XANES-based comparative chemistry & the anatomical evolution of living and fossil plants

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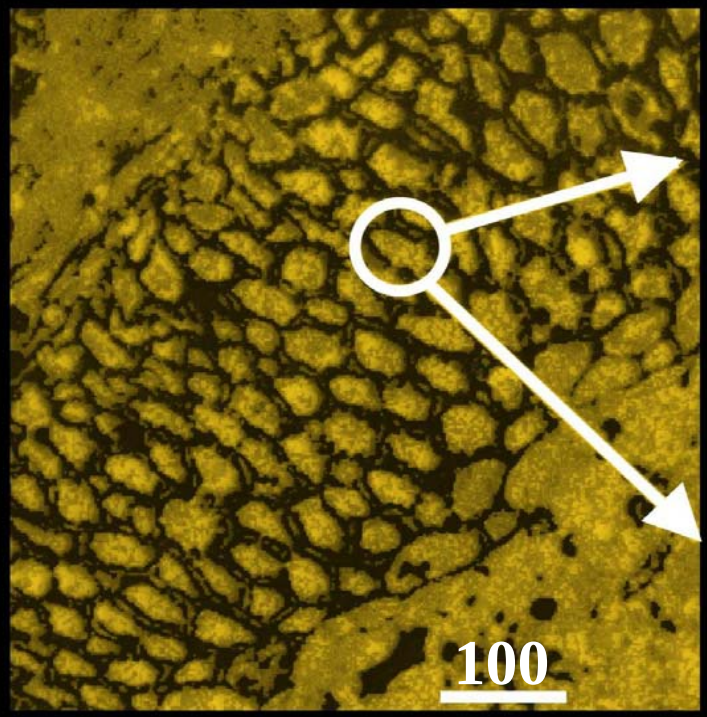
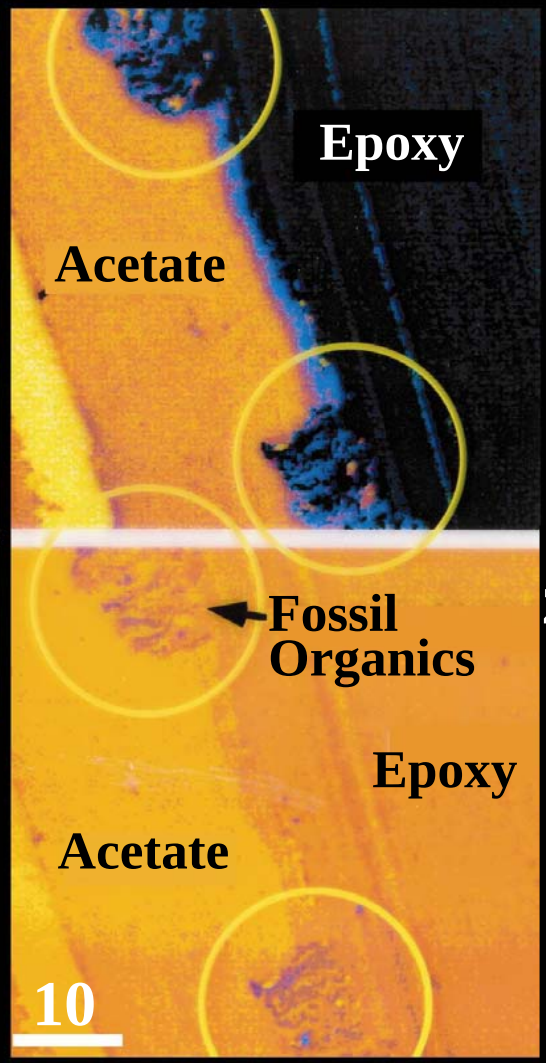
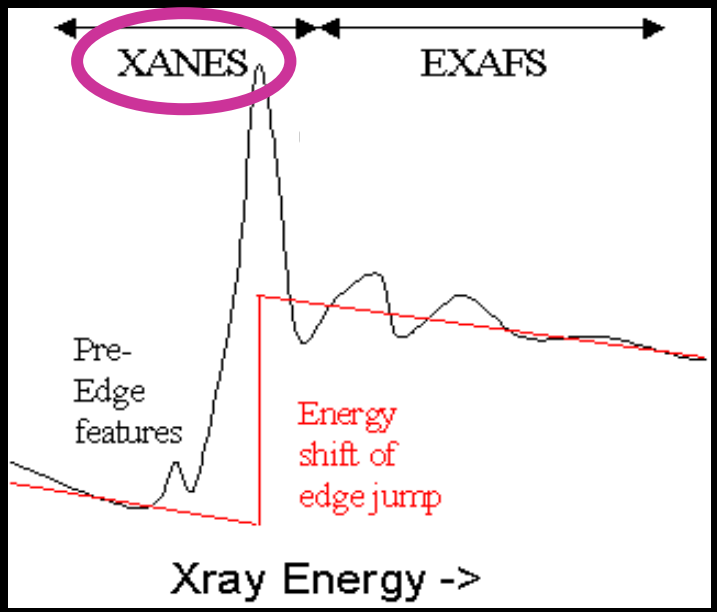
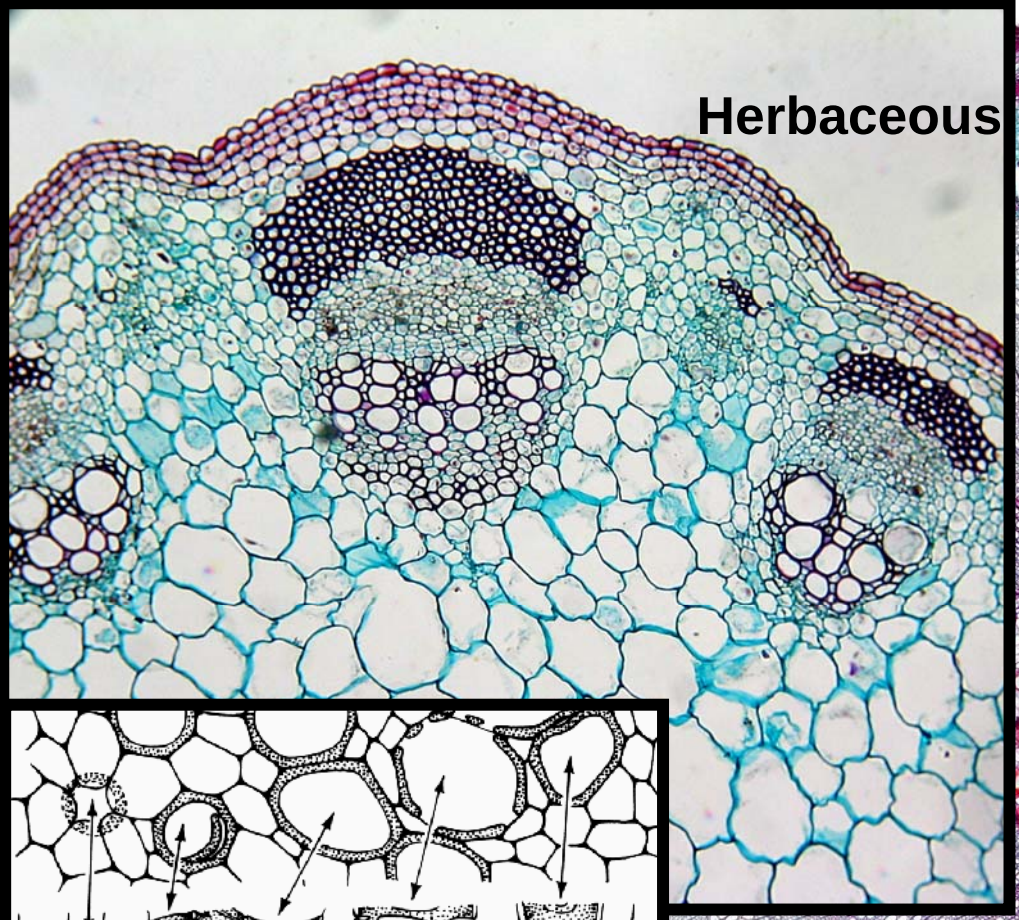
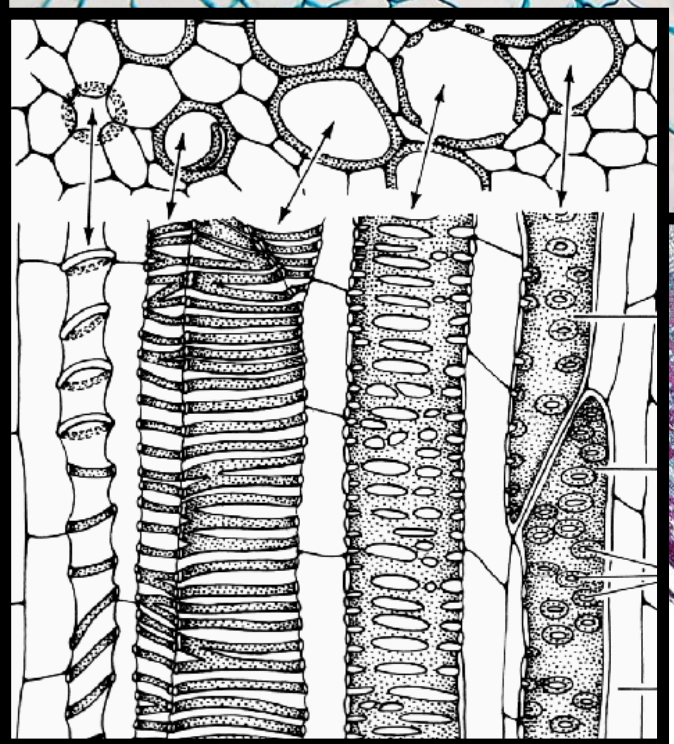


