

# Newsprint Research

- This is a summary of research conducted at the Smithsonian Center for Materials Research and Education (SCMRE) during the summer of 2003.
- This work was conducted by two interns, Evan Quasney and Kathy Hufford, under the supervision of David Erhardt and Charles Tumosa.
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# Newsprint

## permanence and degradation: newsprint over the last 100 years

new research presented by:

kathy hufford  
massachusetts institute of technology

evan quasney  
university of michigan

13 august 2003  
10:00 am  
scmre theater



Smithsonian Center  
for Materials Research and Education

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# **Permanence and Degradation: Newsprint Over the Last 100 Years**

**Kathy Hufford**  
**Massachusetts Institute of Technology**

**Evan Quasney**  
**University of Michigan**

Charles Tumosa, Ph.D.  
W. David Erhardt, Ph. D.

# Introduction

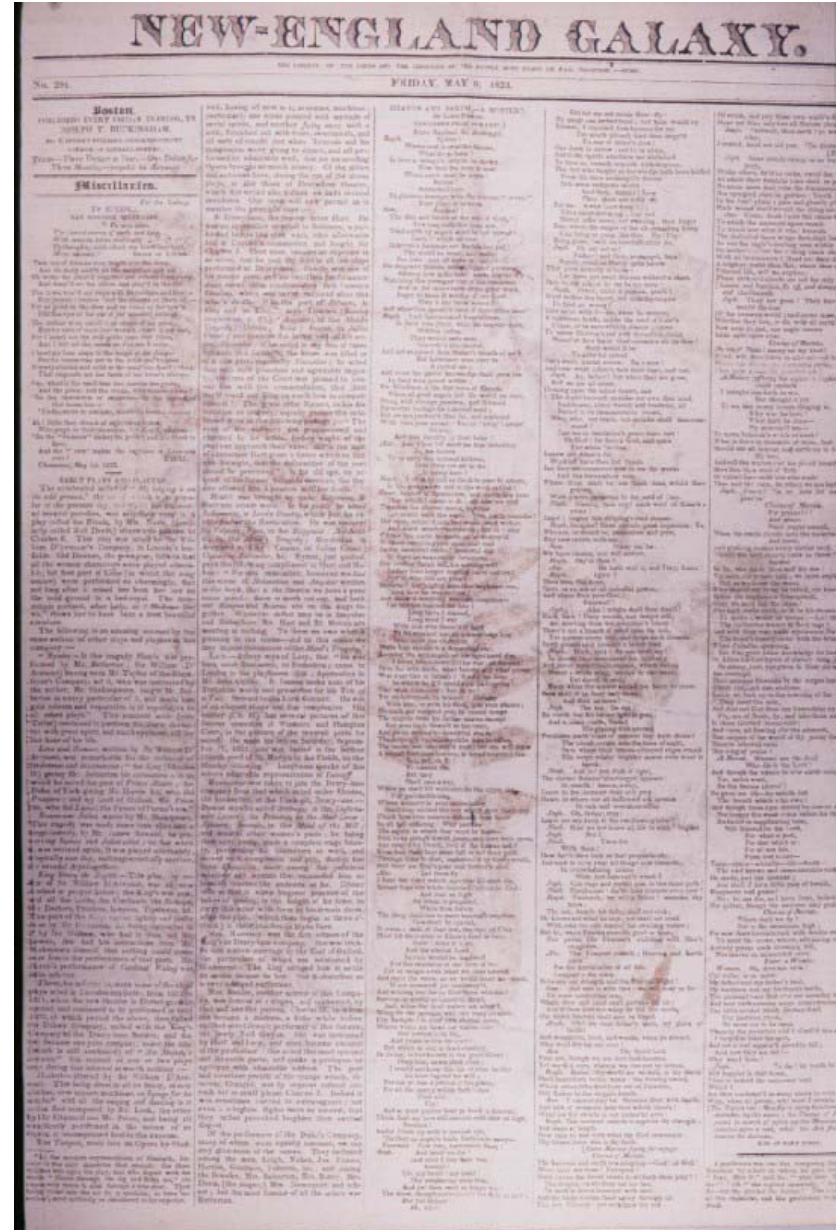
- Printed material on paper dominates written communication
- Paper records have finite life ... how finite?
- Mechanical concepts addressed and discussed
- Chemical concepts linked to mechanical properties
- Scope of research newsprint-specific





# Wood-based Newspapers Tested

06/01/2003	Washington Post
11/17/2001	Washington Post
11/27/2000	Washington Post
08/03/1999	Washington Post
12/02/1998	Washington Post
11/02/1997	Washington Post
07/10/1997	Washington Post
01/26/1997	Washington Post
05/07/1995	Washington Post
11/14/1993	Washington Post
02/08/1983	Washington Post
10/20/1983	Washington Post
07/07/1985	Washington Post
09/11/1985	Washington Post
12/14/1988	Washington Post
12/15/1988	Washington Post
10/25/1999	Washington Post
07/01/1975	Vineland Times Journal
12/11/1960	New York Times
09/13/1950	Christian Science Monitor
12/02/1934	Topeka Daily Capital
04/11/1915	Detroit Free Press
10/07/1905	Detroit Free Press
01/03/1890	The World
05/07/1875	New York Semi-Weekly Times



# Definitions

## Strain = $\Delta$ length / length

- extensibility of paper
- change in length

$$\varepsilon = \Delta L / L$$

## Stress = Force / Area

- 'strength' of the paper
- randomized based on sizing or technology

$$\sigma = F / A$$

## Stress-Strain Curve

- Graph of stress versus strain
- Basis for finding plastic and elastic regions

## Tensile (Young's) Modulus

- Numeric value of the flexibility / stiffness of the paper

$$E = \sigma / \varepsilon$$

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$\varepsilon$

$\sigma$

$\sigma$

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# Definitions

## Isotropic:

- Specimen behaves the same in all directions

## Orthotropic:

- Specimen behaves differently in mutually perpendicular directions

## Breaking Strain:

- Percent elongation at which a specimen fails

## Breaking Stress:

- Pressure at the breaking strain; tensile strength of specimen

## Region Deformation:

Elastic – Flexible Modulation of Specimen

Plastic – Permanent Irreparable Damage to Specimen

E

$\epsilon$

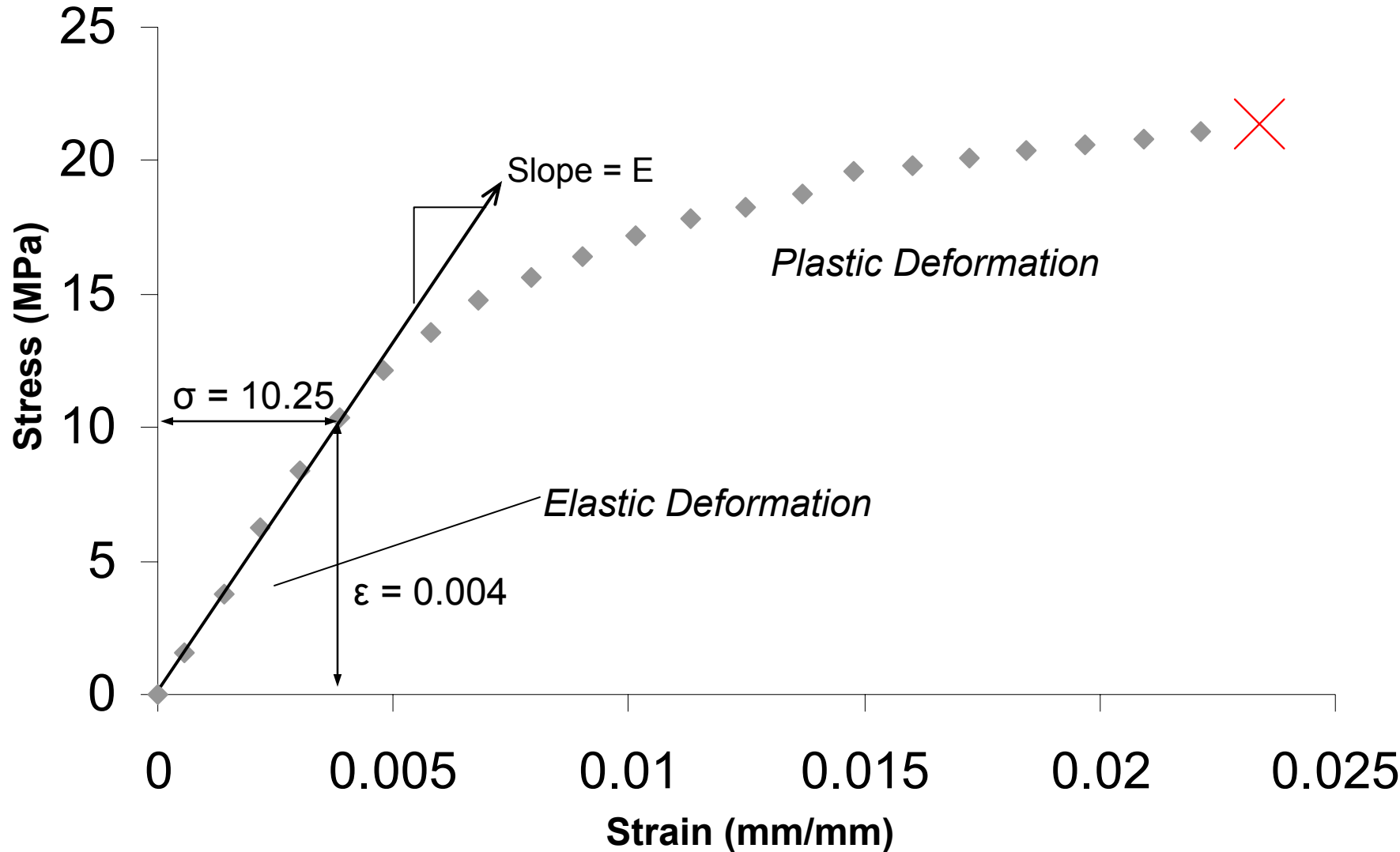
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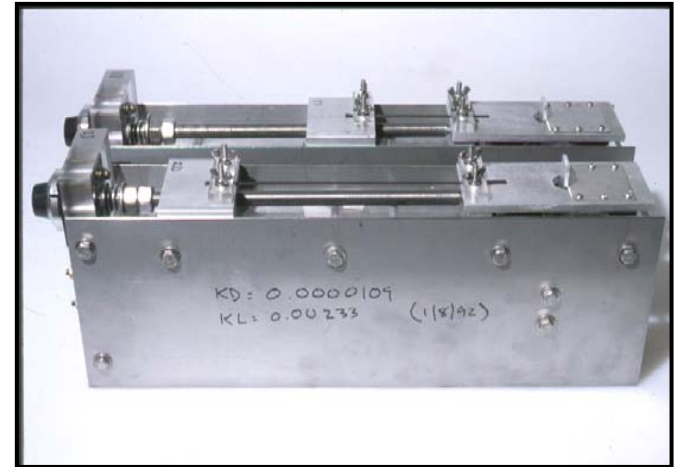
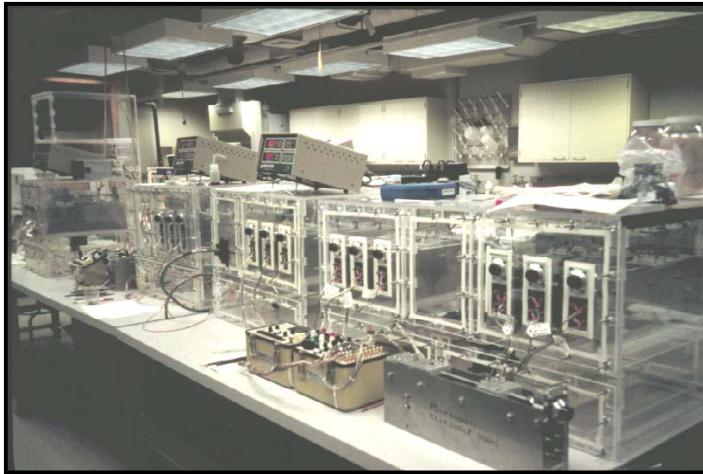
# General Stress-Strain Curve

