Aalto University
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Alterations in wood ultrastructure induced by drying

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Outline

- **Background**
  - motivation
  - fiber cell wall alterations upon drying (chemical pulp / hornification)
  - deuteration of cellulose / detection with IR spectroscopy
- **Experimental design**
  - sampling / deuteration / controlled drying design
- **Results**
  - method validation – deuteration reversibility, repeatability, reproducibility
  - drying of wood: impact of temperature and relative humidity
  - drying comparison: wood and pulps
  - water retention of pulps – WRV and D_2O / FT-IR correlation

Background

Motivation and significance

Drying-induced changes in native wood cell wall structure

Fundamental study – initial changes on ultrastructural level

- **trees grow in water-swollen conditions**
- **drying of wood after felling unavoidable – logistics or process requirement**
- **changes in physical properties of wood after drying are well-known**

Affects the "novel" utilization of cellulose from wood

Biofuels production

- **accessibility of cellulose – acid and enzymatic treatments**

Cellulose nano-objects fabrication

- **microfibril separation – accessibility/aggregation of individual microfibrils**

Background

Approach

Drying-induced changes in native wood cell wall structure

Fundamental study – initial changes on ultrastructural level

Analytical techniques vs. sample preparation

- **water removal or replacement with solvent**
- **alteration of native wood cell wall ultrastructure**

Deuteration of wood

- **no sample preparation**

FT-IR analysis of deuterated samples

- **minimal sample preparation**

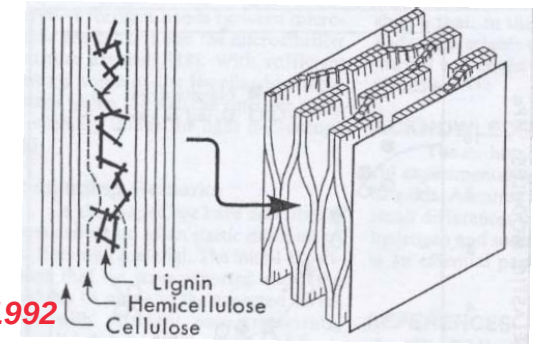
Background

Pulp drying – hornification

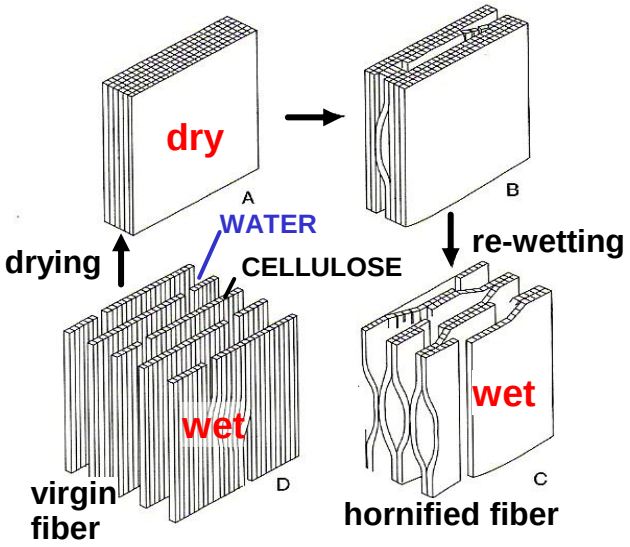
Irreversible changes in wood pulp upon water removal

Reduction of swelling ability – feature of low yield (chemical) pulp

- **structural changes – internal fiber volume decrease**
- **collapse of pores between walls and closure of capillary voids**
- **hydrogen bonding / increased degree of cross-linking within cell wall**
- **tighter packing of cellulose chains – aggregation of fibrils**



Scallan & Tigerström; JPPS 1992

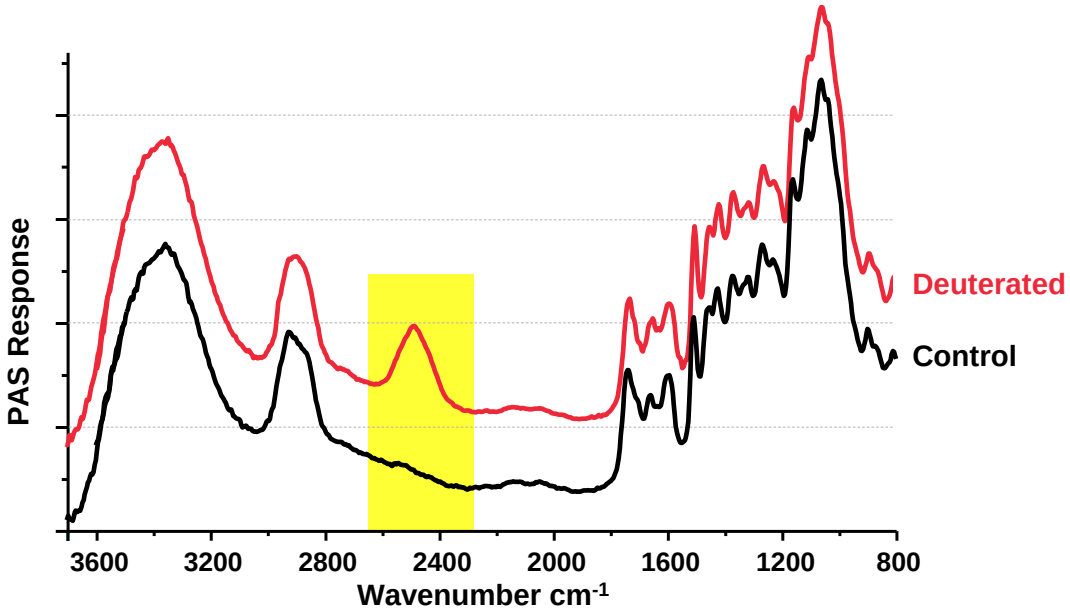


Background

Experimental concept

Deuterium exchange coupled with FT-IR spectroscopy

Exposure of cellulose to D_2O – accessible OH groups readily exchanged:
R-OH → R-OD



