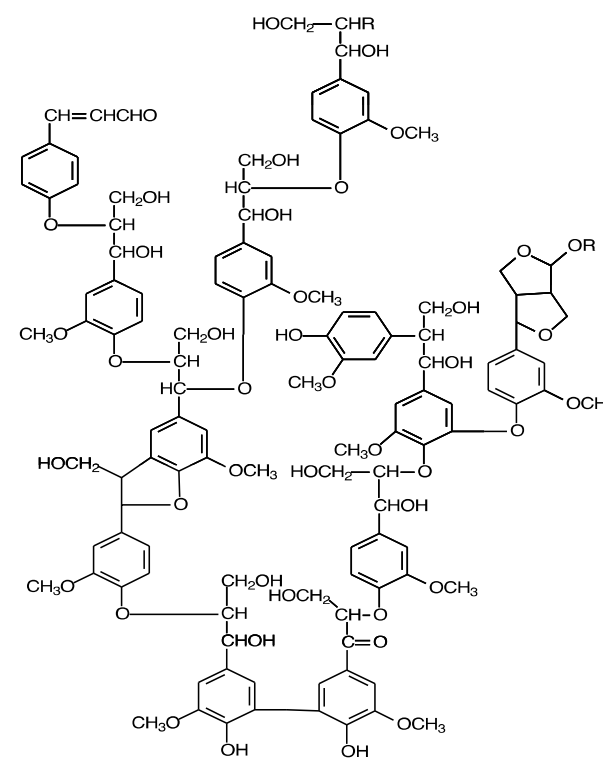
Hemicelluloses

Basic chemical composition of generic hardwoods and softwoods. Values were taken both from the literature (Picollo et 2011)

Wood contents	Hardwoods (%)	Softwoods (%)
Cellulose	40-50	40-50
Hemicelluloses	30-40	20-35
Lignin	20-25	25-35
Extractive and mineral substances	4-10	4-25



Cellulose



Lignin

## Archaeological Wood

Archaeological wood is found in bad state due to attack by biological agents.

Physical and chemical properties of archaeological wood vary depending on environment conditions.

Its inner parts are better preserved than its outer parts that are more degraded.



A Roman ship being excavated - Museum of Roman Ships:  
[www.comune.pisa.it](http://www.comune.pisa.it)

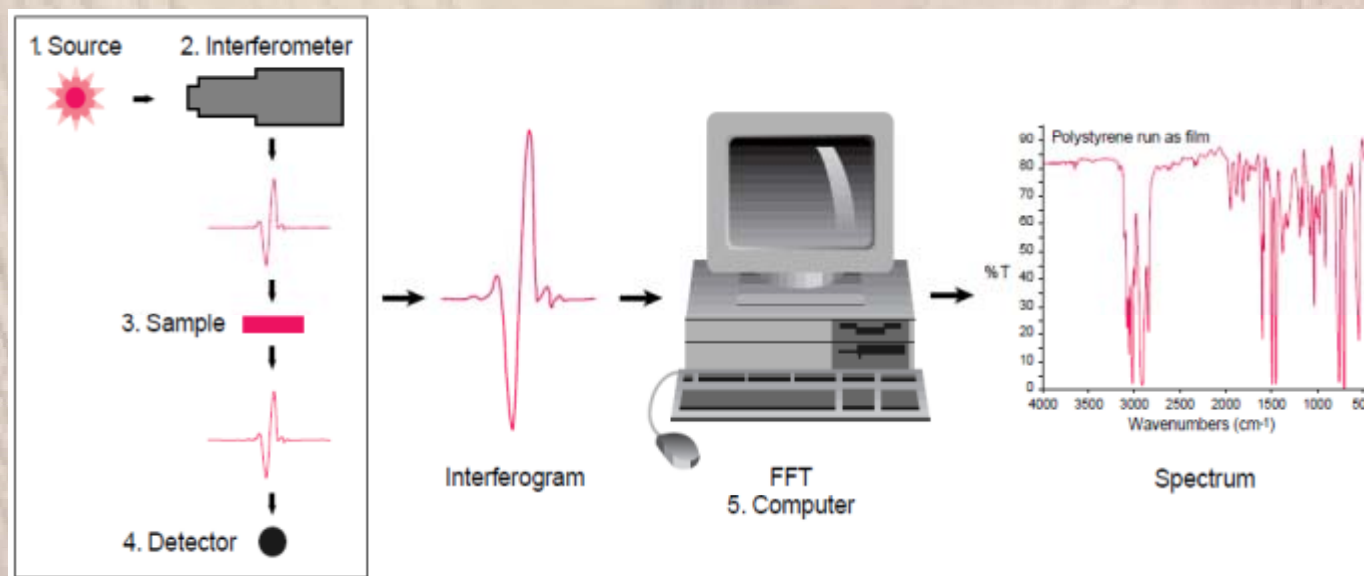


View along the keel of the remains of the Tantara B wreck being excavated  
photo ©1996 Institute of Nautical Archaeology

Archaeological wood can be specially cellulosic or lignitic or any combination of these, due to chemical changes underwent.

## FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance

The radiation emerging from the source passes through an interferometer to the sample before reaching a detector

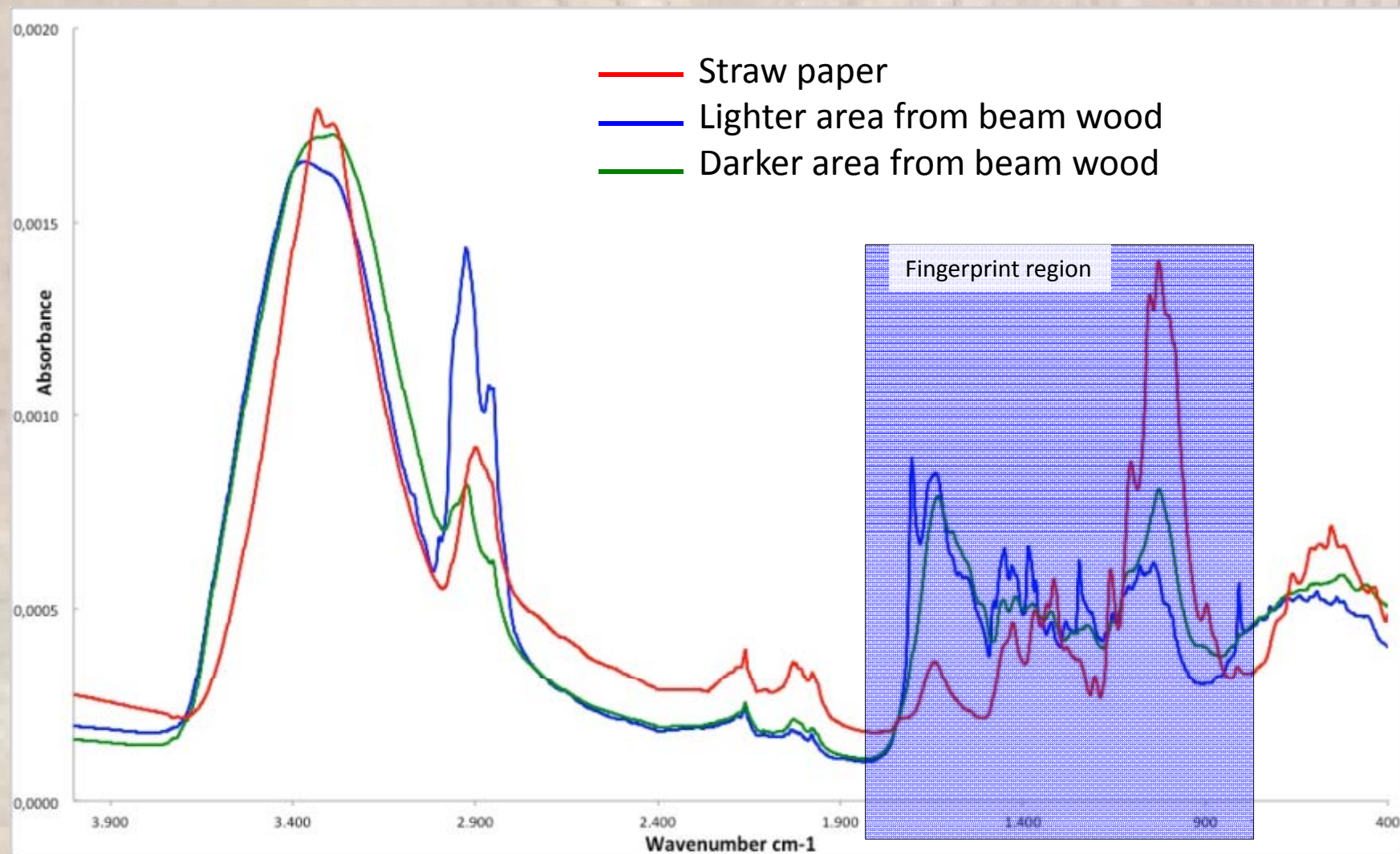


Basic step of an FTIR spectrometer

The beam is splitted when it passes through the sample, due to changes in the vibrational energy of the molecules.