Mancellinus Antonius, circa 1500, Vertical Dir





# Method

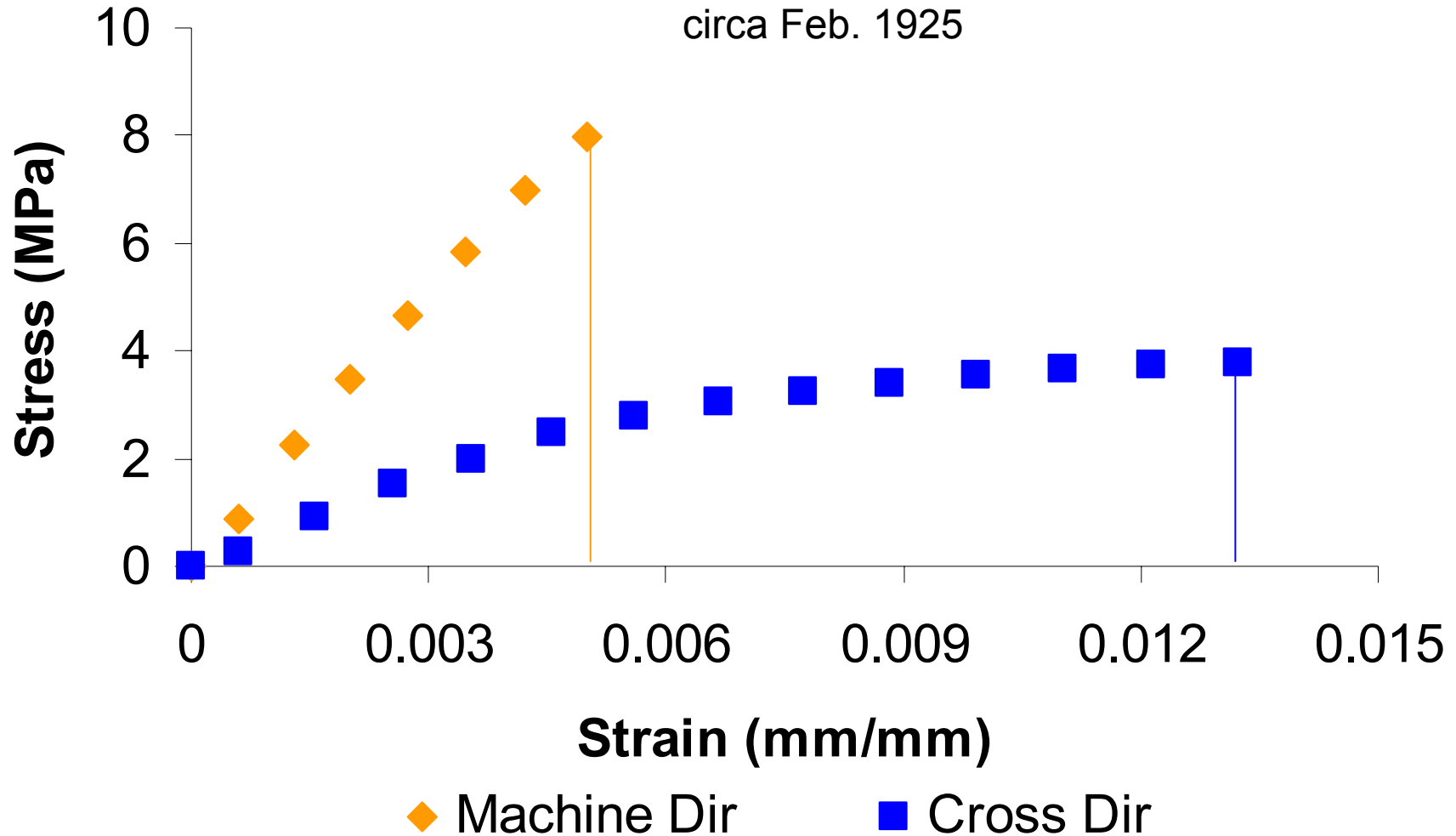


- Tests performed on screw-driven tensile tester in environmental chambers
- Incremental length change standard: 30-seconds, 1/200 (0.005) inches
- Tests performed between 42 – 52% RH and 22.5 – 24.2 deg. C
- 4 distinctly different sub-variations of each specimen examined