Background

Experimental concept

Deuterium exchange coupled with FT-IR spectroscopy

Exposure of cellulose to D_2O – accessible OH groups readily exchanged:
R-OH → R-OD

Photoacoustic (PAS) detection

- **special sample cell**
- **absorbed IR radiation >> heat in sample >> partial release to gas at interface**
- **resulting pressure changes detected with sensitive microphone**

- **no sample preparation (requires dry sample*)**
- **measurement depth (10-100 µm)**

Background

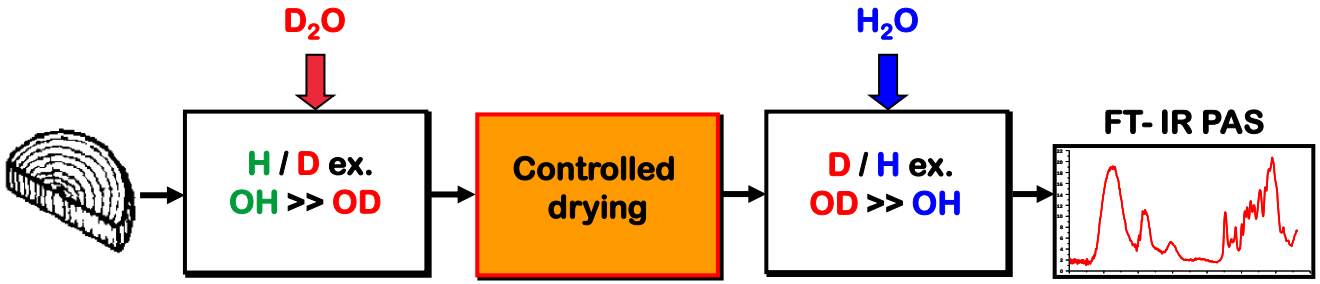
Overall objective and approach

Changes in wood ultrastructure during initial dehydration

Deuteration of accessible OH groups originally present in fresh wood / fiber

Monitoring their conversion to inaccessible OD during drying:

Detection of inaccessible OD groups by FT-IR

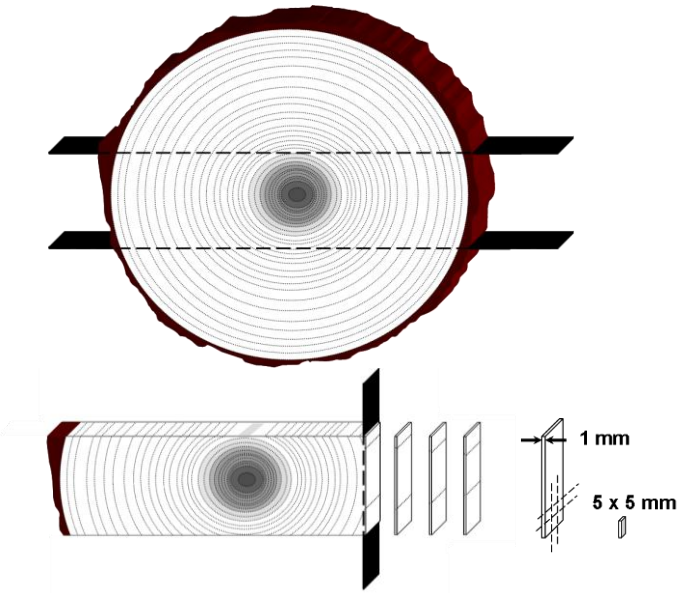


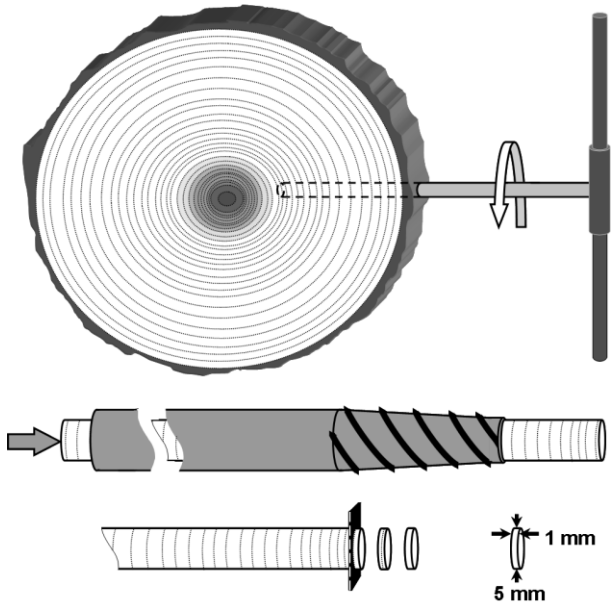
Analysis and correlation of pulp and wood testing results