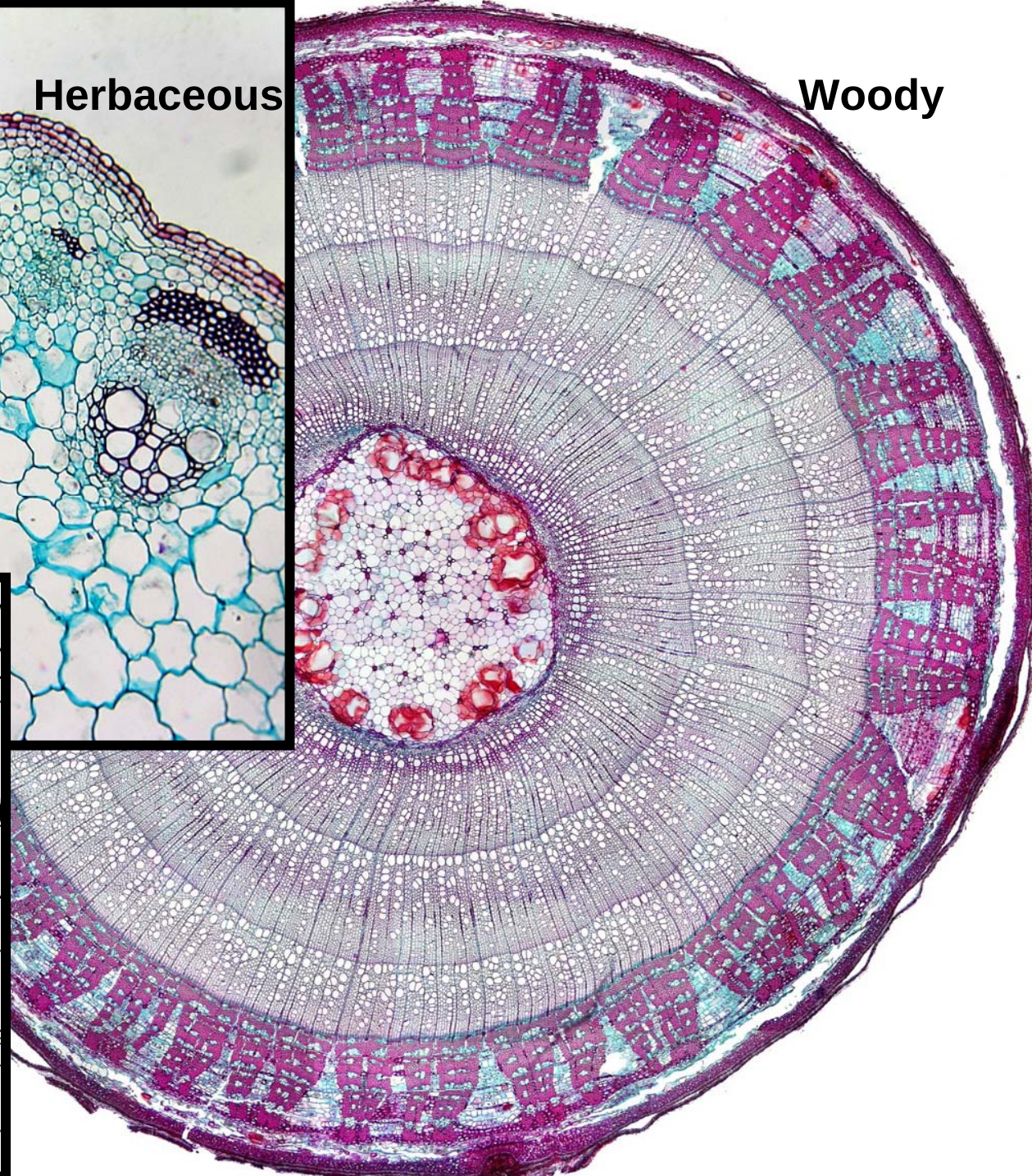


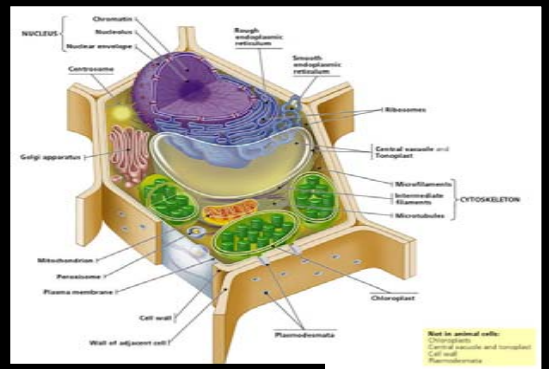


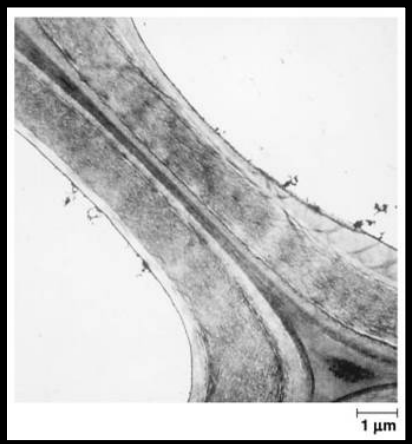
Scanning Transmission Xray microscopy
(NSLS, X1A beamline)