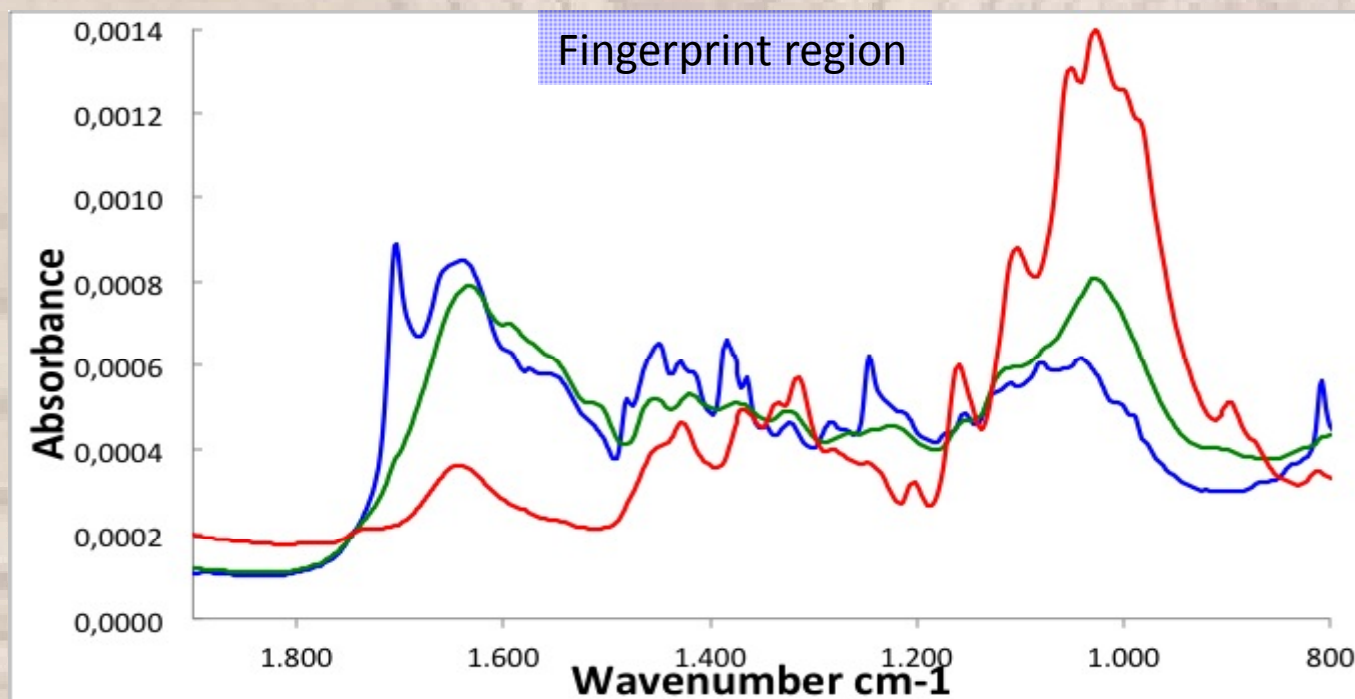
The absorption spectrum allows identifying bands that characterize vibration of atoms functional groups present in the molecule.

## FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance



FTIR spectra of beam wood and straw paper

## FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance



- Straw paper
- Lighter area from beam wood
- Darker area from beam wood

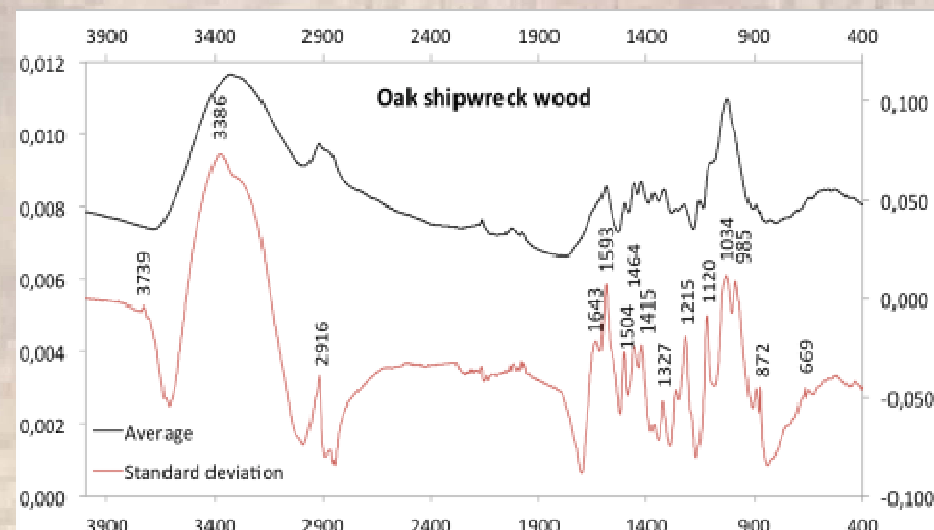
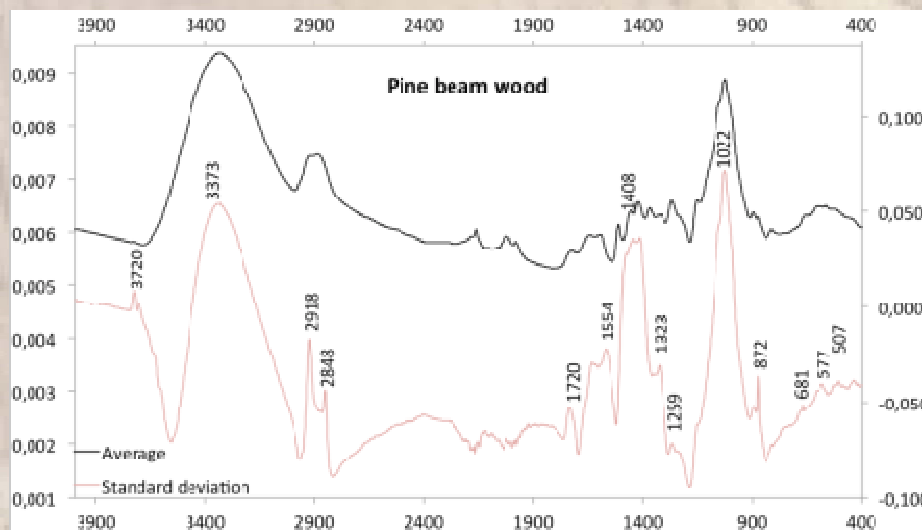
Wavenumber (cm <sup>-1</sup> )	Functionality
3400	O-H of alcohols, phenols and acids
2970-2850	CH <sub>2</sub> , CH- and CH <sub>3</sub>
1750-1720	C=O of esters, ketones, aldehydes
1700-1550	Conjugated C=O and C=C
1600	Aromatic ring
1515-1500	Aromatic ring
1460	CH
1420	Aromatic ring and CH
1240-1330	Lignin S and G unit and OH
1140	G-Guaiacyl lignin and C-O
1128	S-Syringyl lignin and C-O
1025-1035	C-O-C
897	Anti-symmetric out of phase stretching in pyranose ring

Main bands of infrared spectrum of wood and their assignment to functionality (Esteves et al 2013)



## FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance

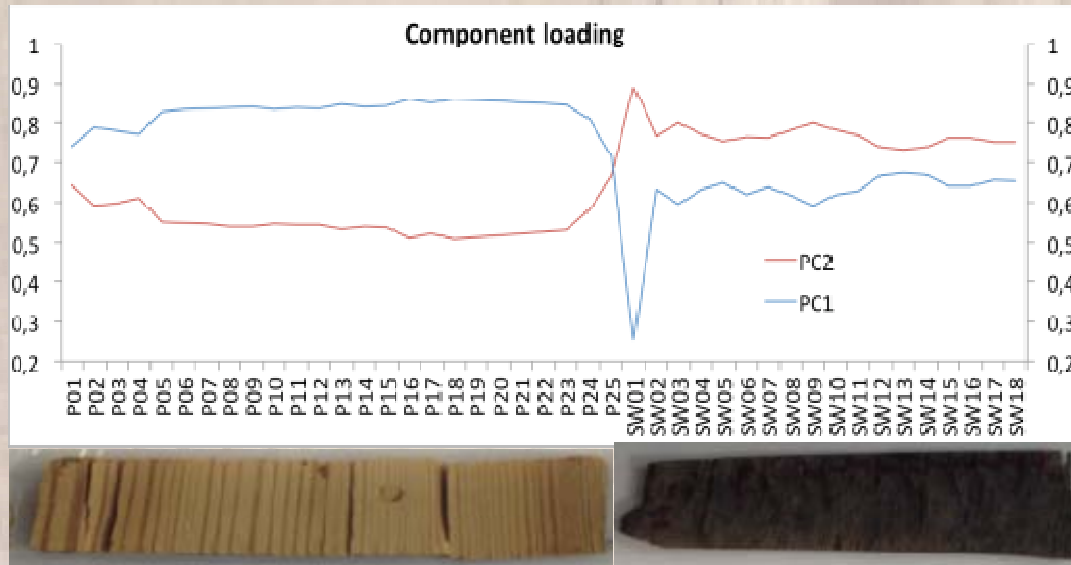
### Variations in FTIR spectra



	Pine beam wood	Oak shipwreck wood
Cellulose peaks	1009, 3373	995, 1034, <b>3386</b>
Hemicellulose peaks	872, 3373	872, 1034, <b>3386</b>
Lignin peaks	1259-G, 1323, 1554, 2840, 3373	1120-S, 1215, 1327-S, 1464, 1504, 1593, <b>3386</b>
Other compounds	507, 577, 681, 2818	669, 2916



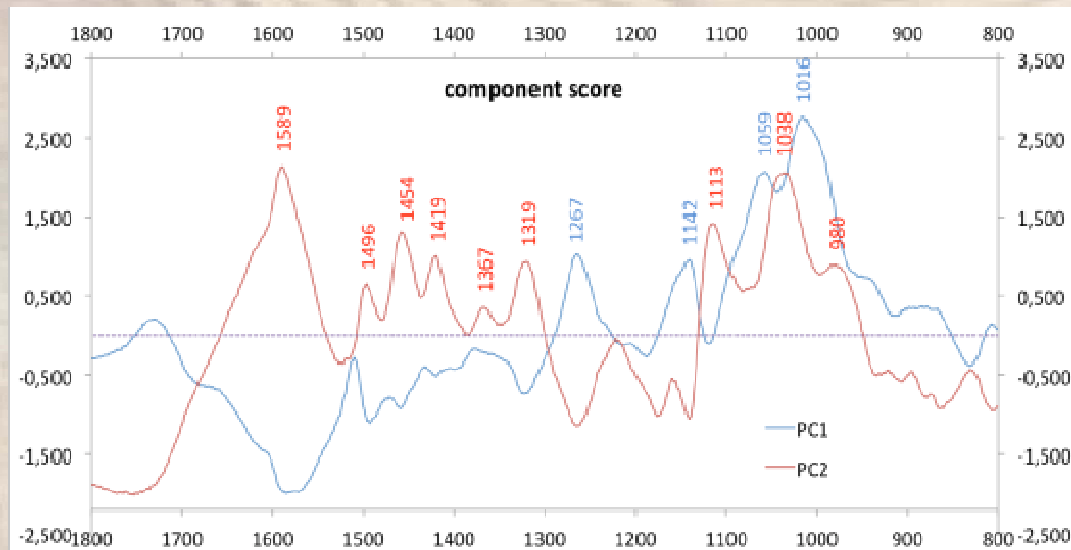
# FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance



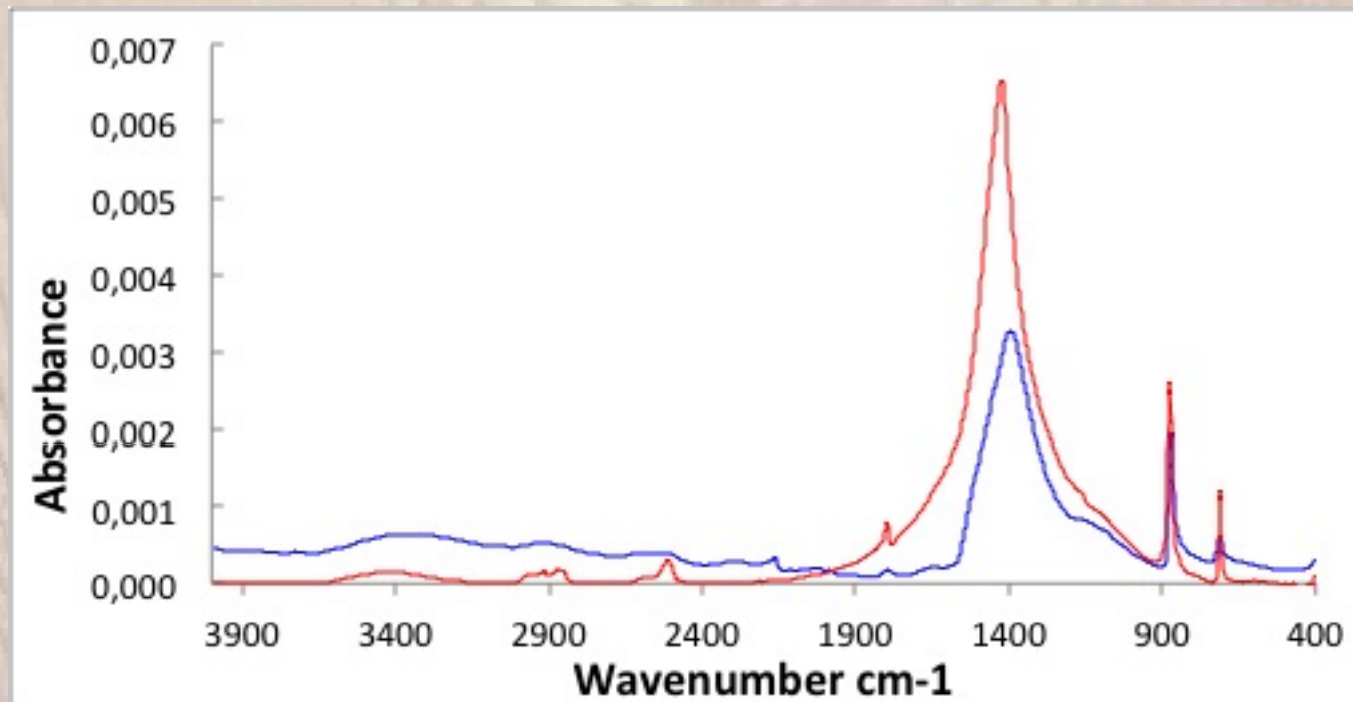
Principal component analysis

Discrimination by sample type

Discrimination by component



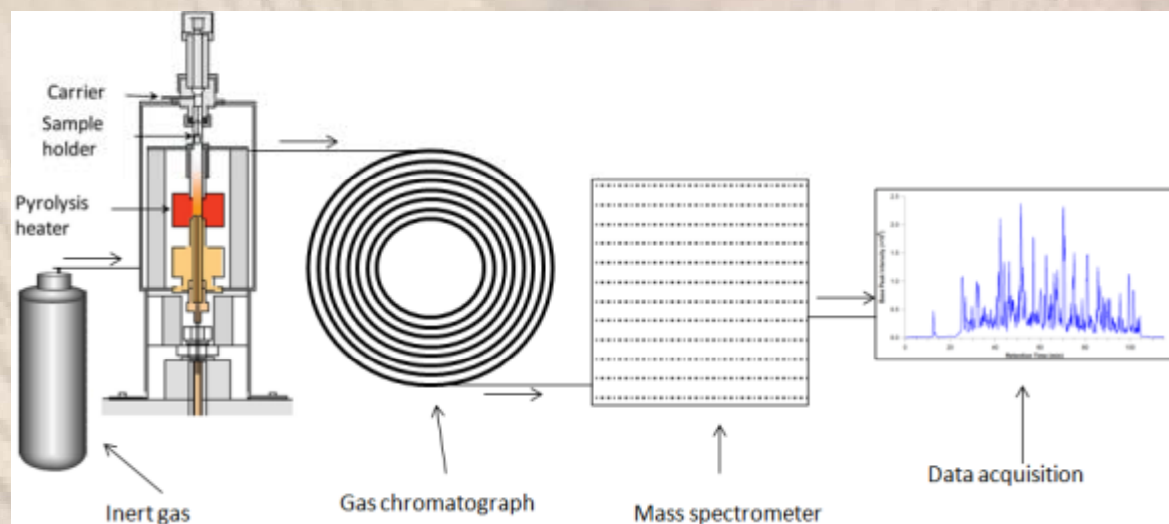
## FTIR-ATR: Fourier Transform Infrared-Attenuated Total Reflectance



- Pure carbonate
- Wall of hole in shipwreck wood (biogenic carbonate)