Experimental

Wood sampling and pulps

- freshly felled pine and spruce wood

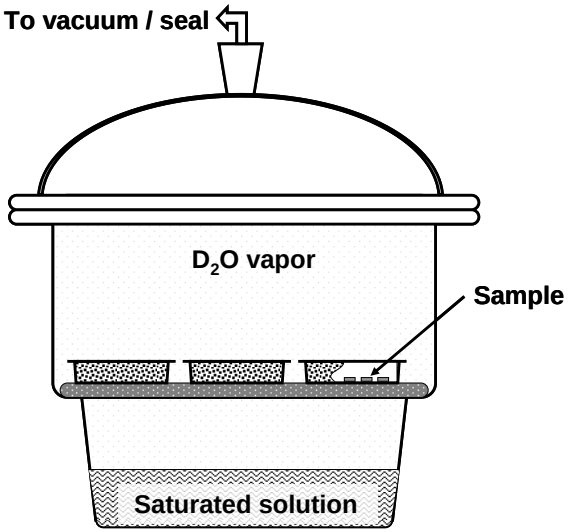




Experimental

Deuteration and controlled drying

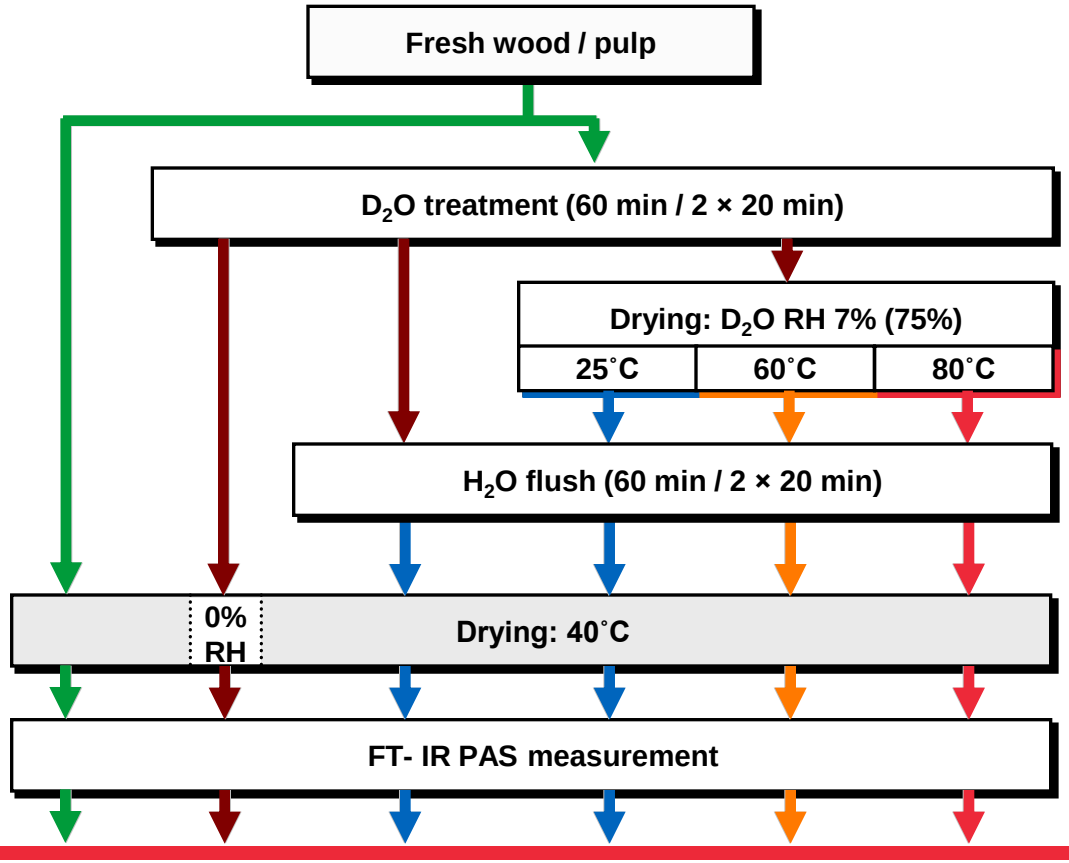
- wood immersed in liquid D_2O, pulps deuteration in plastic bags
- controlled D_2O RH drying: saturated salt solutions for RH control
- desiccators placed in oven; time of drying: 7 days