Herbaceous

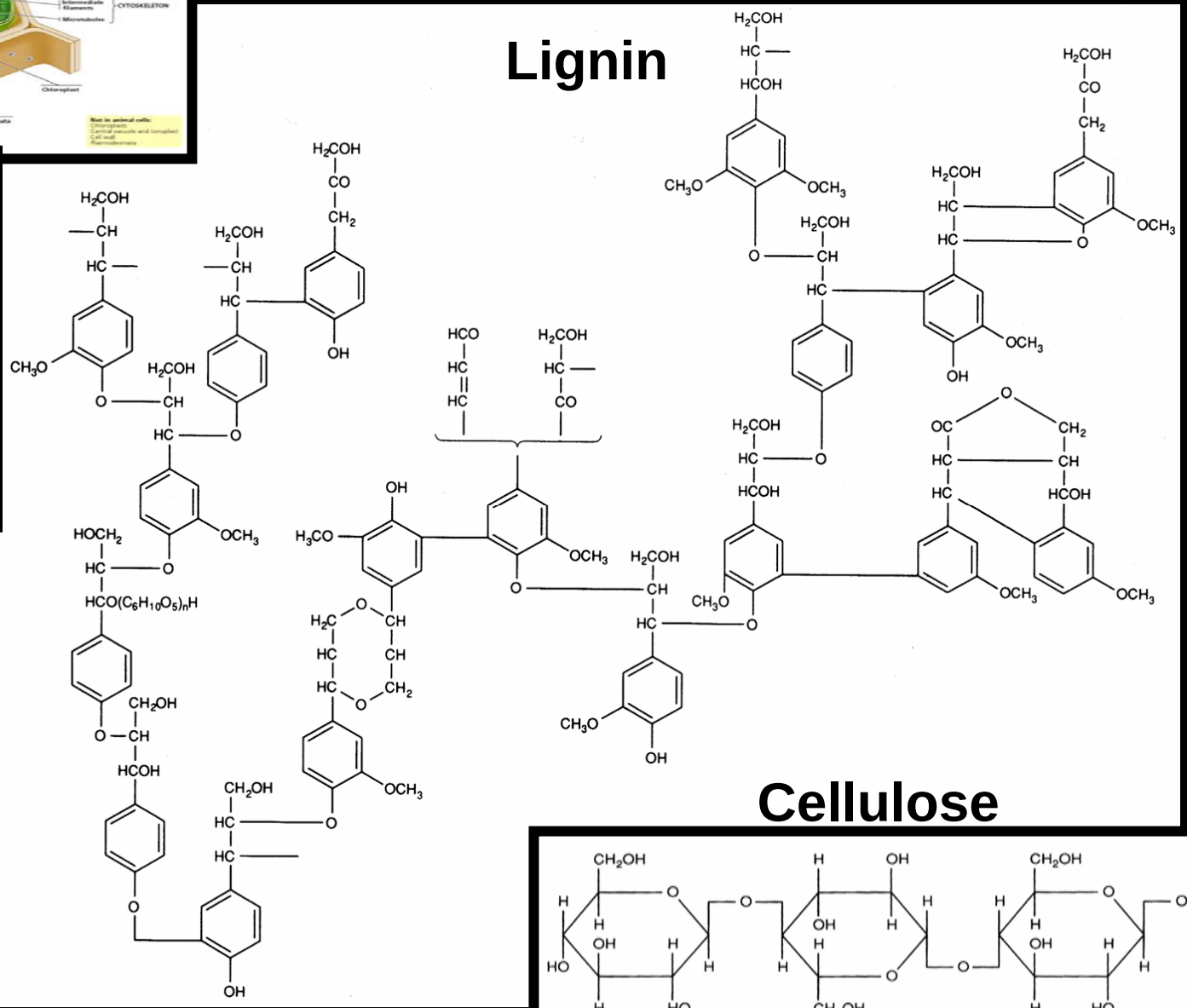



Woody

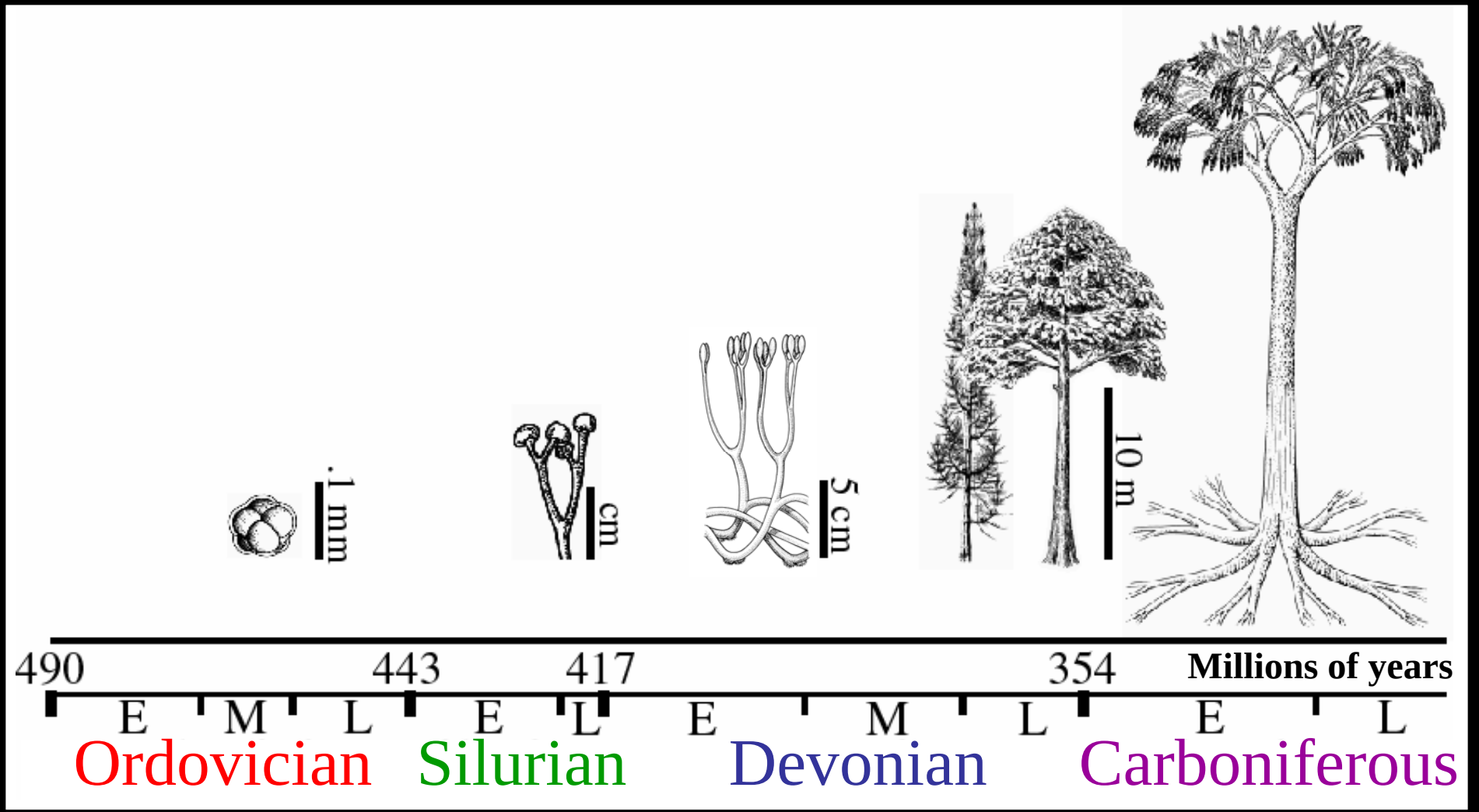




Lignin

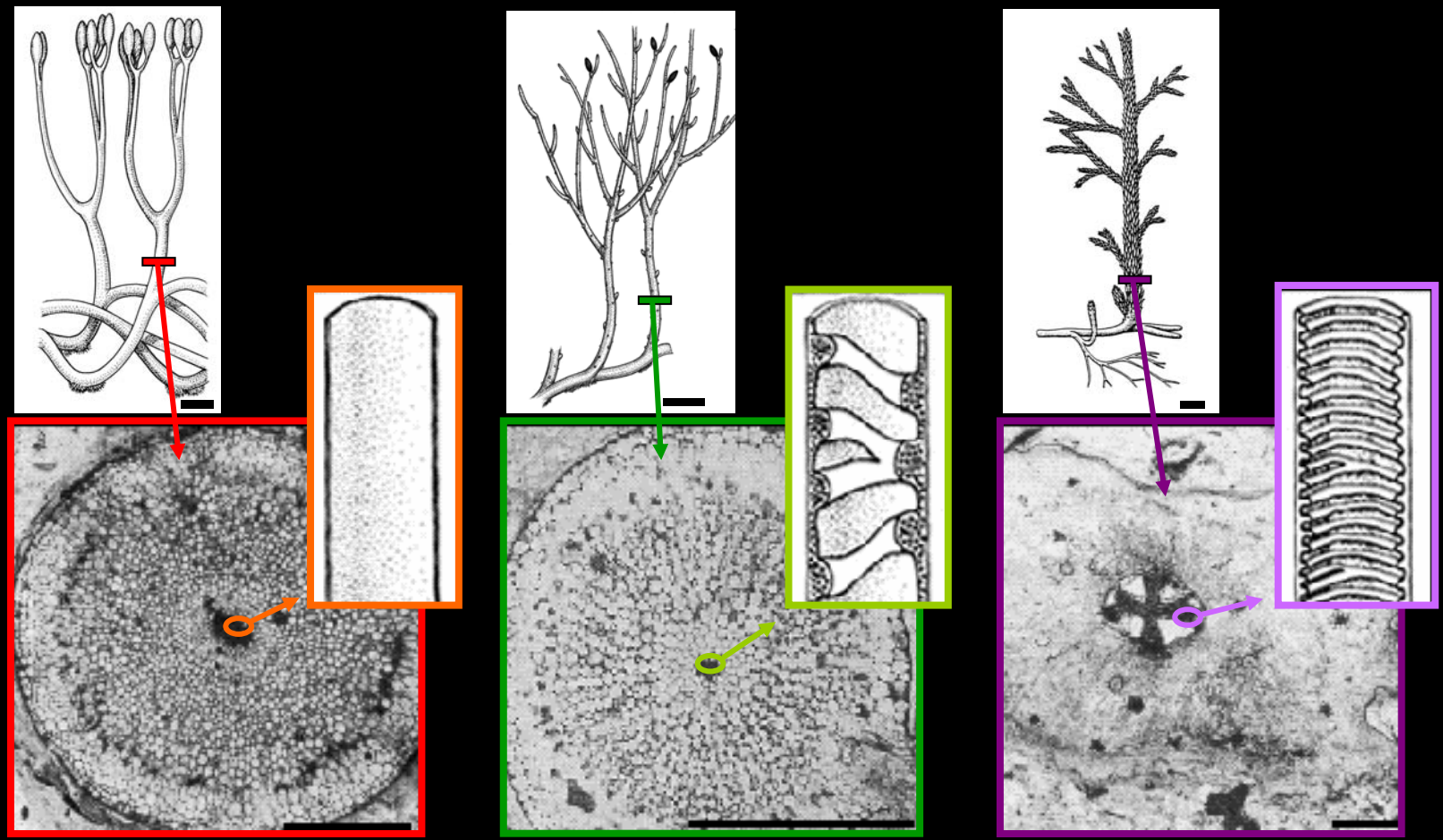


Cellulose


1 mm
cm
5 cm
10 m
490
443
417