# Machine v. Cross Direction

## Directional Comparison of *Century Magazine*

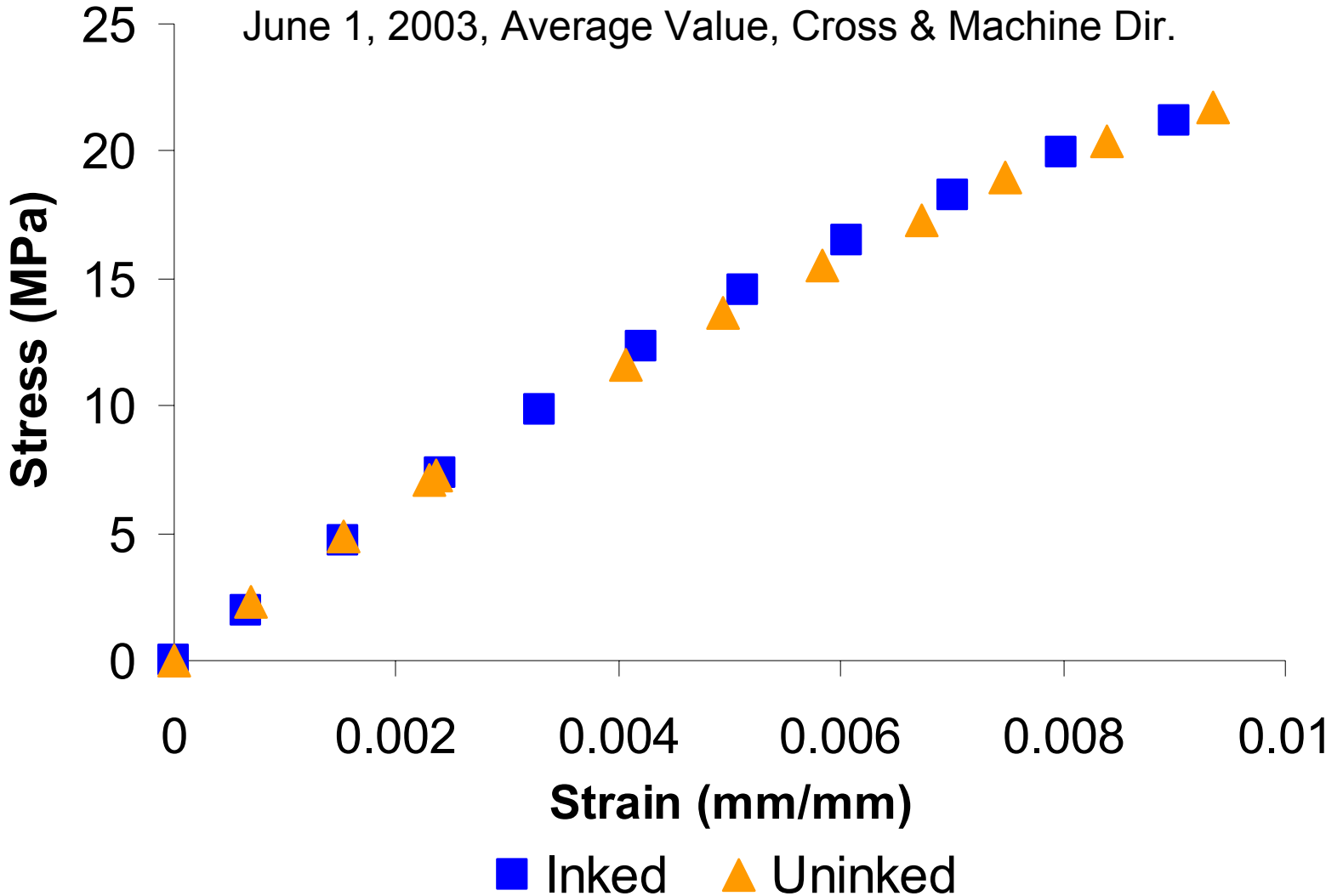
circa Feb. 1925



# Initial Application

## Tensile Strength of *The Washington Post*

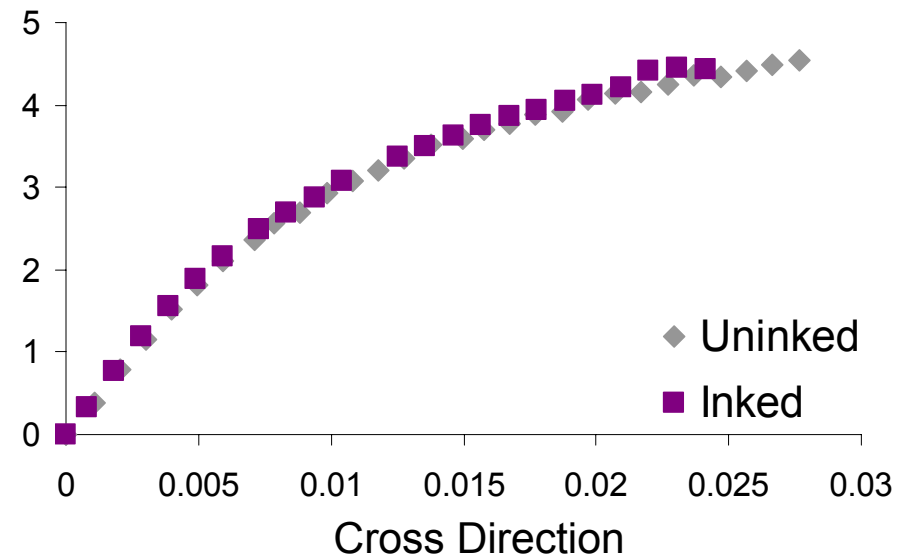
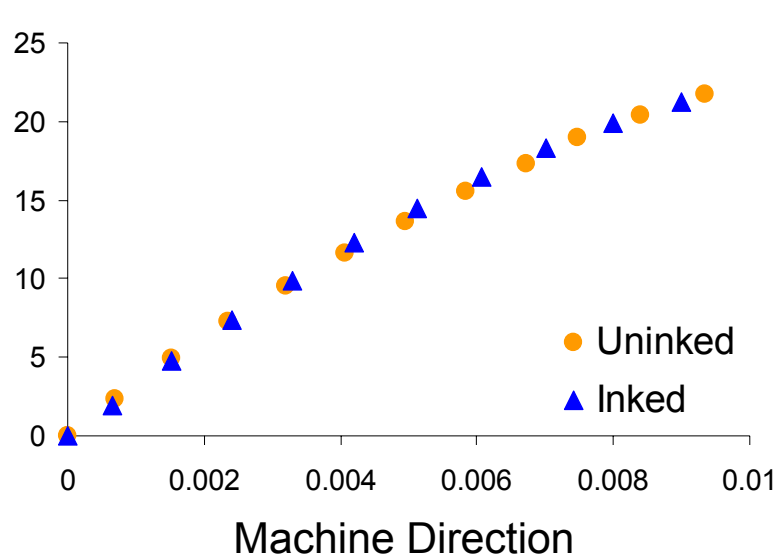
June 1, 2003, Average Value, Cross & Machine Dir.



# Initial Application

## Individual Axial Comparison of Inked v. Uninked Paper

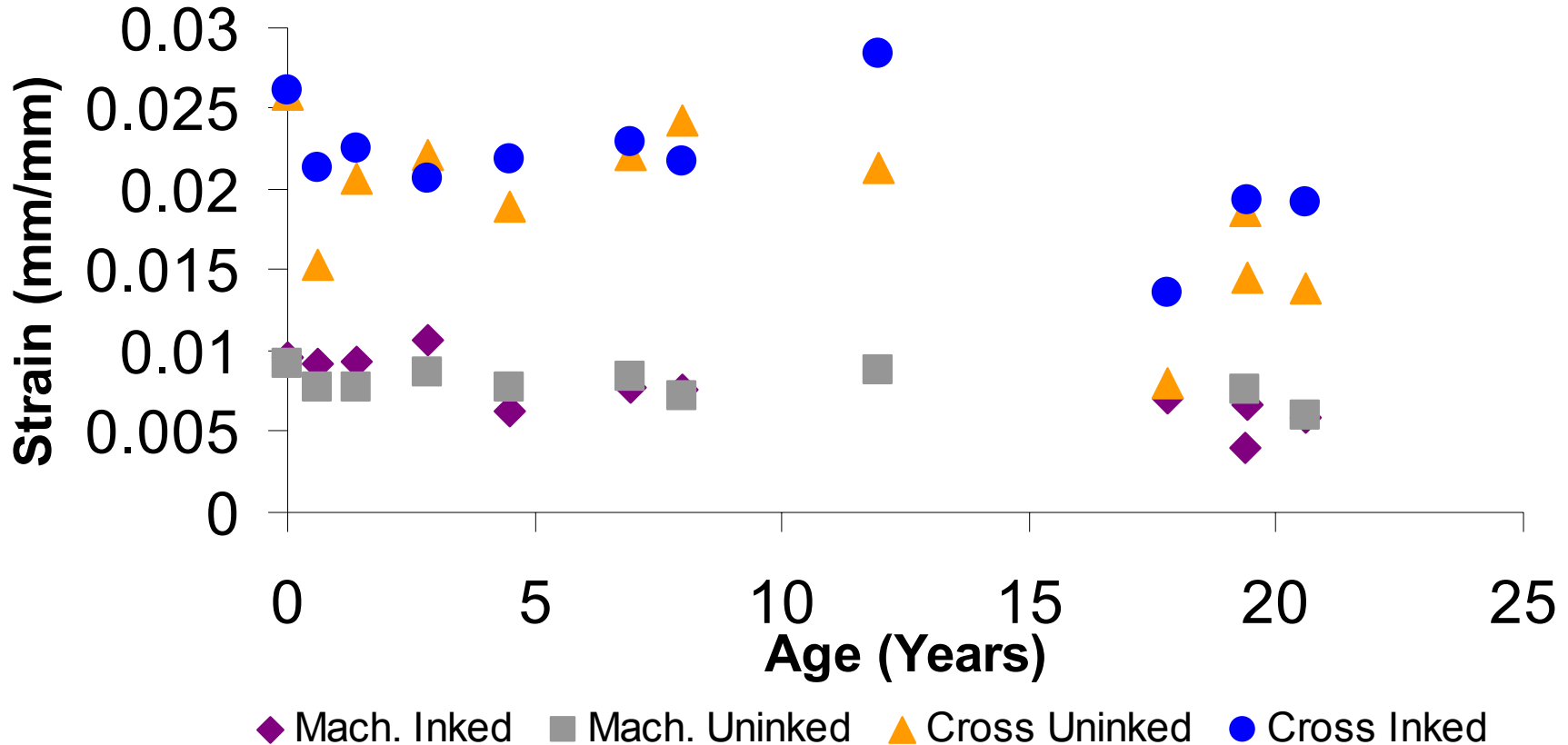
*The Washington Post*, June 1, 2003



- Orthotropic behavior present in specimens
- Very little difference between inked and uninked strains