	25º C	80º C
	Estimated RH %	Estimated RH %
NaCl	75…77	74…76
NaOH	6…7	~7

Experimental

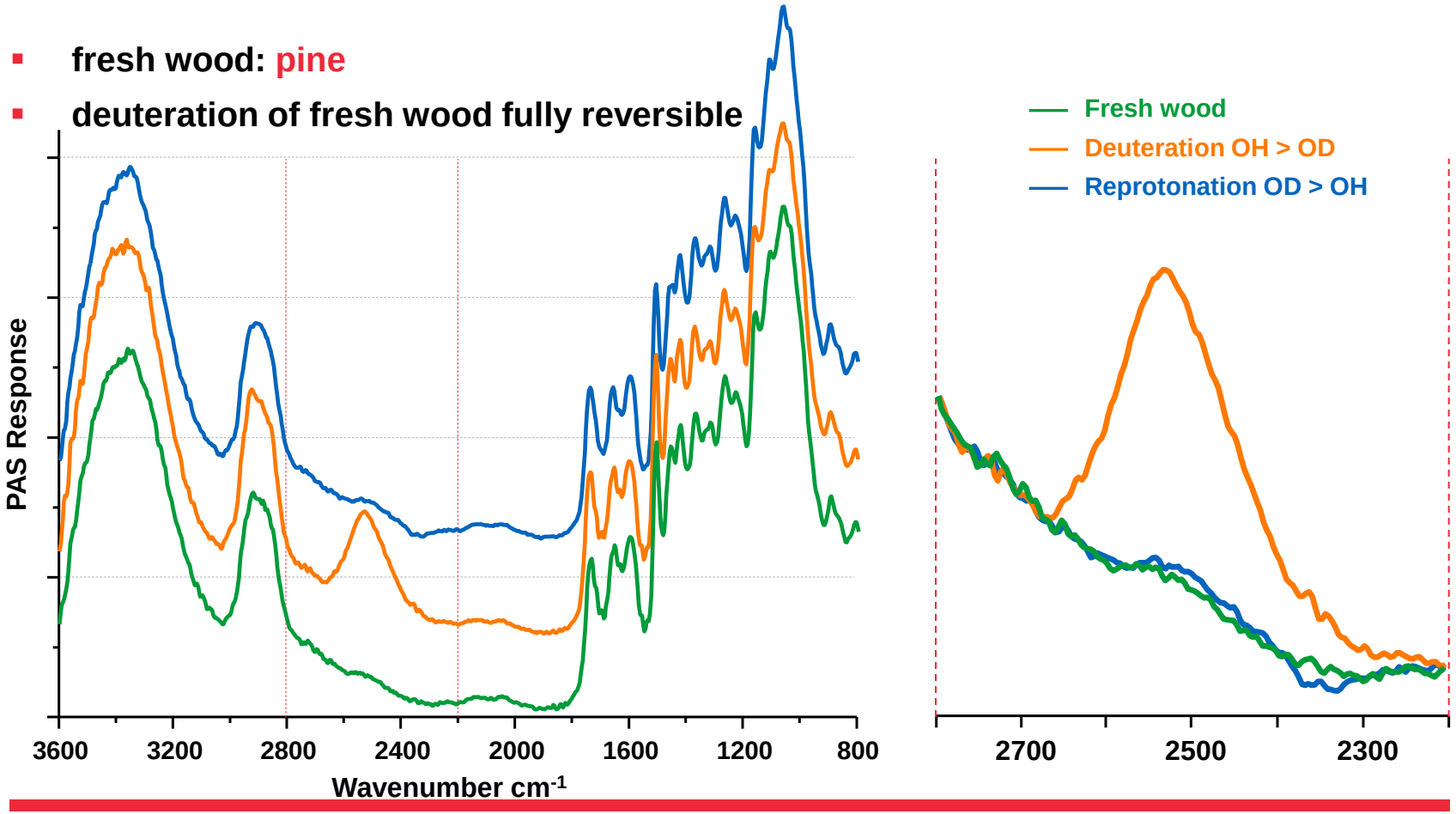
Design of experiments



Deuteration reversibility

Extent of OD exchange and reprotonation

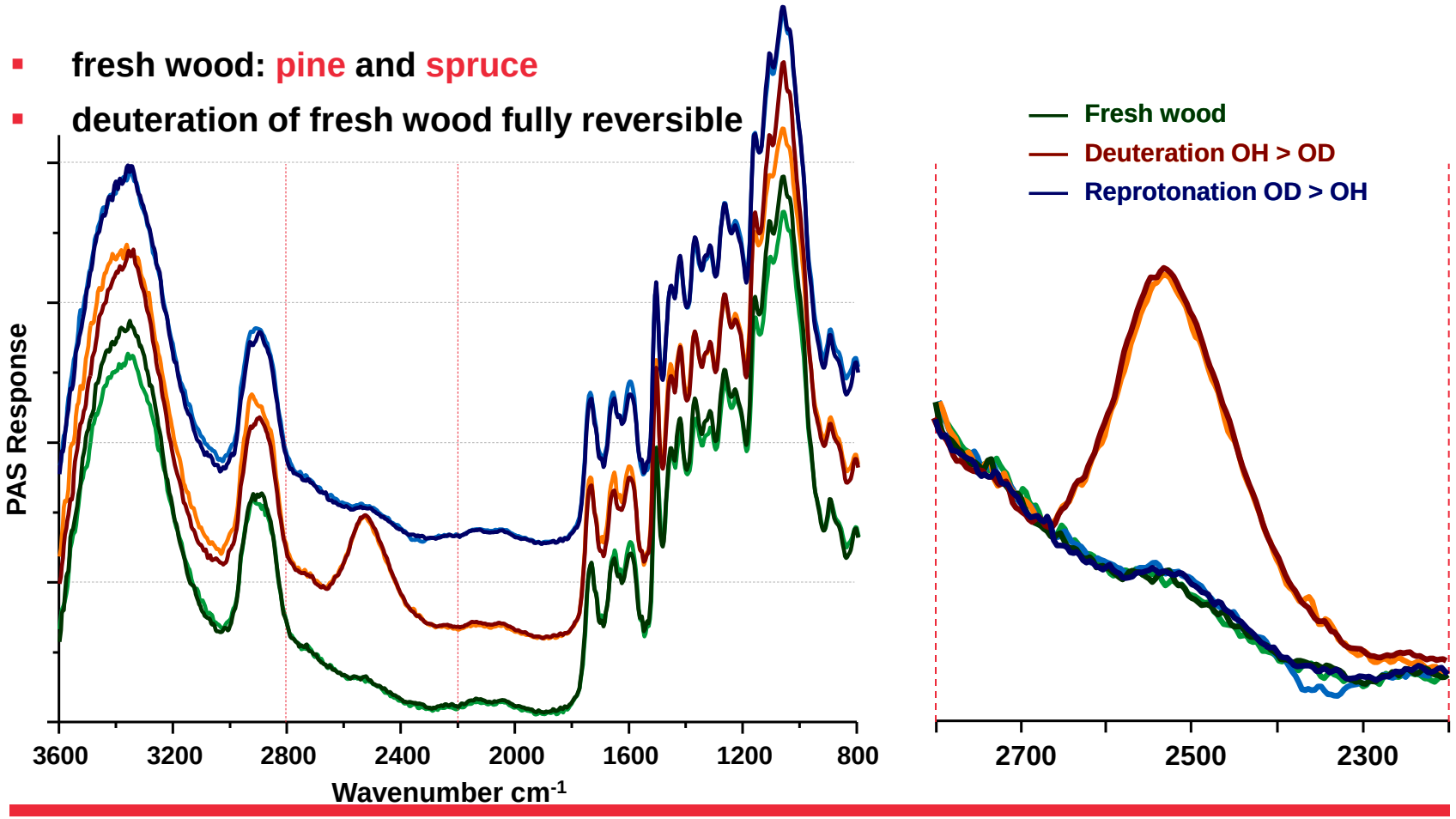
- fresh wood: pine
- deuteration of fresh wood fully reversible