354
Millions of years
E
M
L
E
L
E
M
L
E
L
Ordovician
Silurian
Devonian
Carboniferous

Evolution of vascular cells

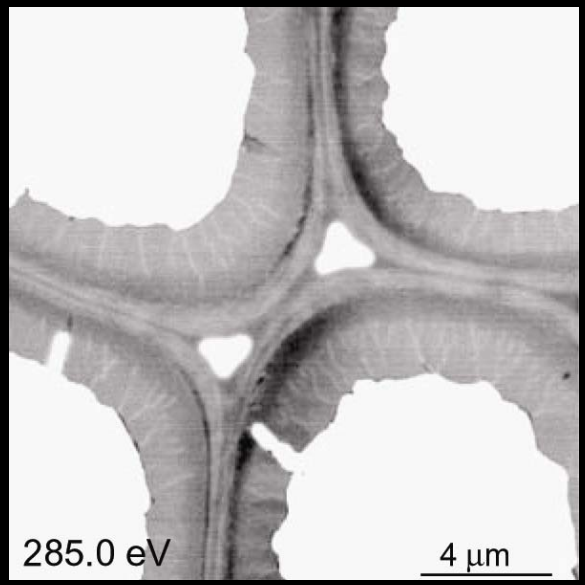
Lower Devonian (400 million years ago)