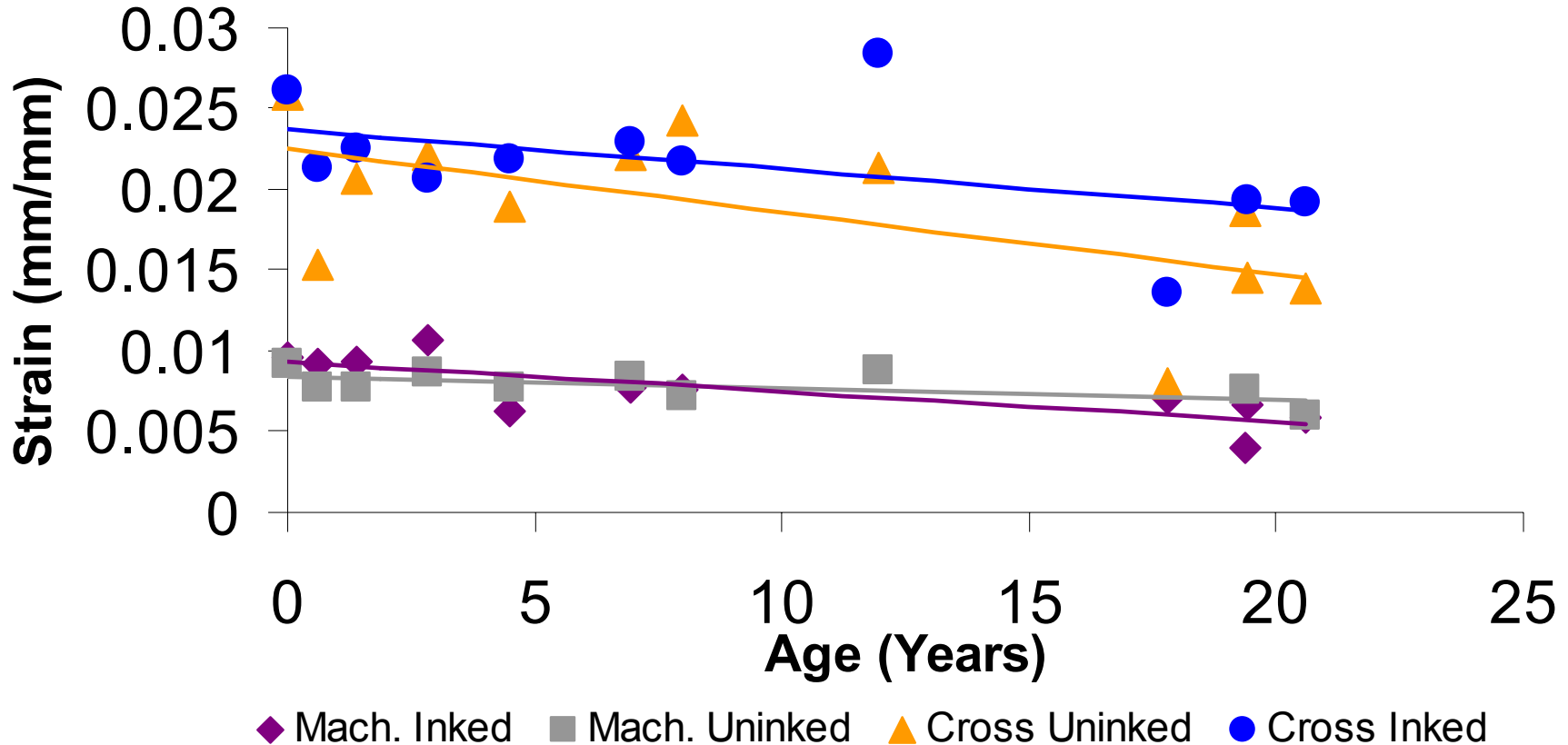


# 20 Year Study in Lab Environment



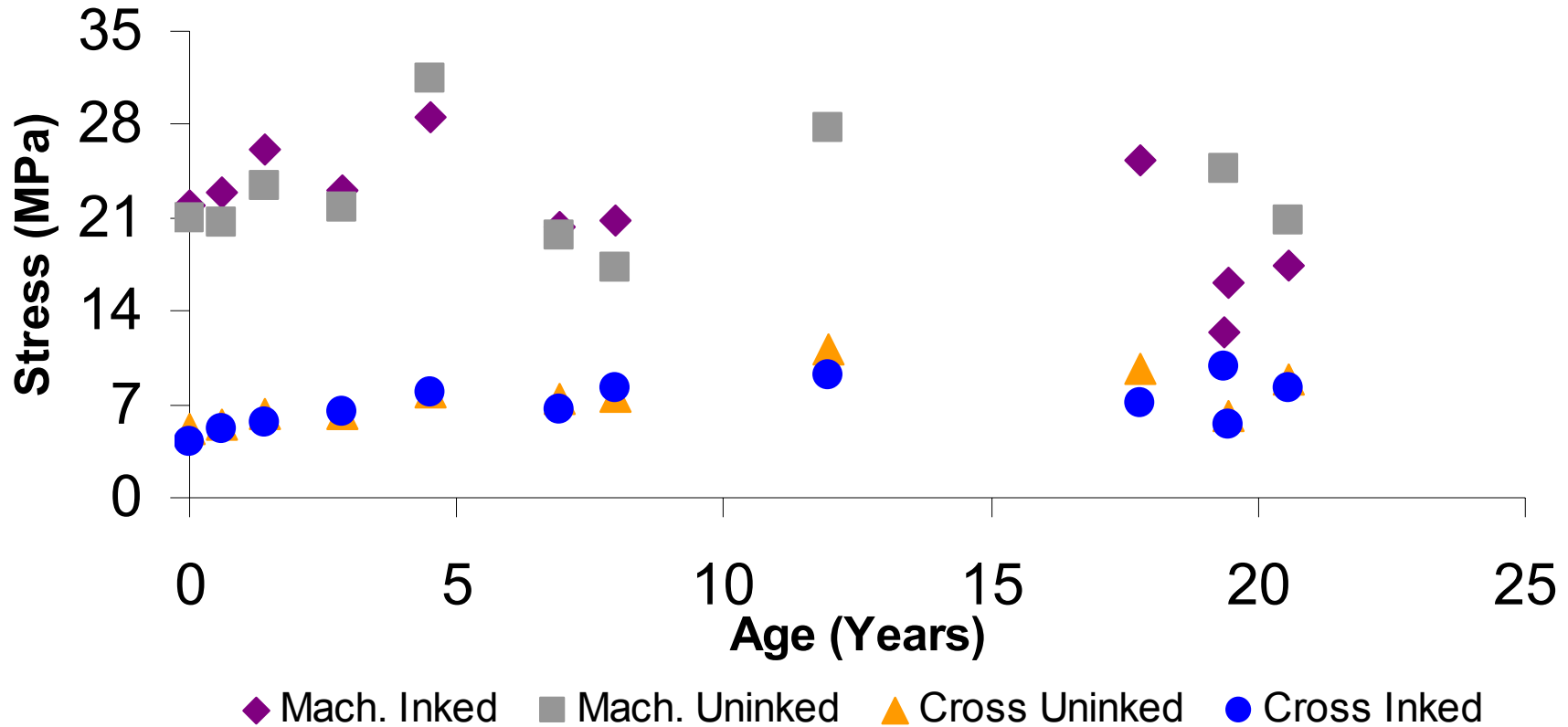
- No great change, but a slight decreasing trend is exhibited
- Degradation small enough that overall damage is minimal
- Specimens could last 100-150 years

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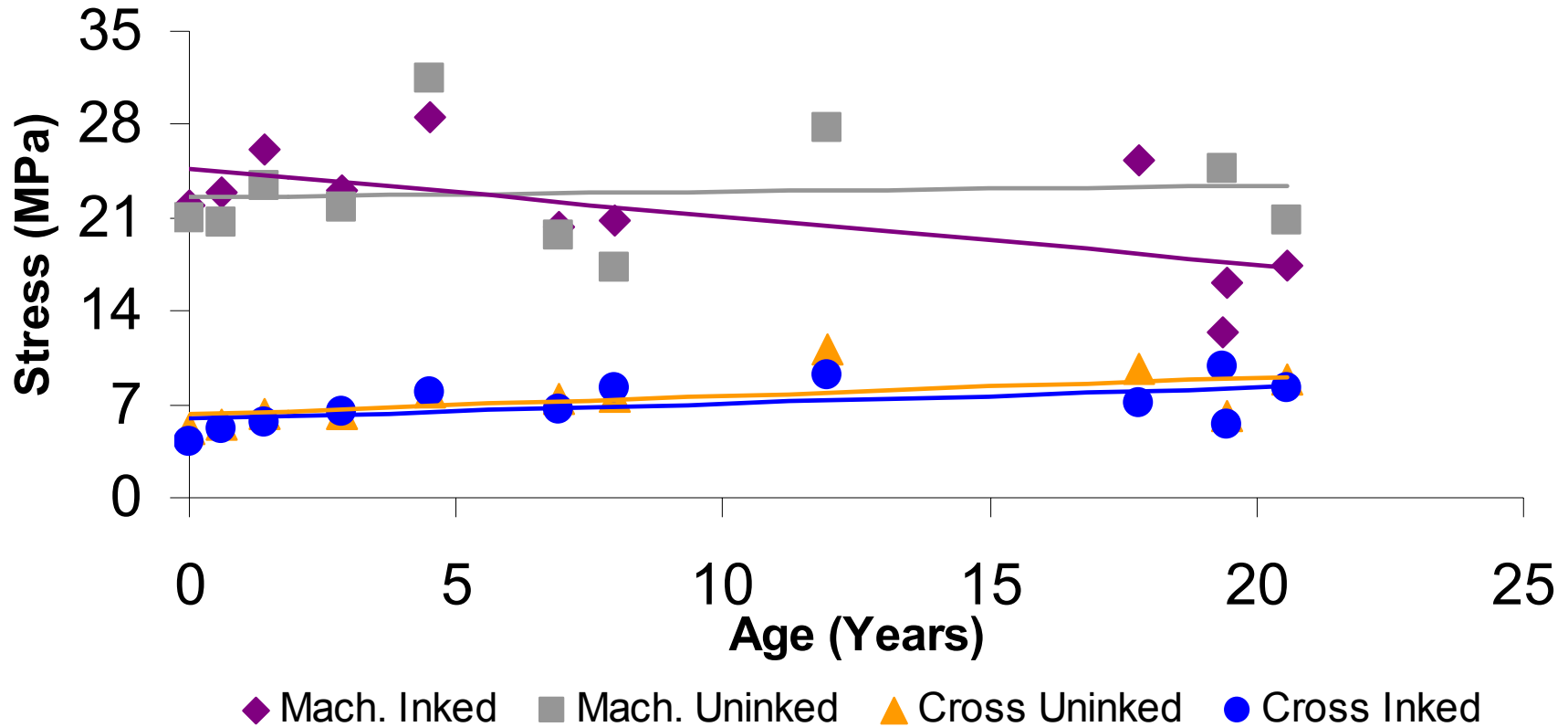
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# 20 Year Study in Lab Environment



- No distinguishable change in strength of specimens
- Specimens will last a long time under Standard Laboratory Conditions

# 20 Year Study in Lab Environment



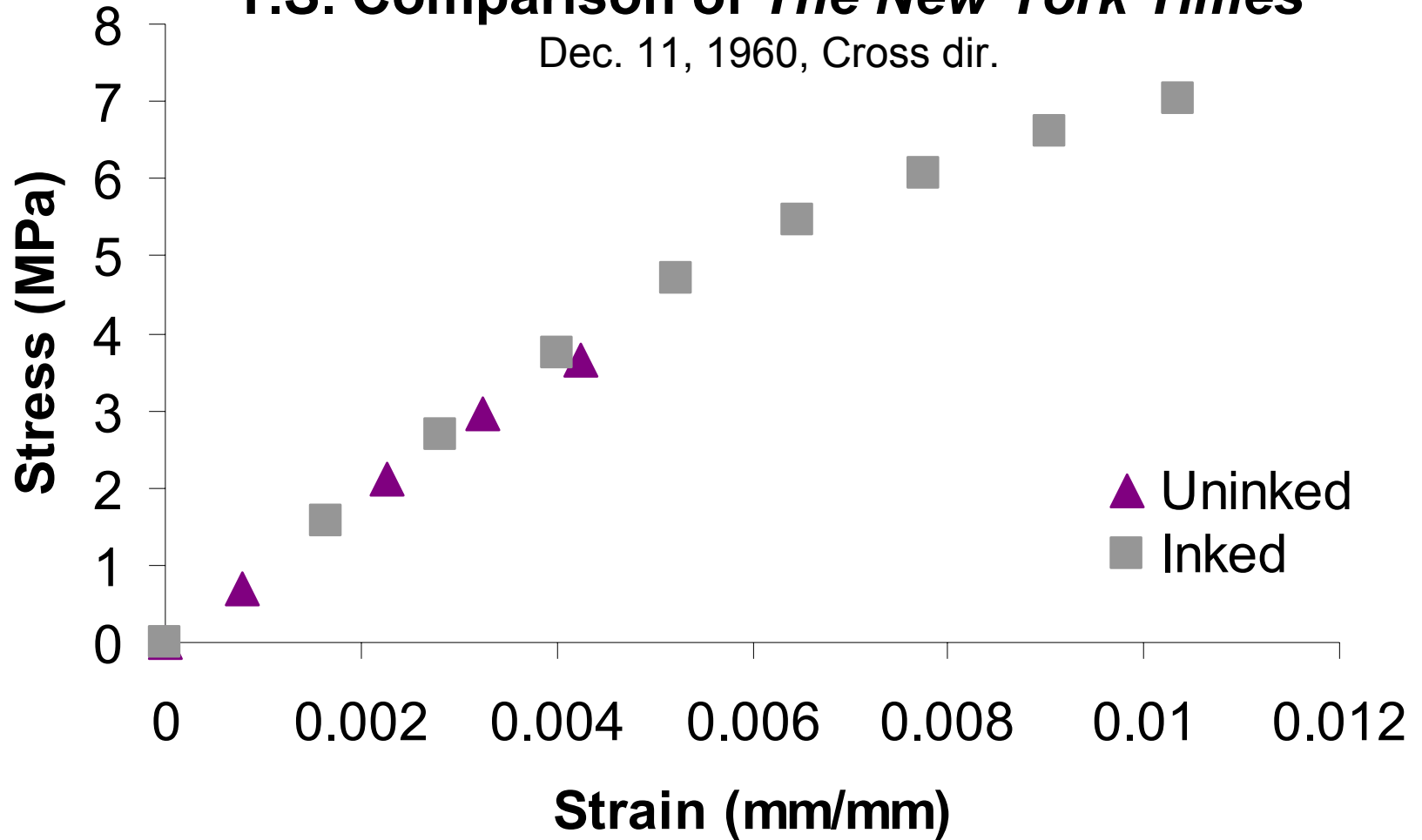
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# Inked v. Uninked Paper