Deuteration reversibility

Extent of OD exchange and reprotonation

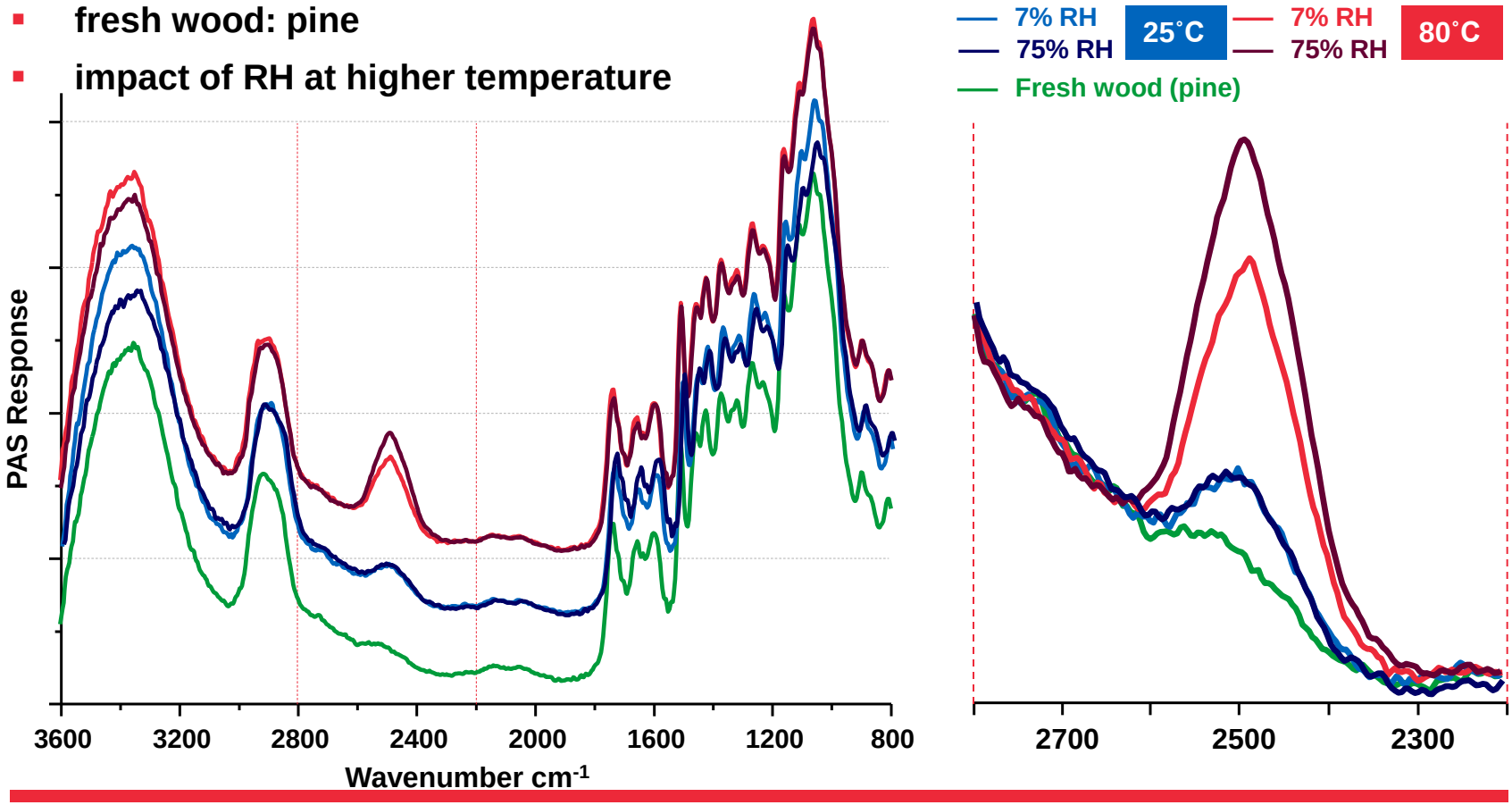
- fresh wood: pine and spruce
- deuteration of fresh wood fully reversible