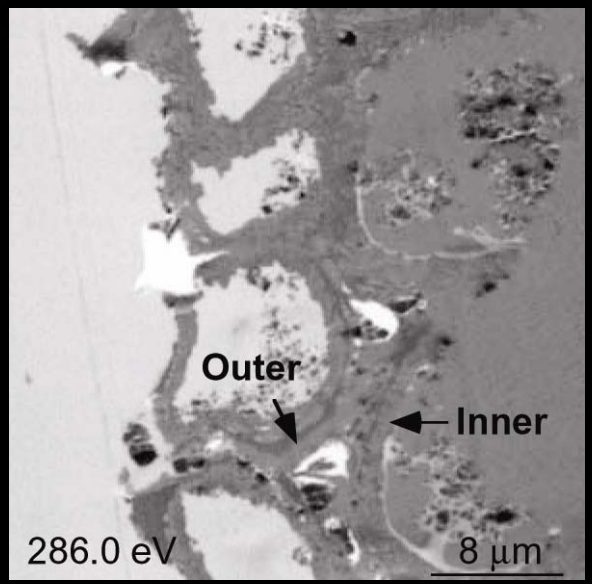
Aglaophyton *Rhynia* *Asteroxylon*

(Boyce et al. IJPS 2003)

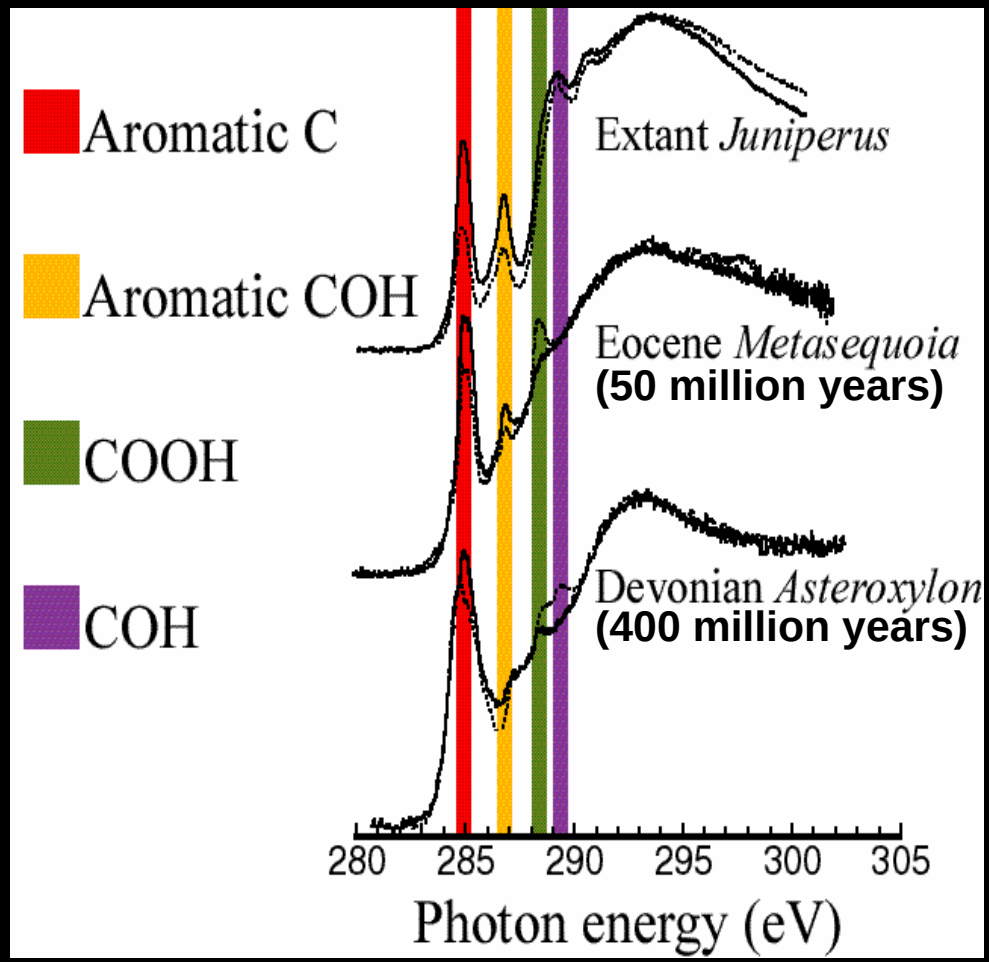
Cell wall chemical differentiation in living plants and fossils