## Py-GCMS: Pyrolysis coupled to gas chromatography and mass spectrometry

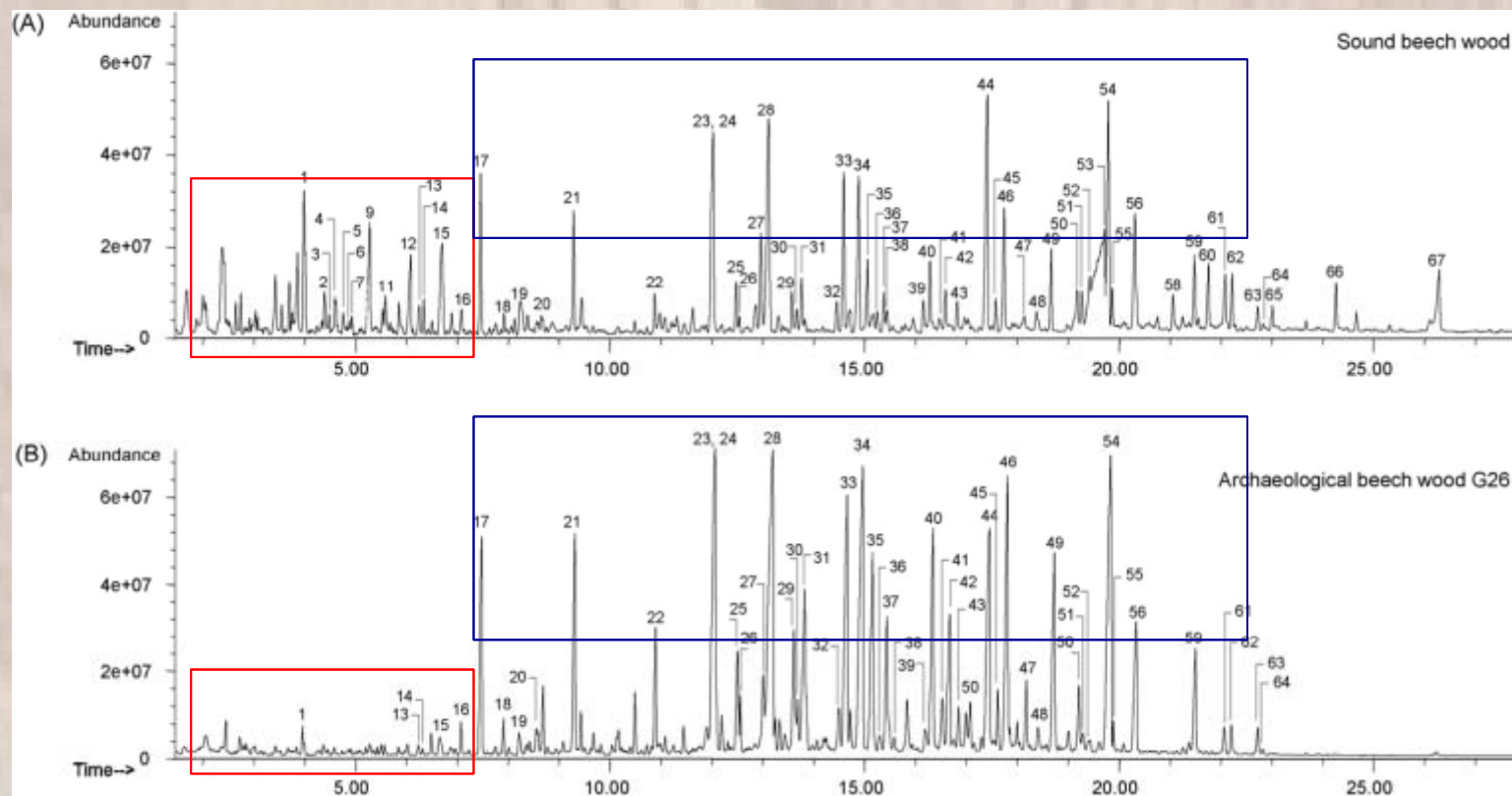
Pyrolysis is a thermochemical degradation reaction caused by heating samples at temperatures of 400-900°C in an inert atmosphere during a short time.



Integrated system Py-GC-MS

Products yields are transported by a flow of inert gas to the chromatographic column, where compounds are separated. Following in the mass spectrometer that is equipped with an ion trap where it takes place the separation based on the mass to charge ratio ( $m/z$ ) of the ions. The signal from the detector is computed and converted in a mass spectrum.