Controlled drying

Impact of temperature and relative humidity

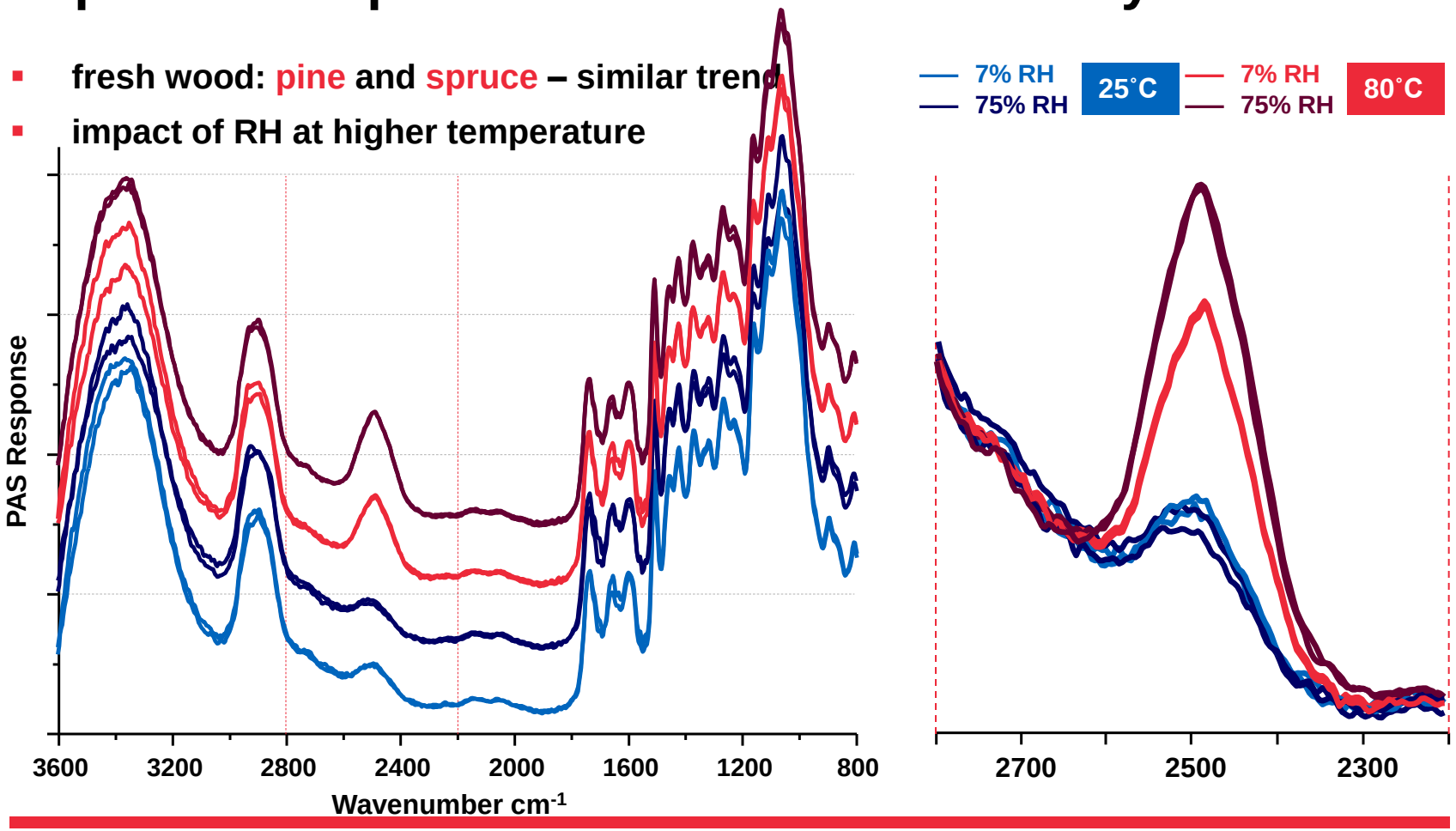
- fresh wood: pine
- impact of RH at higher temperature