Recent wood

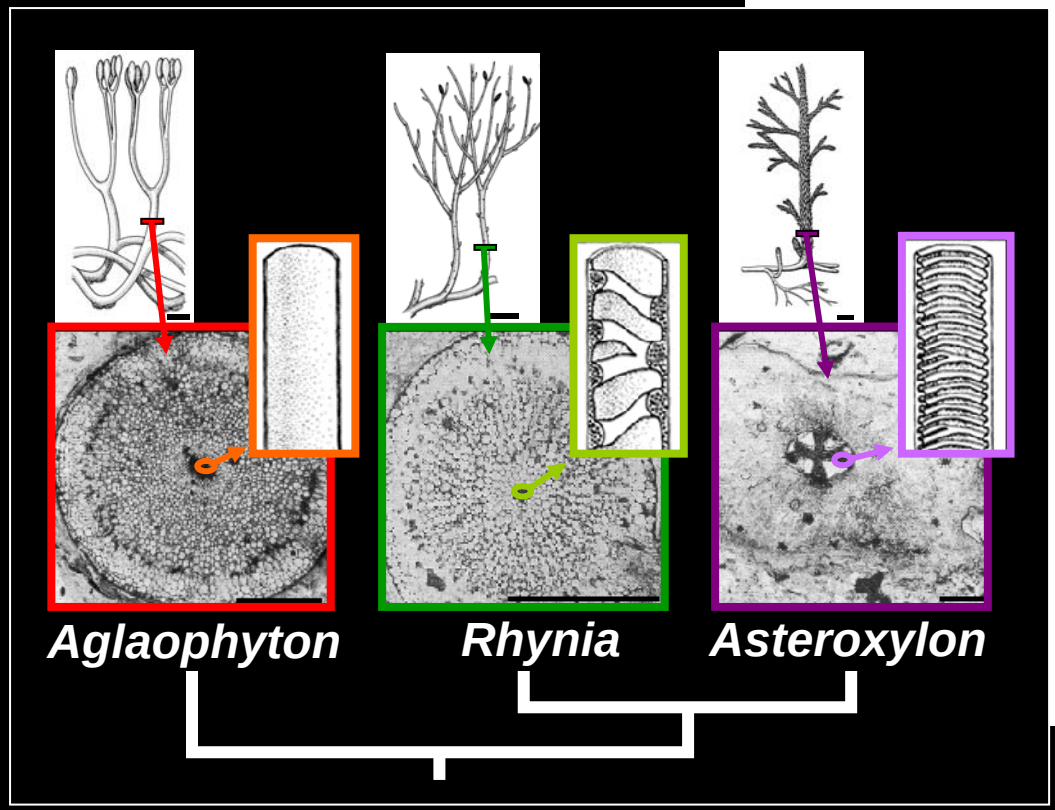


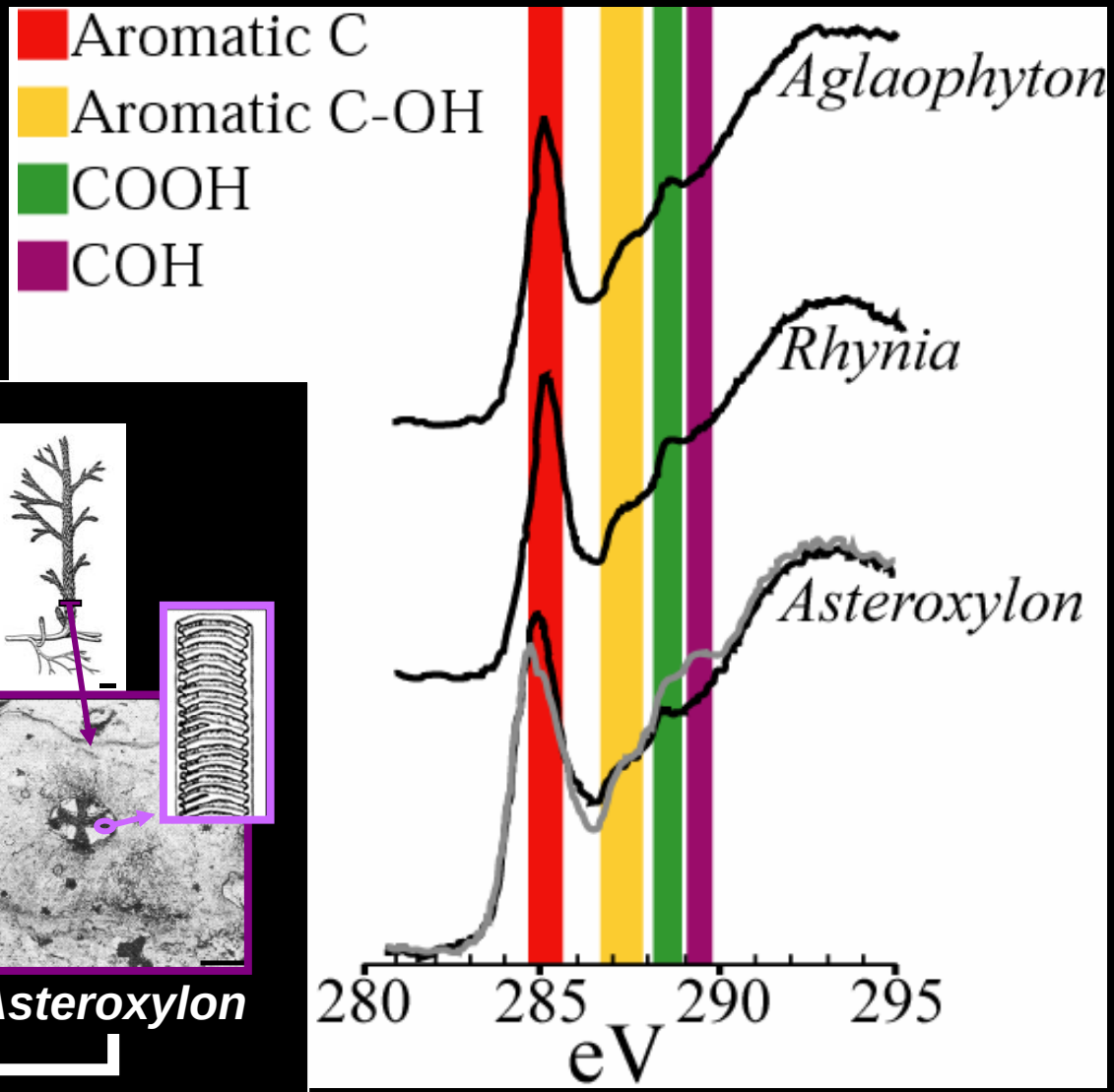
Eocene wood



(Boyce et al. Geology 2002)

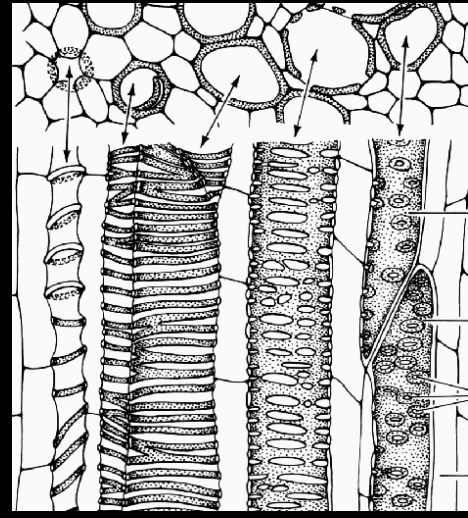
Evolution of vascular cells
Lower Devonian (400 million years ago)



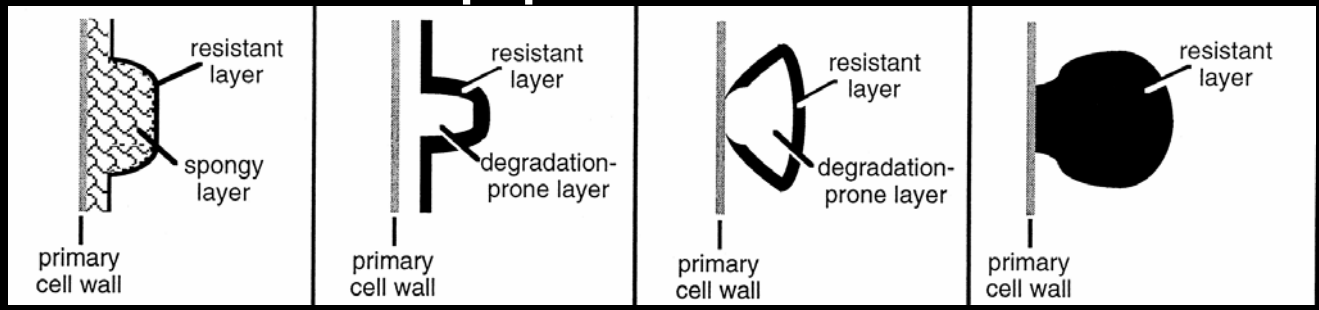


(Boyce et al. IJPS 2003)

Where is the lignin?