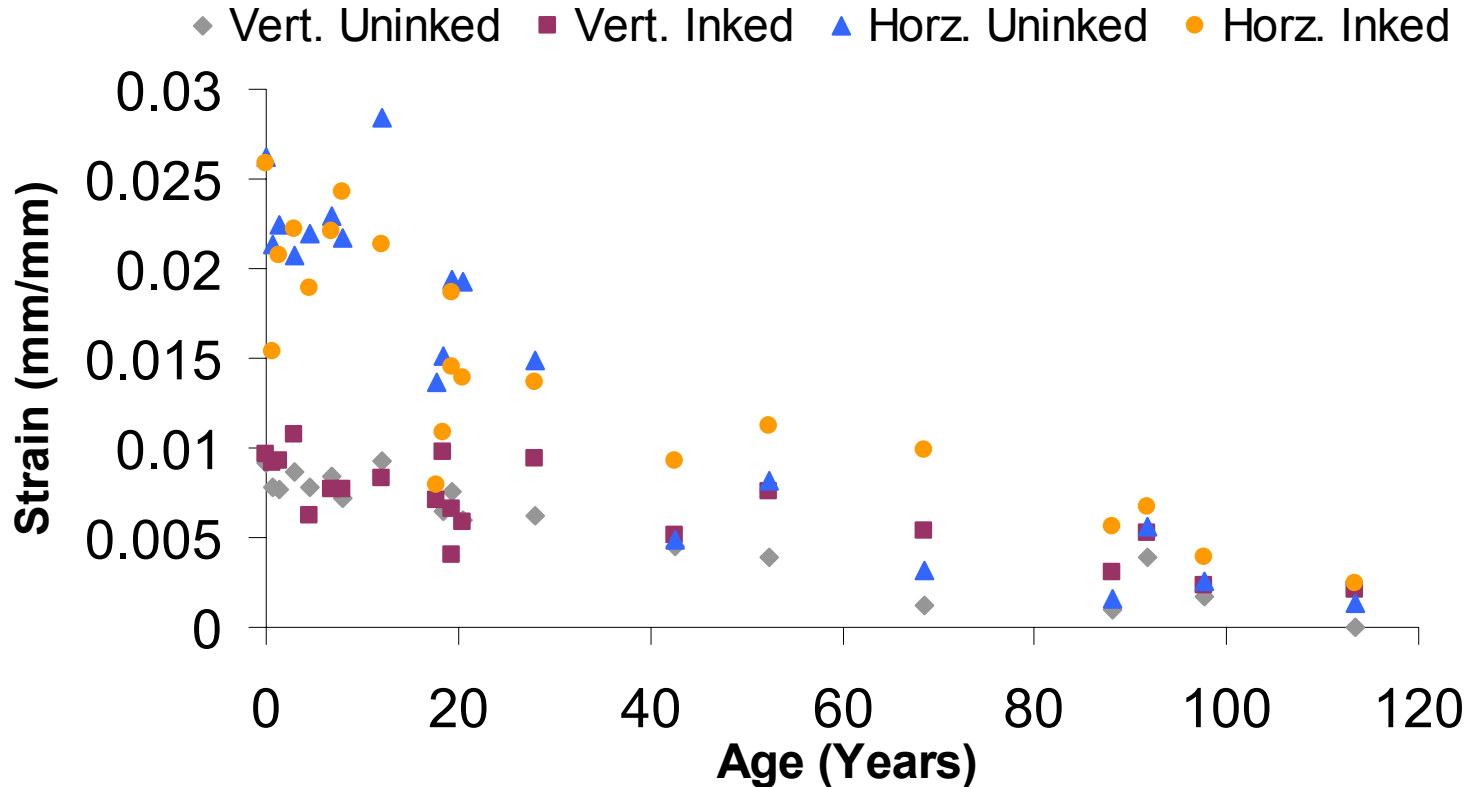
T.S. Comparison of *The New York Times*

Dec. 11, 1960, Cross dir.



# 120 Year Variable Test

## Strain v. Time

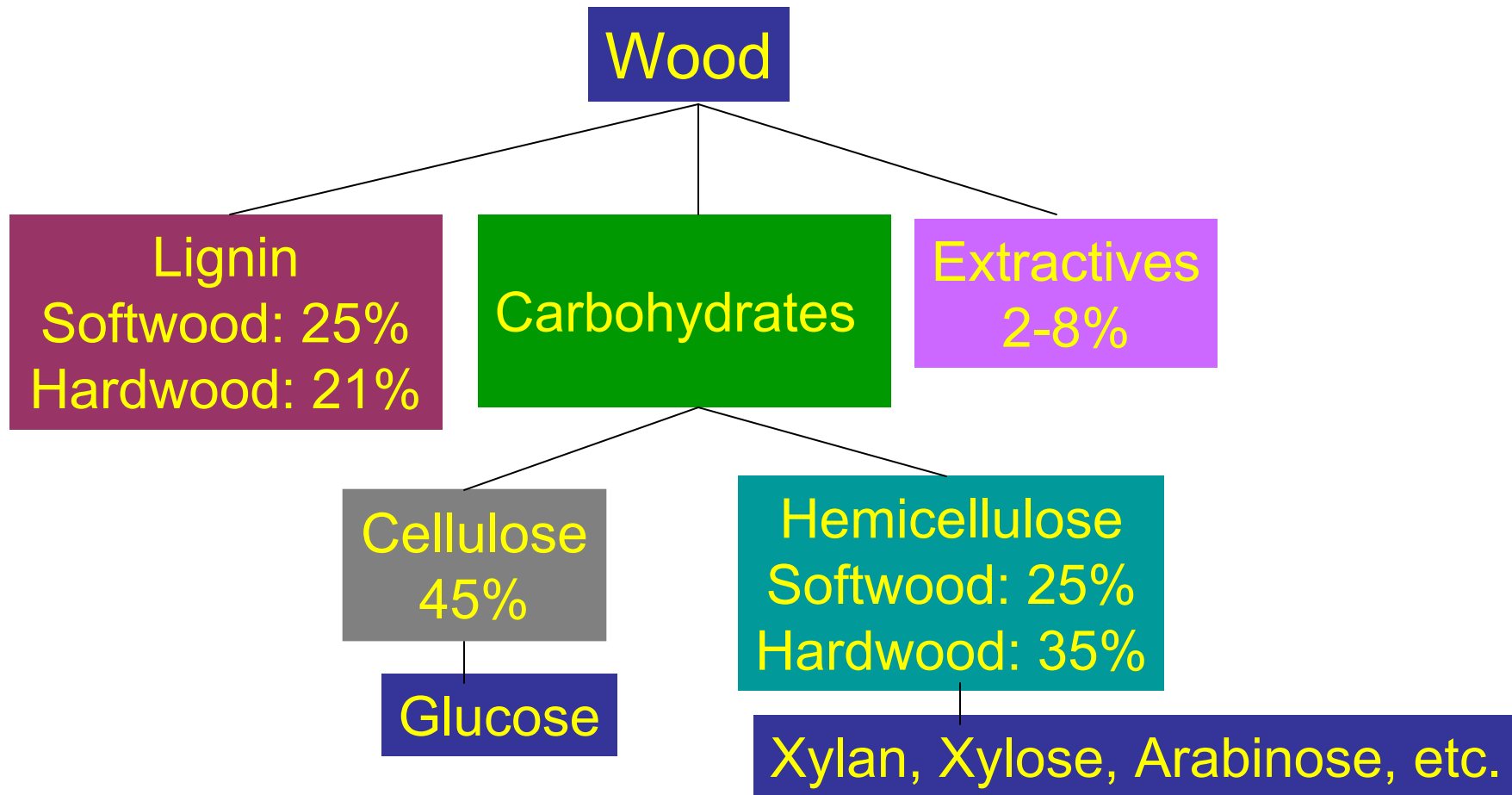


- Loss of elastic region occurs when breaking strains drops below 0.005
- Acute fragility not present until samples are 80 years old
- Total specimen disintegration only occurs after ALL breaking strains are less than 0.003

# Scientific Significance

- Newsprint can last 100 years if given nominal attention
- Archival facilities can provide up to an additional 50 – 100 years of viable storage
- Flexibility and elasticity data will help build an accurate model to predict degradation

# Chemical Composition of Wood





## Cellulose:



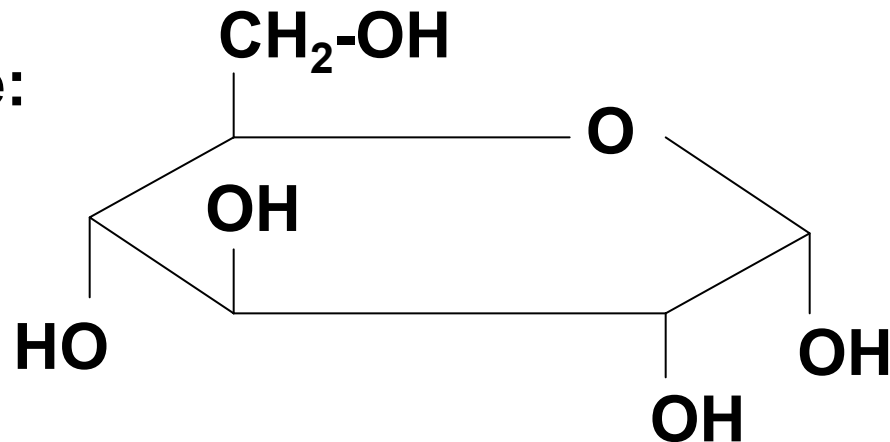
## Glucose Trimer:



## Glucose Dimer:

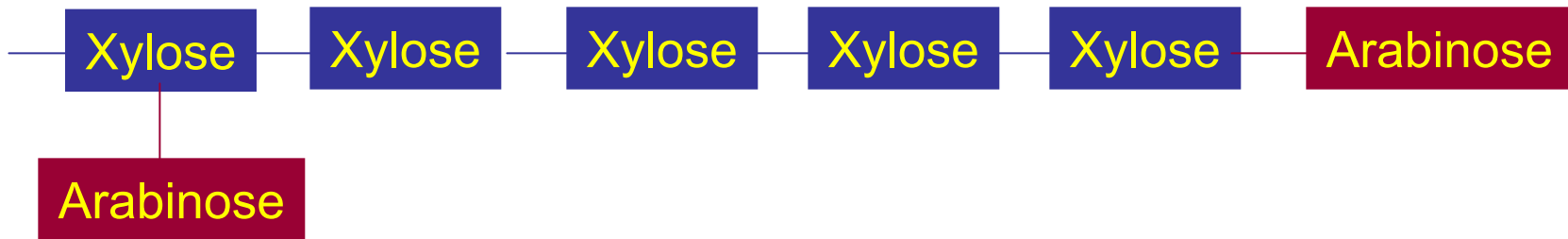


## Glucose:

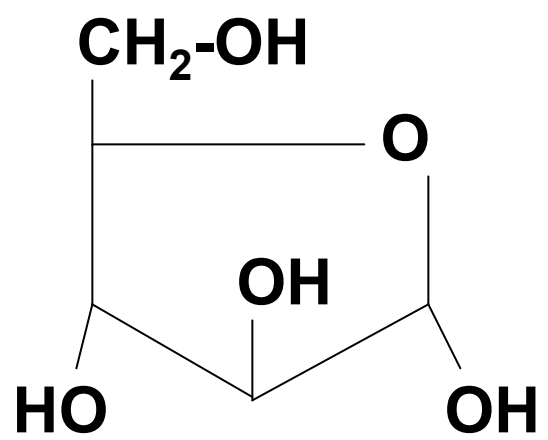


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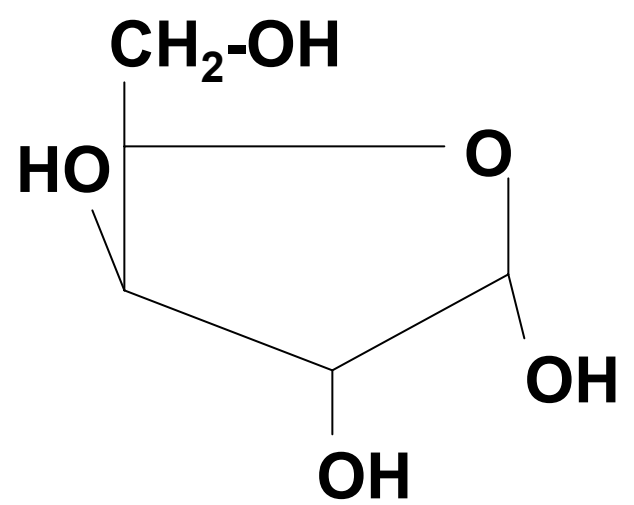
# Xylan:



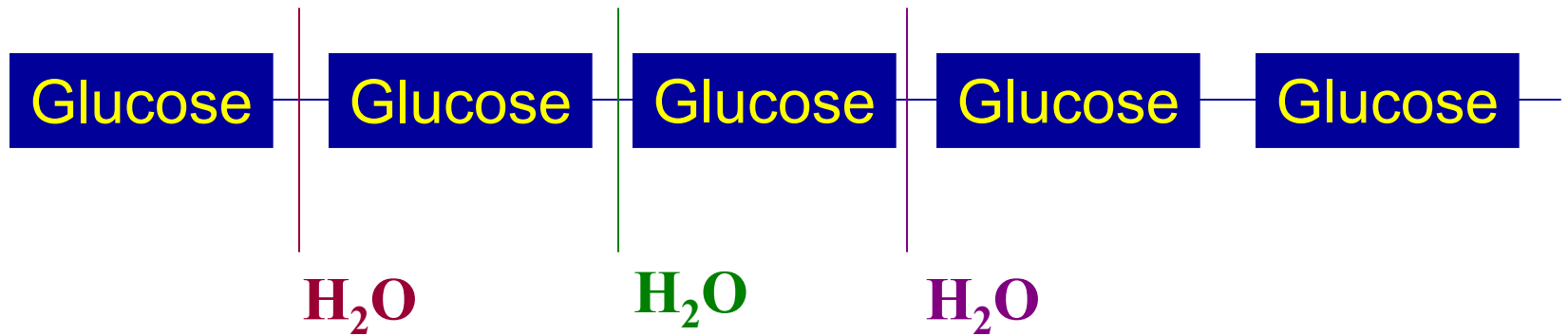
# Xylose:



# Arabinose:



# Hydrolysis of Cellulose



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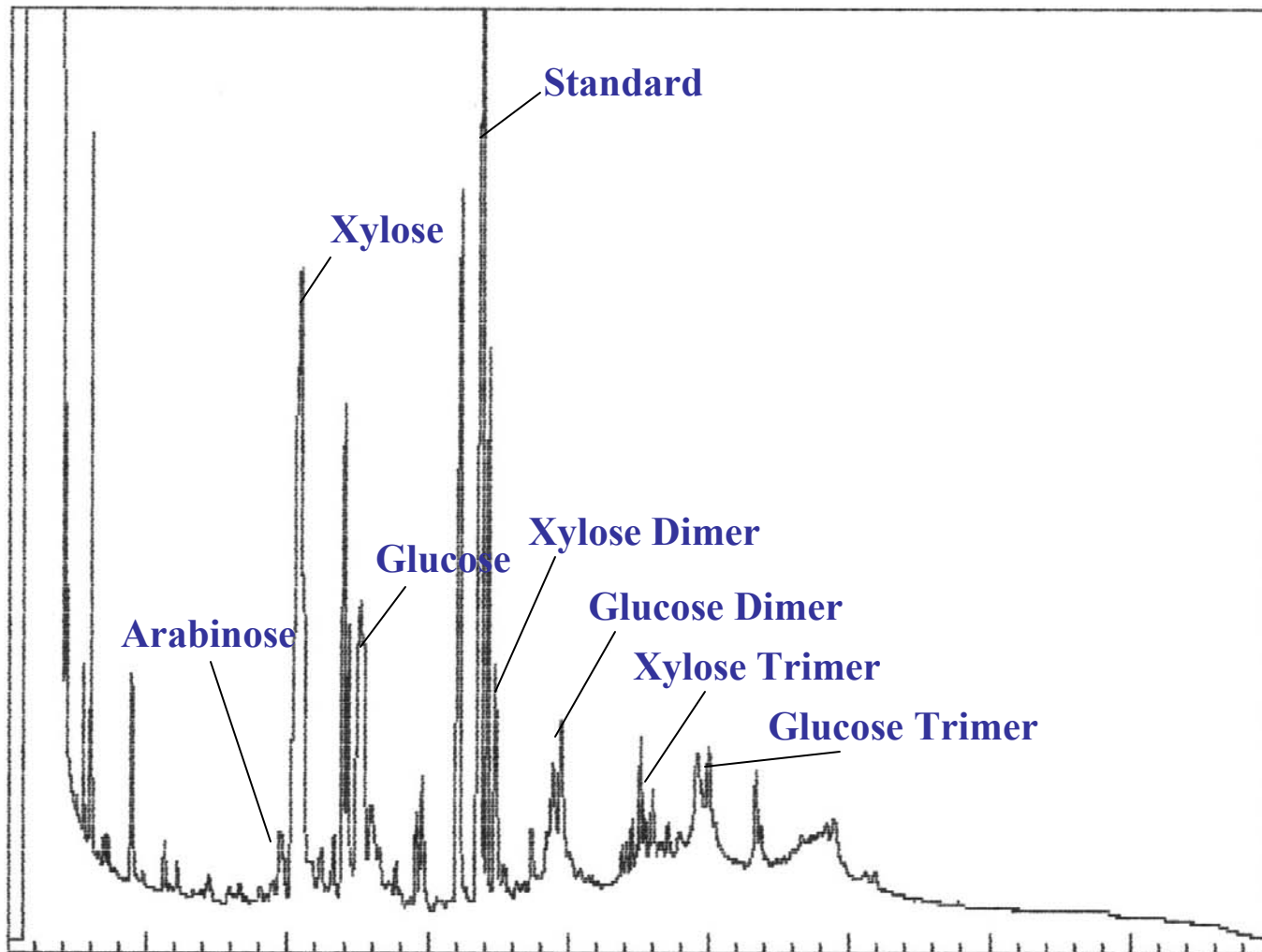
# Method



- Samples prepared, extracted in water, filtered, and evaporated under vacuum
- Derivatized with STOX (commercial reagent containing internal standard), HMDS, and trifluoroacetic acid
- Supernatant analyzed by gas chromatography
- Sugars identified by comparison of retention times against internal standards

Plot of data file: C:\detfree3.PTS  
Date: 07-30-2003 Time: 09:48:30  
Sample Name: DetroitFreePre1905  
Start Time= 0.01 Stop Time = 45.01 Min. Scale=