Species comparison

Impact of temperature and relative humidity

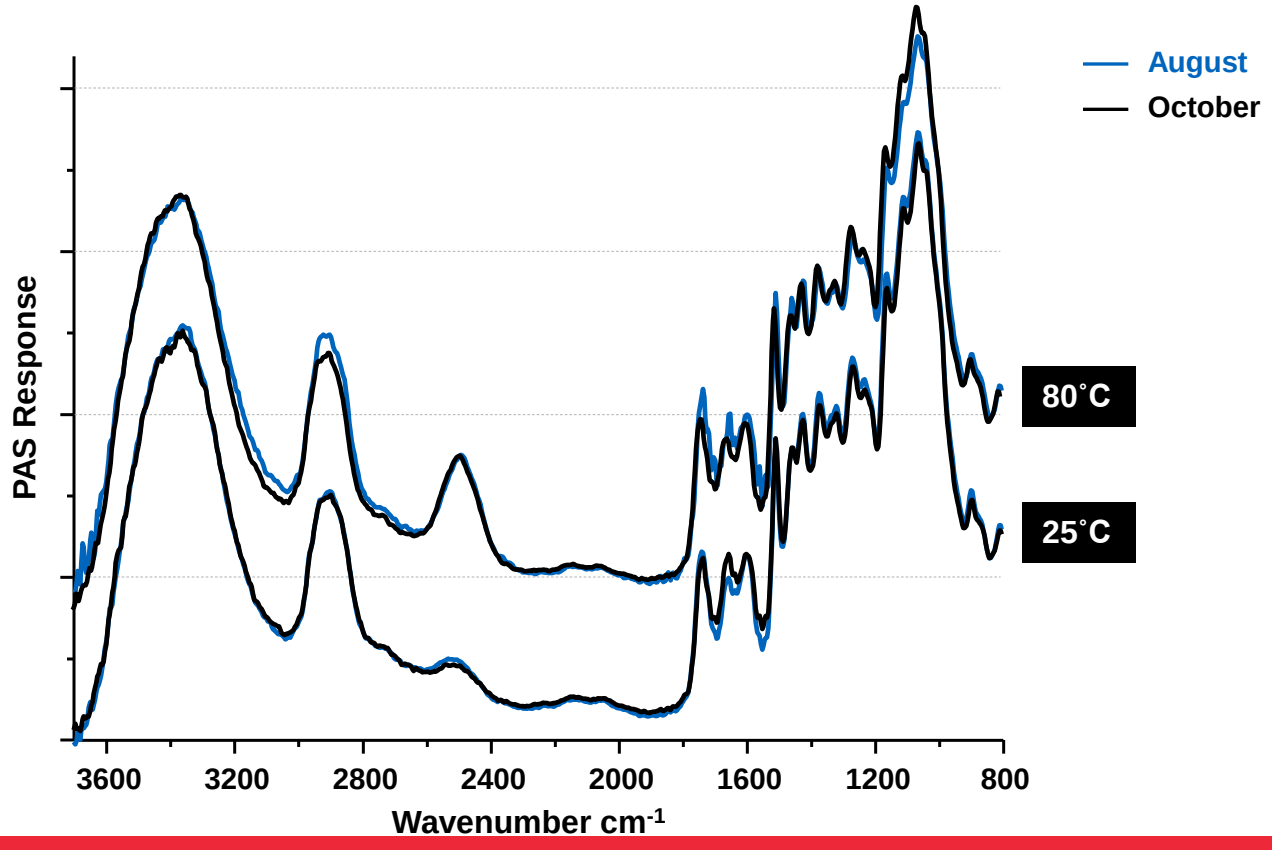
- fresh wood: pine and spruce – similar trend
- impact of RH at higher temperature



Reproducibility

August / October measurement comparison

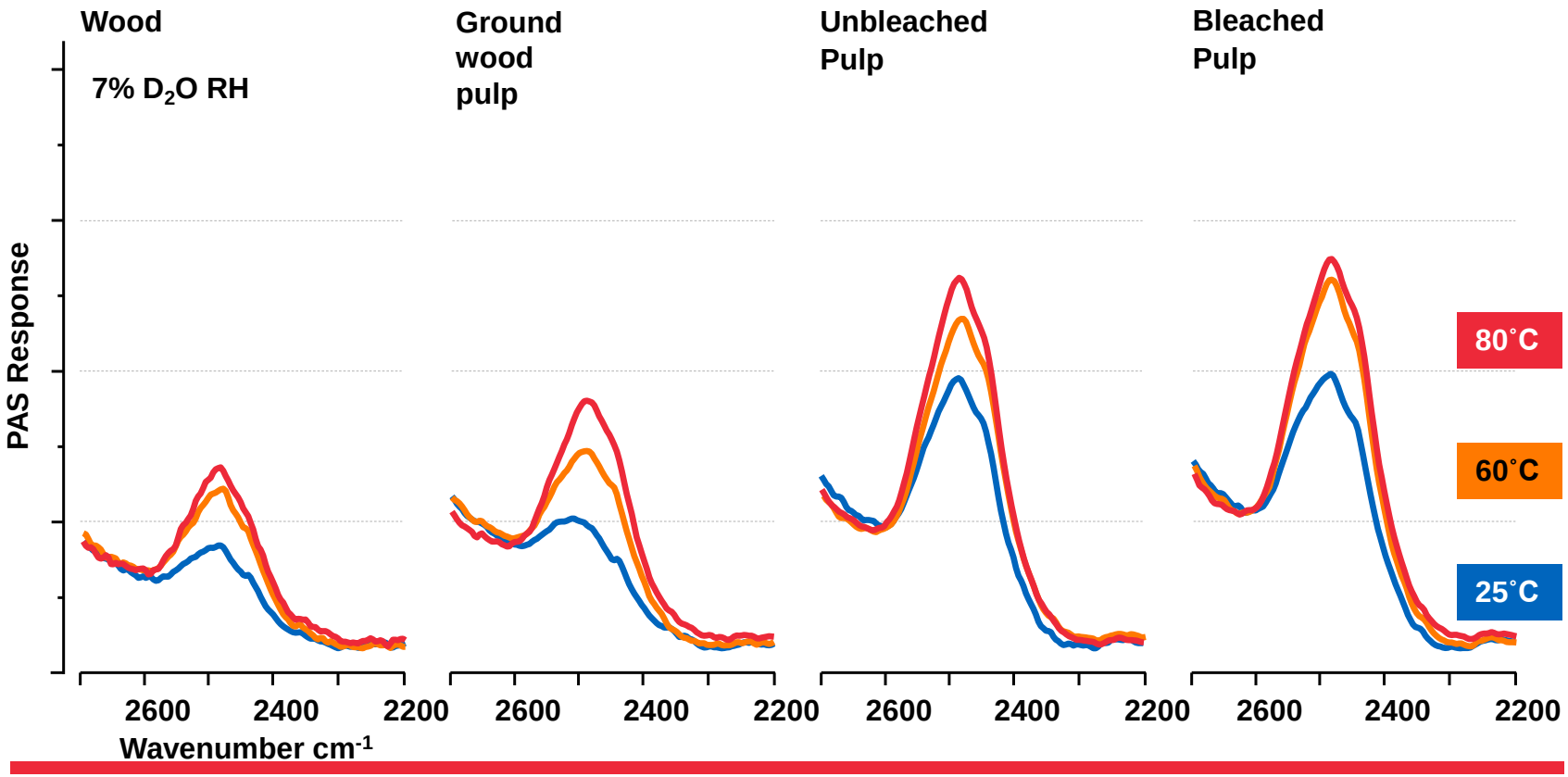
- samples collected in August and October from different locations