From a botanical paper on tracheid cell wall evolution:



(Cook & Friedman 1998)

From an industry book on wood chemistry:

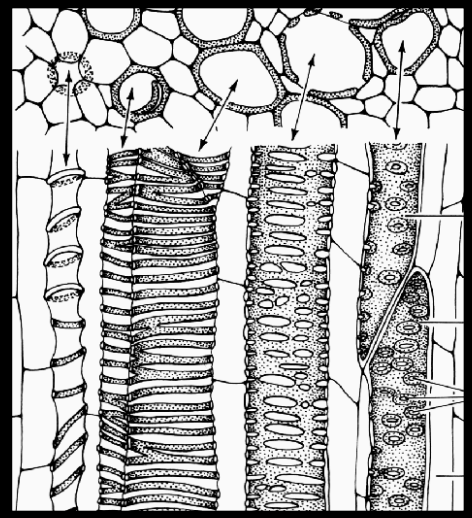
"The primary wall is a thin layer, 0.1-1.0 mm thick, consisting of cellulose, hemicelluloses, pectin, and protein and completely embedded in lignin."

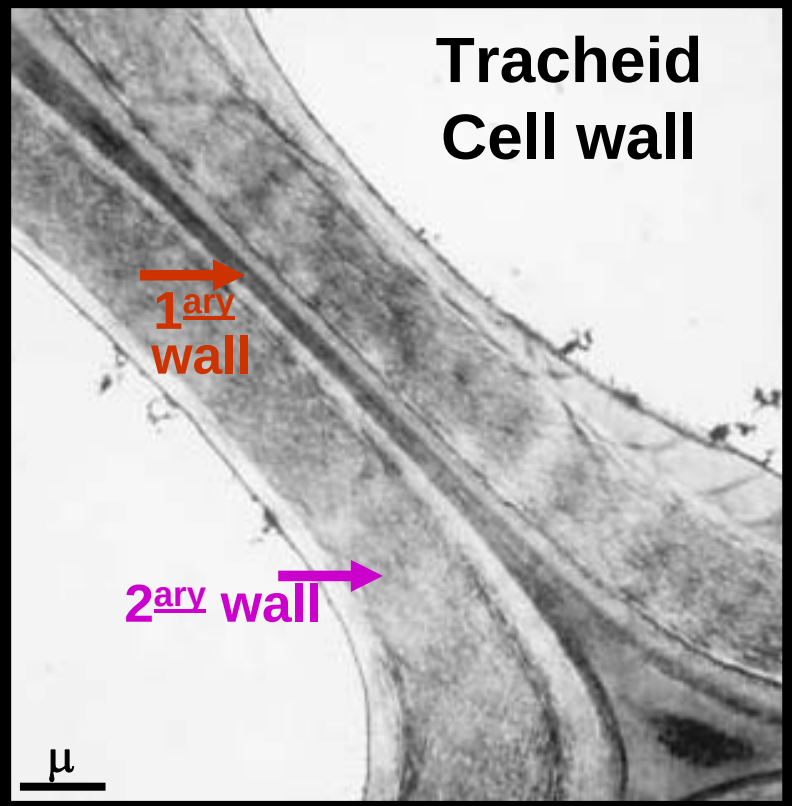
(Sjöström 1993)

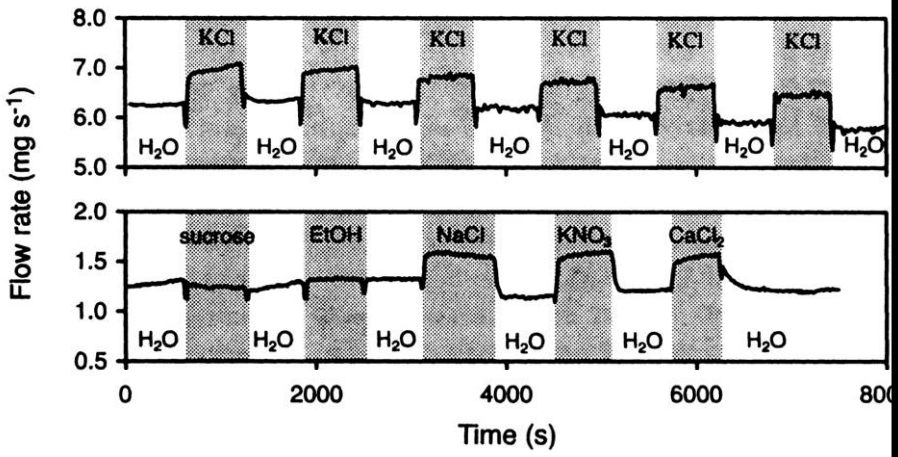
It depends who you ask.

Xylem Function

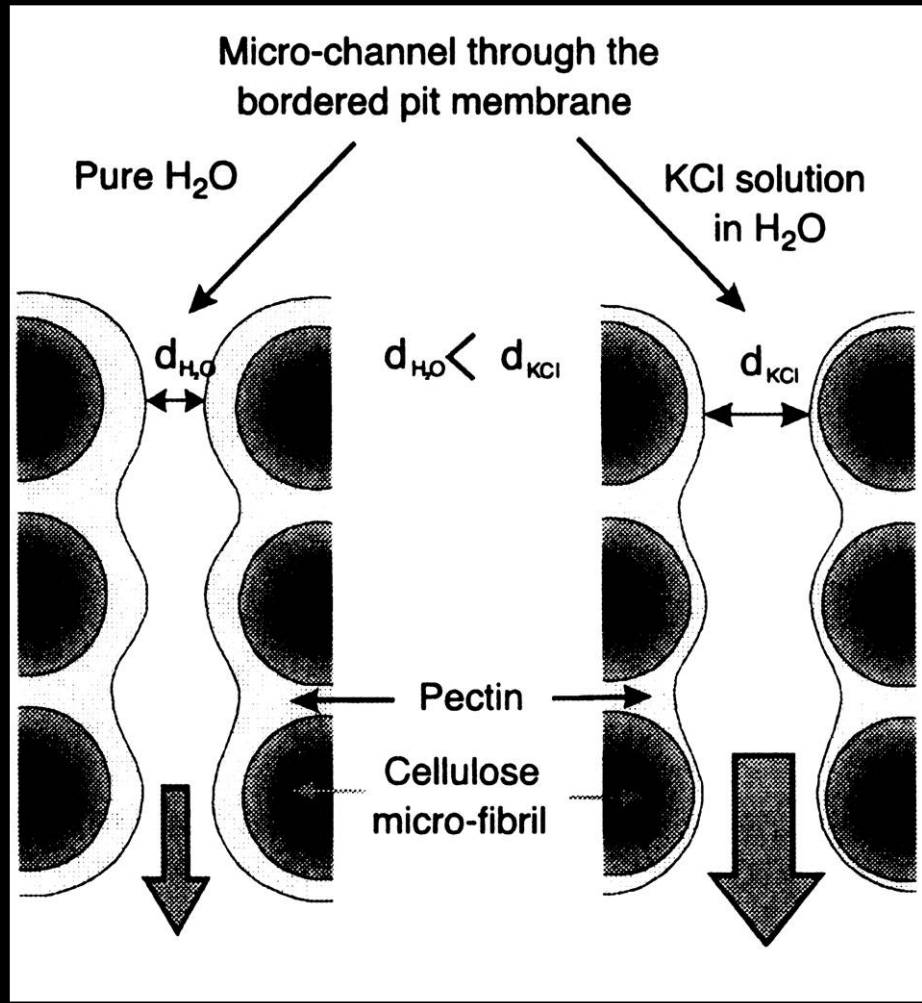
- Hydraulics
  - Short distance distribution
  - Long distance transport
  - Refilling after cavitation
  - Hydrogel transport regulation
- Support
  - Mechanical strength
  - Cell-cell adhesion
  - Withstanding growth stresses