## Py-GCMS: Pyrolysis coupled to gas chromatography and mass spectrometry



Py-GC/MS profiles (Lucejko et al. 2009)

Polysaccharide

Lignin

**Methods testing and ability improving**

Analysis of shipwreck wood by FTIR/PY-GCMS

Analysis of beam wood by FTIR/PY-GCMS

Analysis of pine wood cores by FTIR/PY-GCMS

In process

**Analysis (after crossdating) of pine wood cores collected in Andalusia**

February

**Oak sampling in Basque Country and analysis (after crossdating)**

Must be planned

**Shipwreck woods sampling and analysis (after crossdating)**

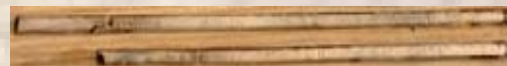


Avoid as much as possible contamination during sampling and dendro-analysis

Coring without lubricating borer



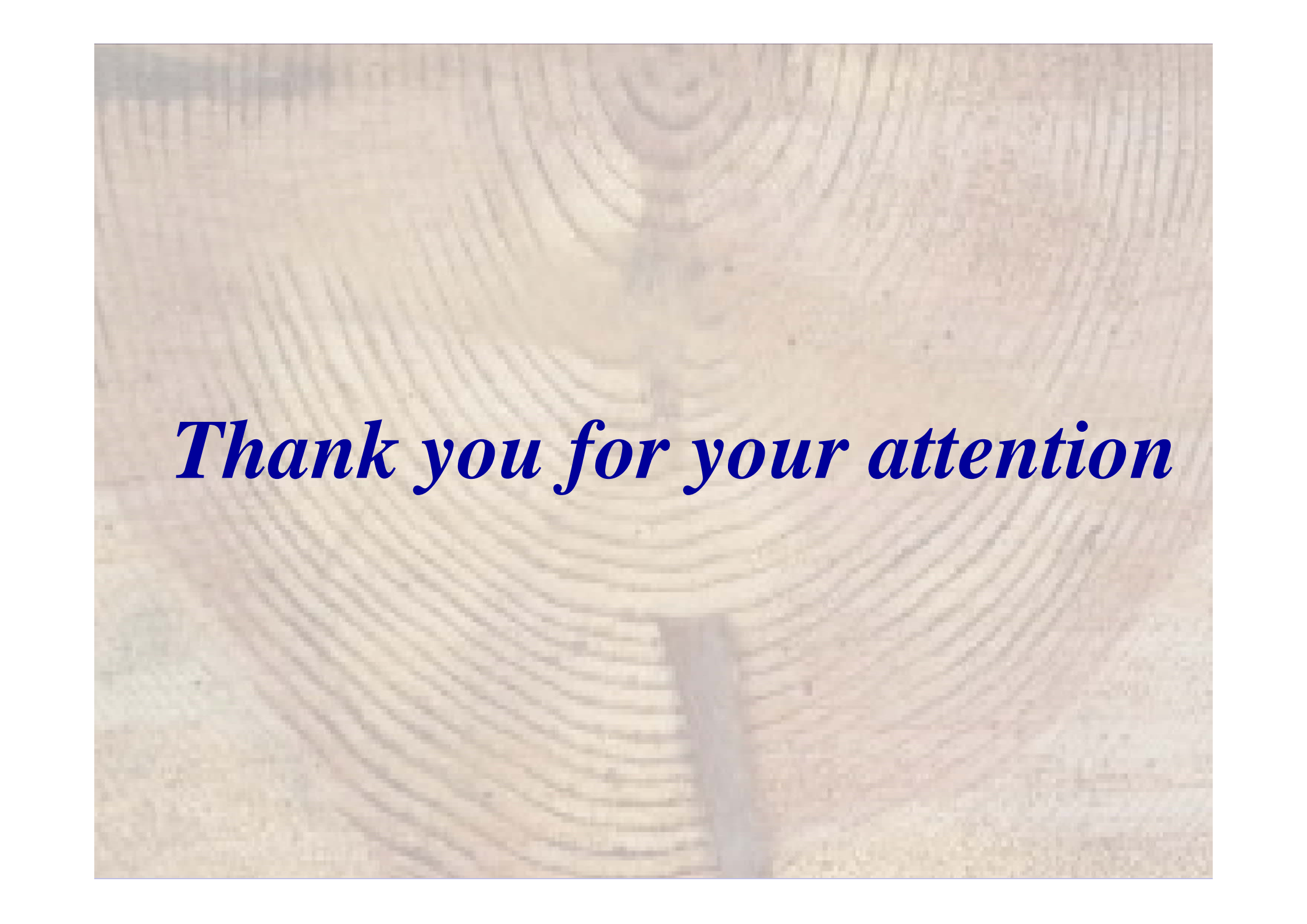
Avoid gluing during crossdating



Sufficient amount of sample (at least two similar cores per tree)



Avoid scarred shipwreck wood (burnt, attacked...)

The background of the slide is a close-up, slightly blurred image of a light-colored wood surface, showing concentric growth rings and a vertical grain pattern. The text is centered over this background.

***Thank you for your attention***