Comparing drying: wood and pulp

Wood and pulps – impact of temperature

- greater extent of alterations at higher temperature; more pronounced in pulps

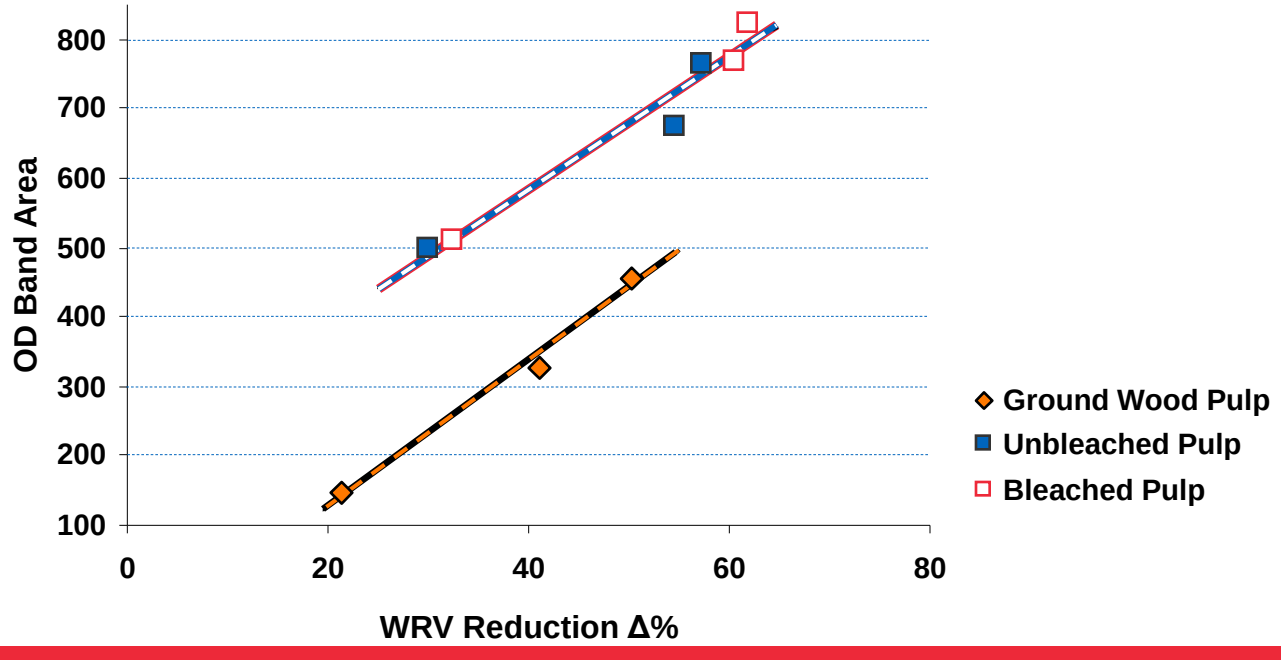


WRV vs. Deuteration / FT-IR

Comparison of techniques for pulp samples

- good correlation in measurement range
- deuteration / FT-IR can indicate hornification in pulps
- similar trend in wood

7% H_2O / D_2O RH



Summary

Main observations

Deuteration reversibility and accessibility for wood

- **fully reversible**

Controlled wood and pulp drying – temperature

- **inaccessible OD in dried sample – irreversible alterations**
- **extent affected by temperature**

Water retention of pulps and correlation with deuteration studies

- **WRV reduction in dried pulps correlates with amount of OD in dried pulps**

Changes in wood ultrastructure occur during initial drying and these alterations appear to be similar to the changes occurring in chemical pulp fibers upon drying.

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Suchy et al. *Biomacromolecules* **2010**, *11*, 515-520.
Suchy et al. *Biomacromolecules* **2010**, *11*, 2161-2168.

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Moisture content after drying
Impact of temperature

- pulps

groundwood		unbleached kraft pulp		bleached kraft pulp	
MC (%)	WRV (%)	MC (%)	WRV (%)	MC (%)	WRV (%)
65.4	146	67.0	146	66.1	143
5.5	124	5.1	117	4.8	110
0.2	105	1.0	92	1.3	82
0.2	96	1.6	89	0.6	81