O Max. Scale= 999999



# Approximate Retention Times of Sugar Peaks

Standard: 16.70

Glucose: 12.57

Xylose: 10.43

Arabinose: 10.20

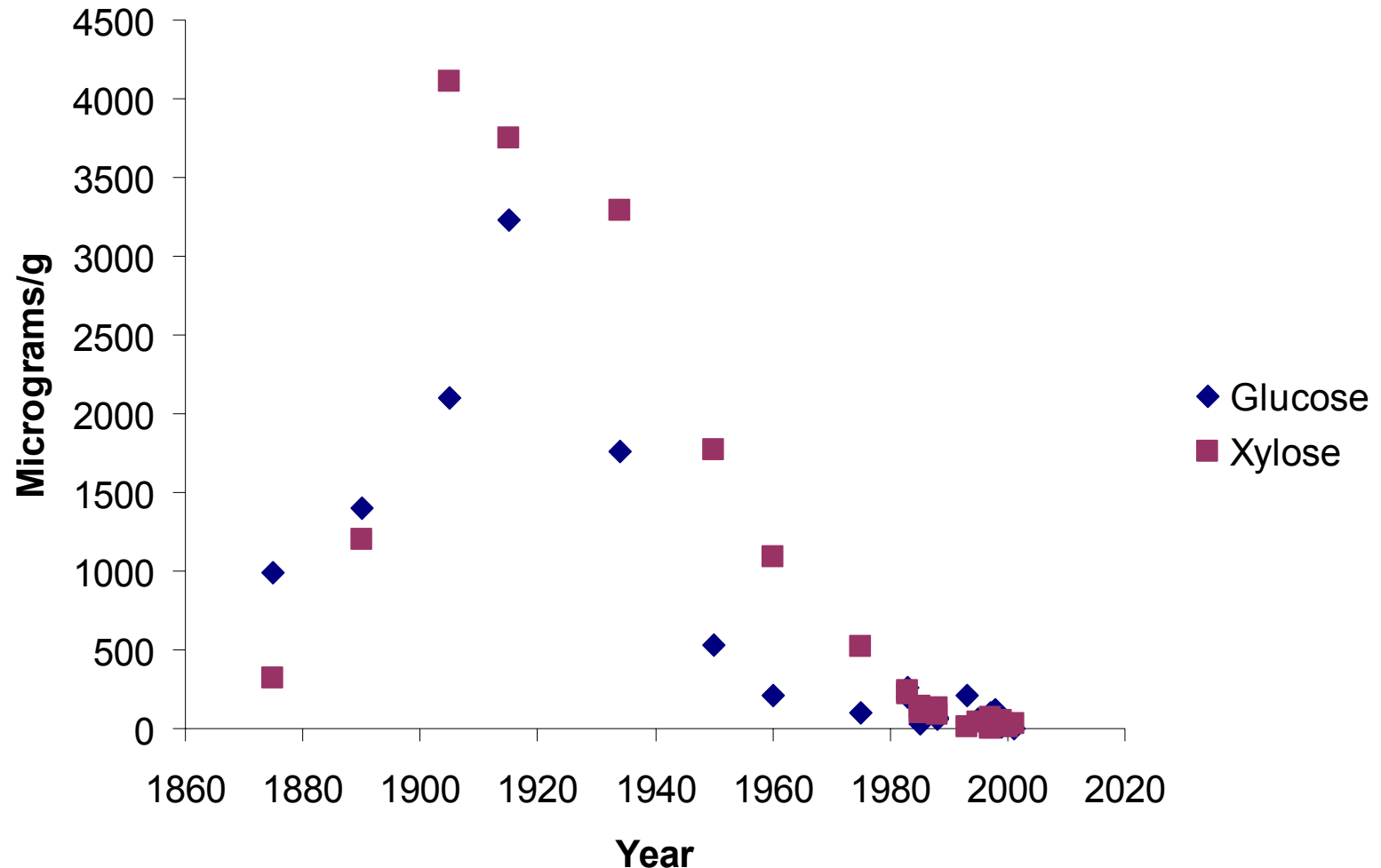
Glucose Dimer: 19.45

Glucose Trimer: 24.55

Xylose Dimer: 17.45

Xylose Trimer: 22.55

# Sugar Content in Wood-based Newspapers



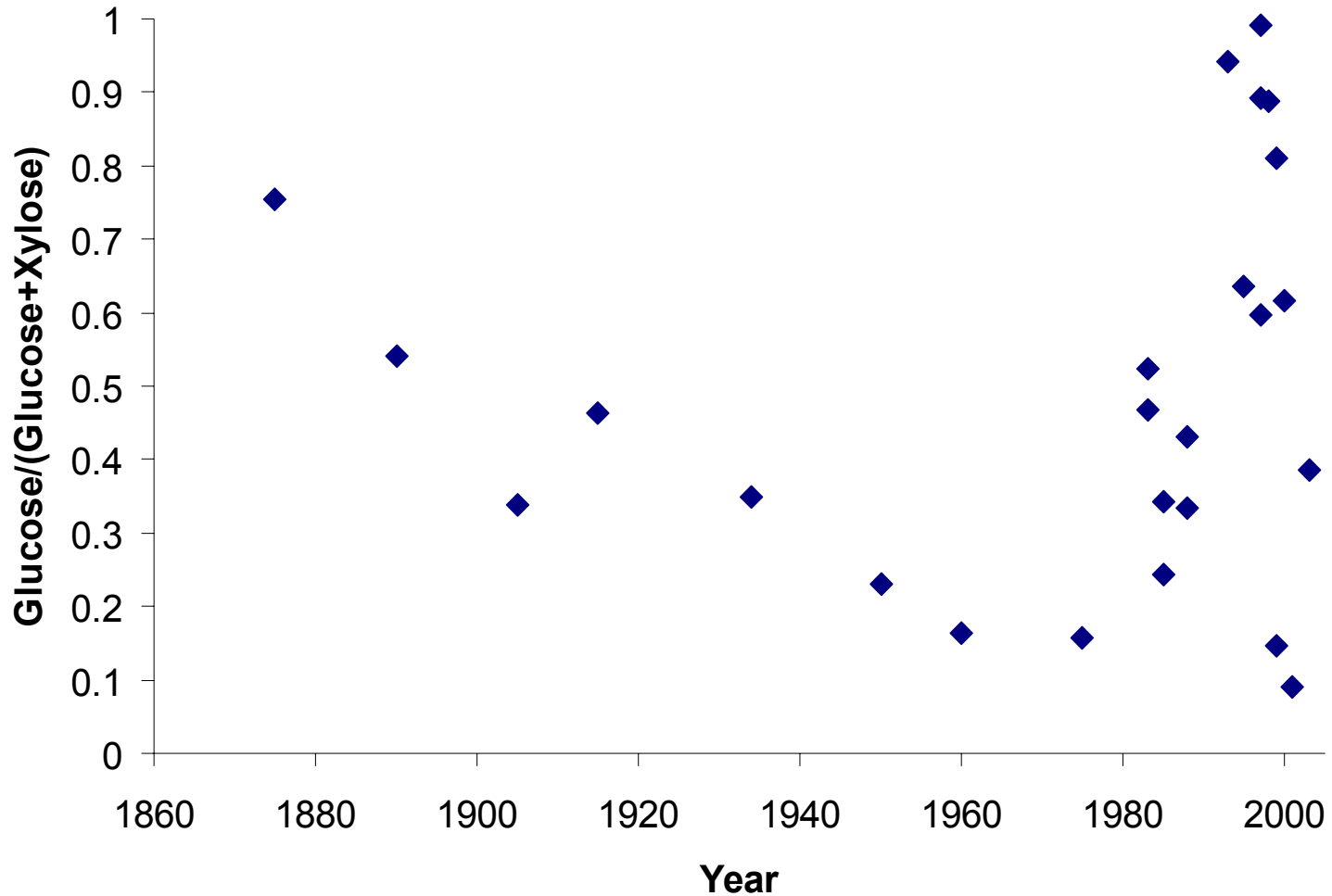
- Glucose and xylose levels highest in newspapers from the Industrial Revolution
- Of interest are the spikes around World War I and the relative stability of the past 20 years



# History of Papermaking Technology

- The Industrial Revolution (1875-1950) brought commercial use of wood-pulp paper and mass production processes
- Commercial use of the acid sulfite process (1880s) and Kraft process with bleaching (1930s) caused a transition from mechanical to chemical processing
- Glucose and xylose levels peak in the World War I era
- After World War I, new technology and processing techniques were invented

# Glucose Fraction in Wood-based Newspapers



- Pre-1980 glucose ratio shows a different mechanism than post-1980
- Kinetics study?
- Changes in data from 1980 to present are particularly interesting

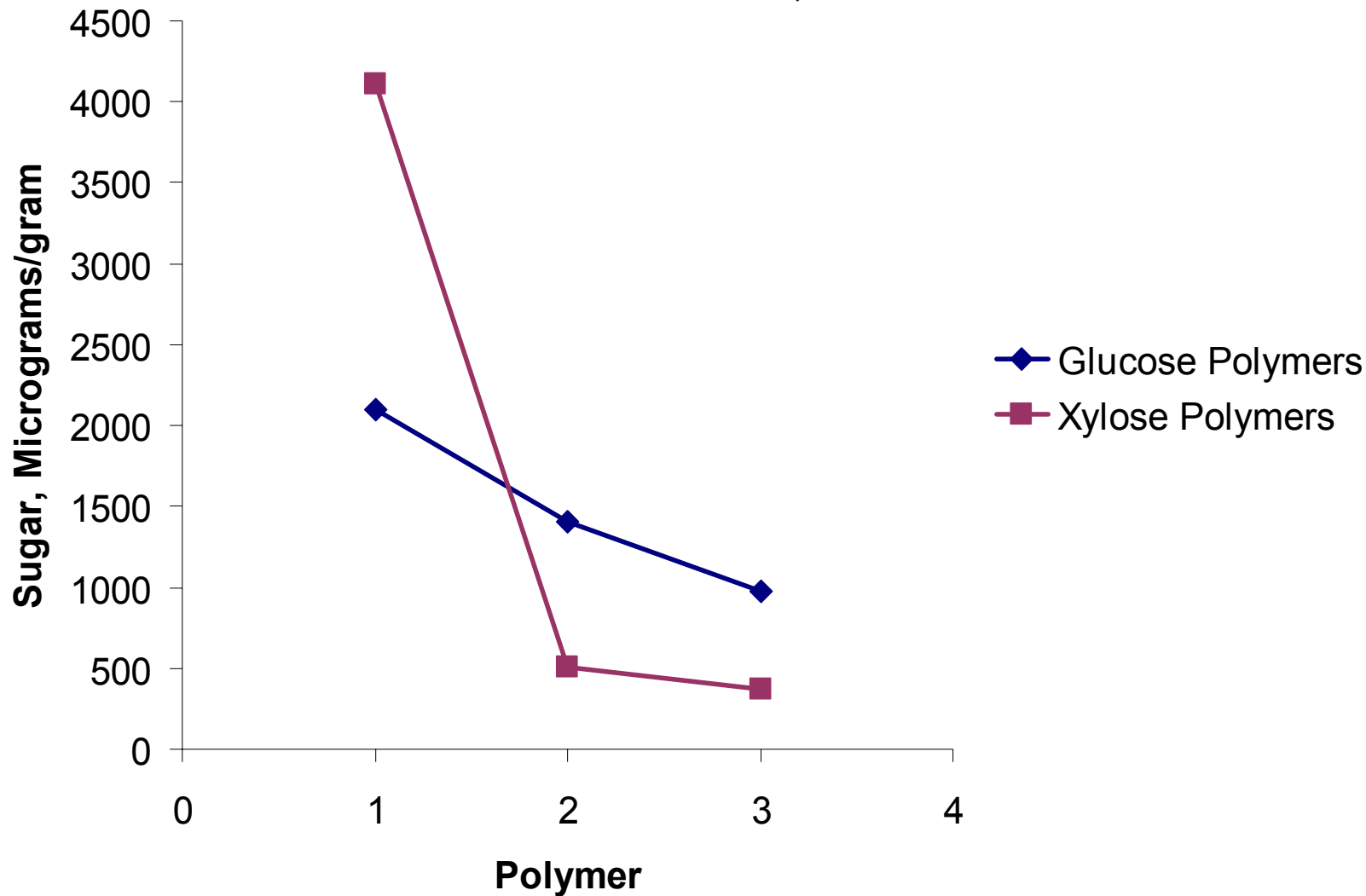
# History of Papermaking Technology

- The USA Today Effect: Launching of the USA Today in 1982 and the use of color in newspapers
- The environmental movement and recycling of newspapers
- Advanced machinery requires thinner material
- Multitude of processes for newspaper manufacturers to choose from: refiner, chemical, thermo, chemothermo, isothermo, etc.
- Further research

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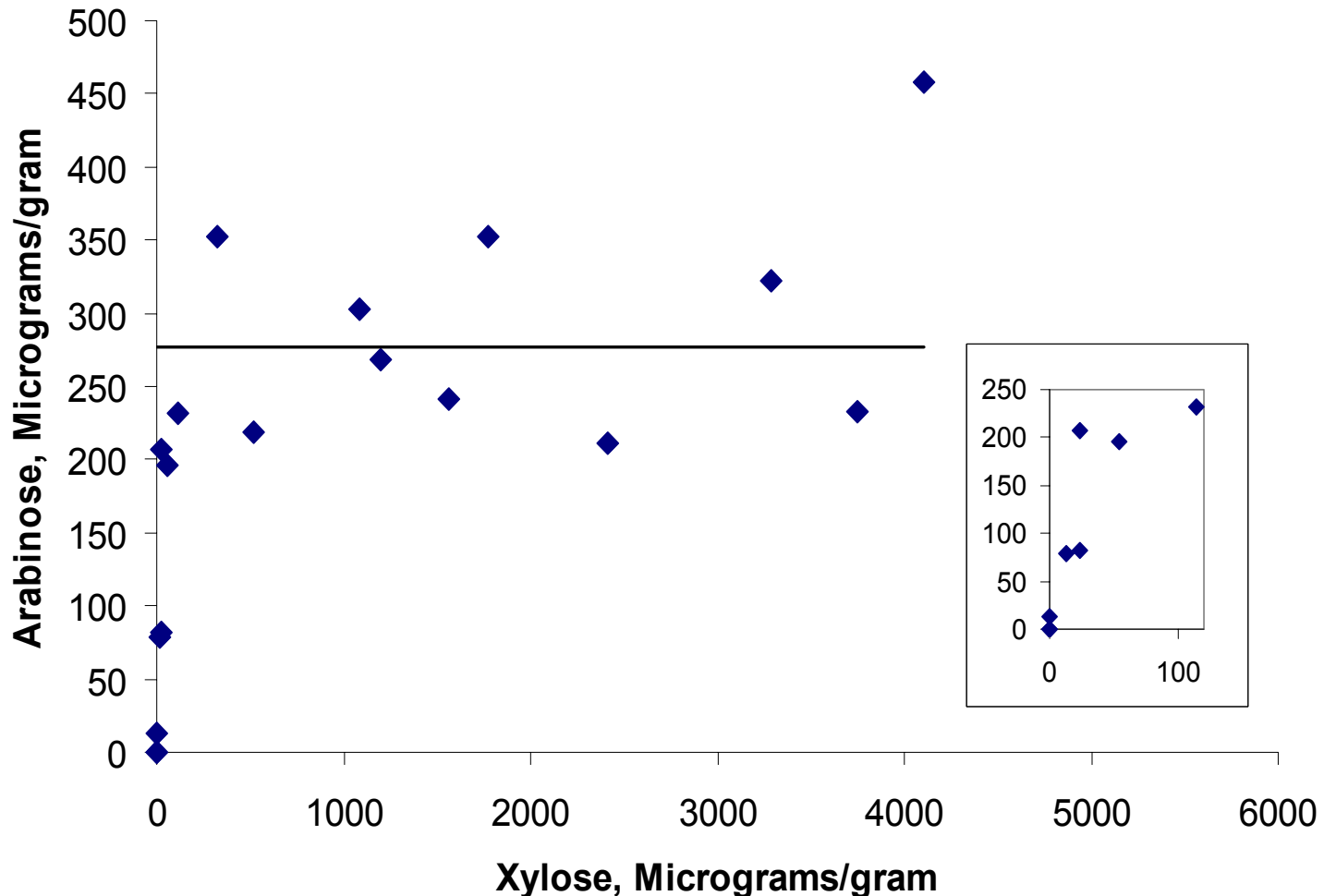
# Sugar Polymers

*Detroit Free Press, 1905*



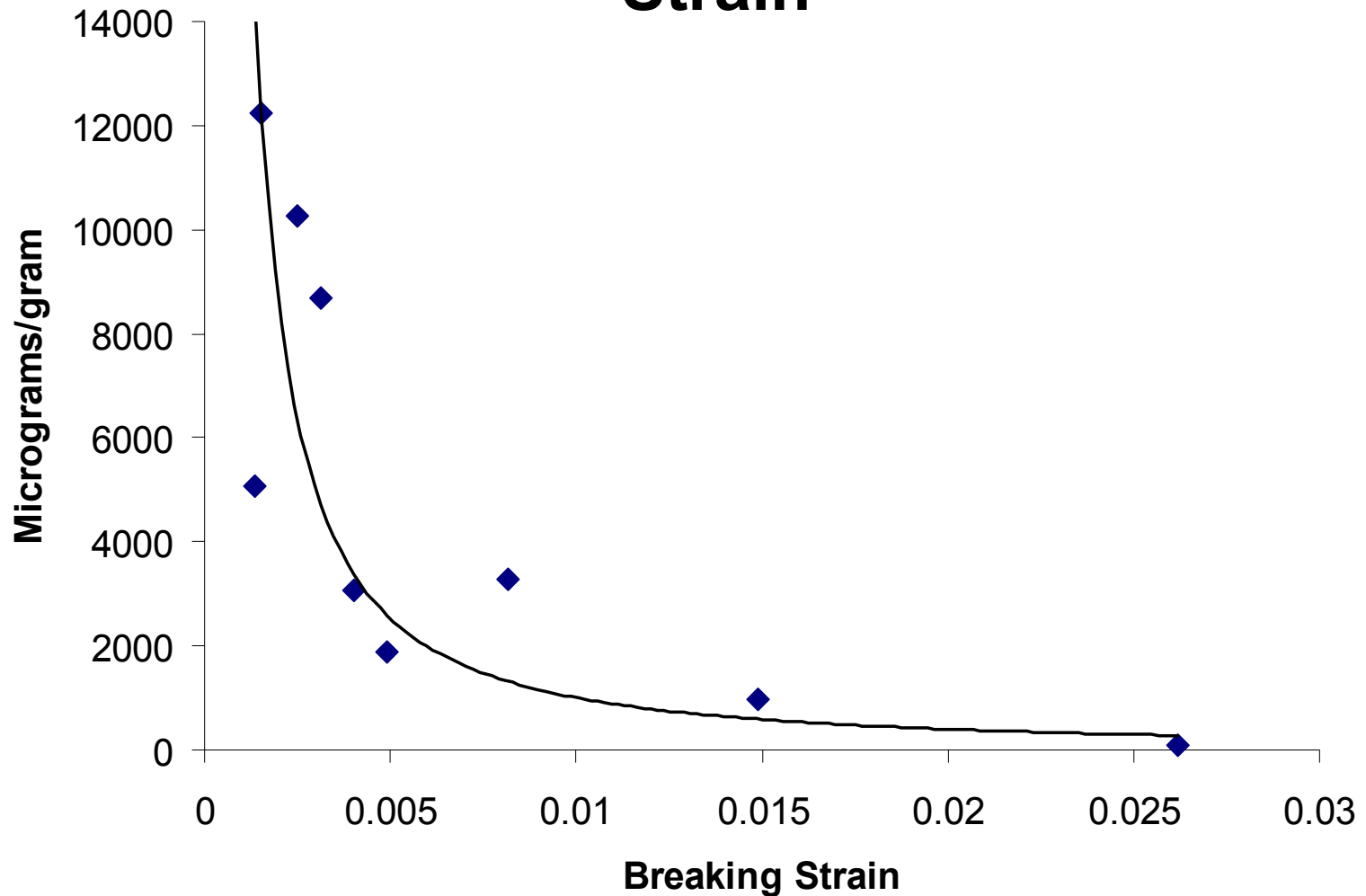
■ Xylose is more hydrolytic and more likely to hydrolyze to monomer than is glucose

# Arabinose and Xylose in Wood-based Newspapers



- Initial, sharp increase in arabinose, and then nearly constant value
- Arabinose molecules must be located at the end of the molecule or on branches, and are hydrolyzed first

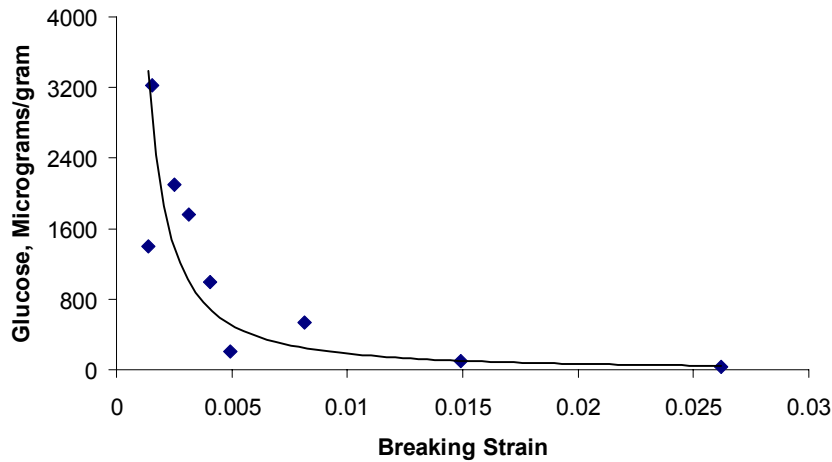
# Total Measured Sugar Content vs. Breaking Strain



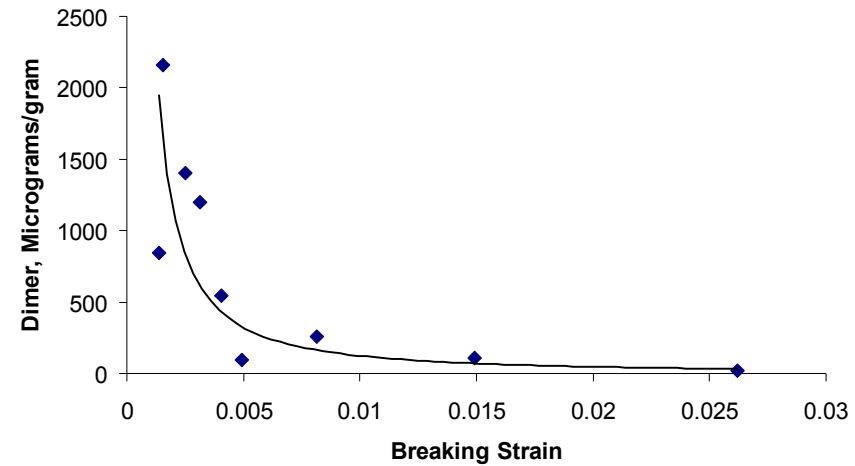
- Similar trends appear across other sugar data
- Illustrates the presence of a surface phenomenon

# Glucose Polymers vs. Breaking Strain

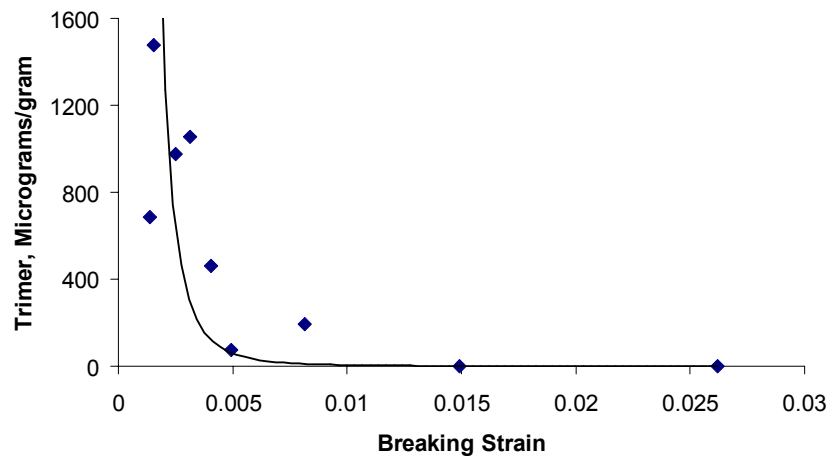
## Monomer



## Dimer



## Trimer



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# Hydrolysis Mechanism Conclusions

- Issue of dueling factors of technology and time in the process of degradation
- Xylan hydrolysis vs. cellulose hydrolysis
- Order of degradation, illustration of mechanistic details of hydrolysis
- Surface phenomenon
- Ideas for further research in kinetics and the history of papermaking technology

# Summary

- Mechanical and physical properties of specimens directly related to hydrolysis of cellulose and hemicellulose
- Hydrolysis of cellulose and hemicellulose affects breaking strain and plasticity of specimen
- Remaining life span of specimen can be estimated via sugar content analysis and/or mechanical testing