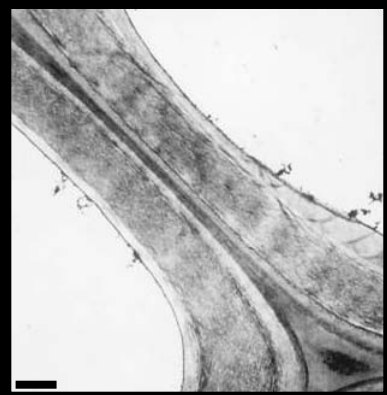


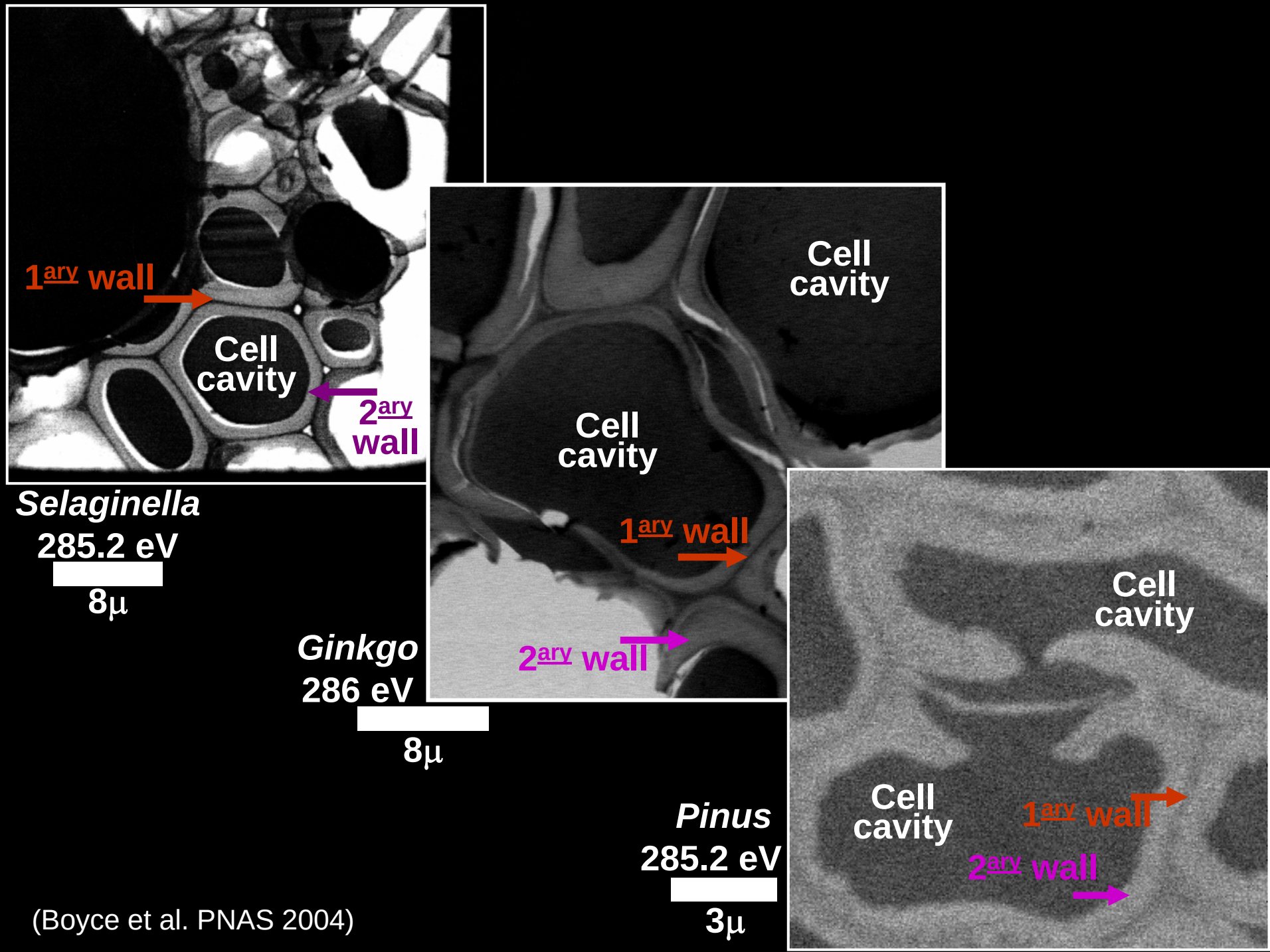
(Zwieniecki et al. 2001)

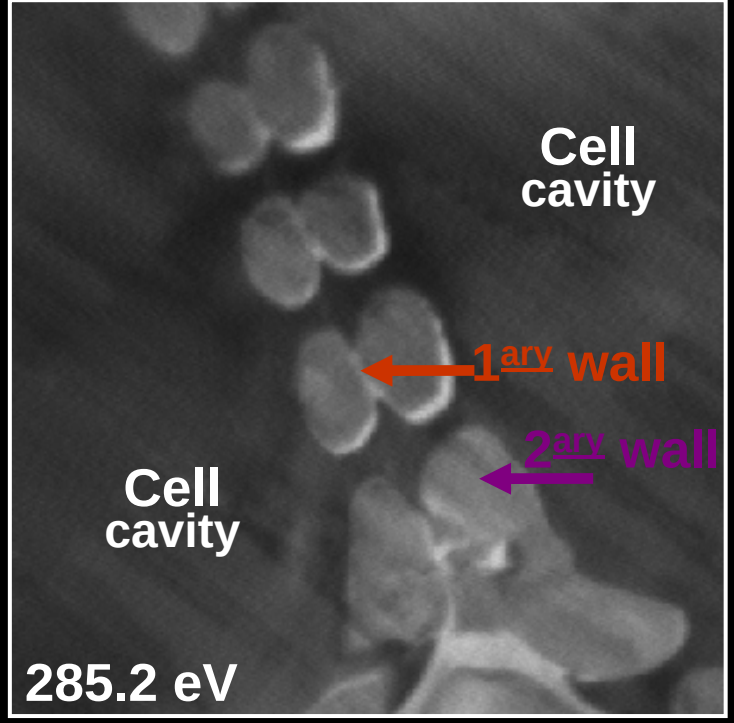


Pectins can act as a hydrogel and alter xylem resistance properties in response to changes in ionic concentration of sap, but…

Xylem Function	Optimal lignin Placement
Hydraulics	
Short distance distribution	2^{ary} wall
Long distance transport	1^{ary} wall
Refilling after cavitation	2^{ary} wall
Hydrogel transport regulation	2^{ary} wall
Support	
Mechanical strength	1^{ary} wall
Cell-cell adhesion	1^{ary} wall
Withstanding growth stresses	2^{ary} wall

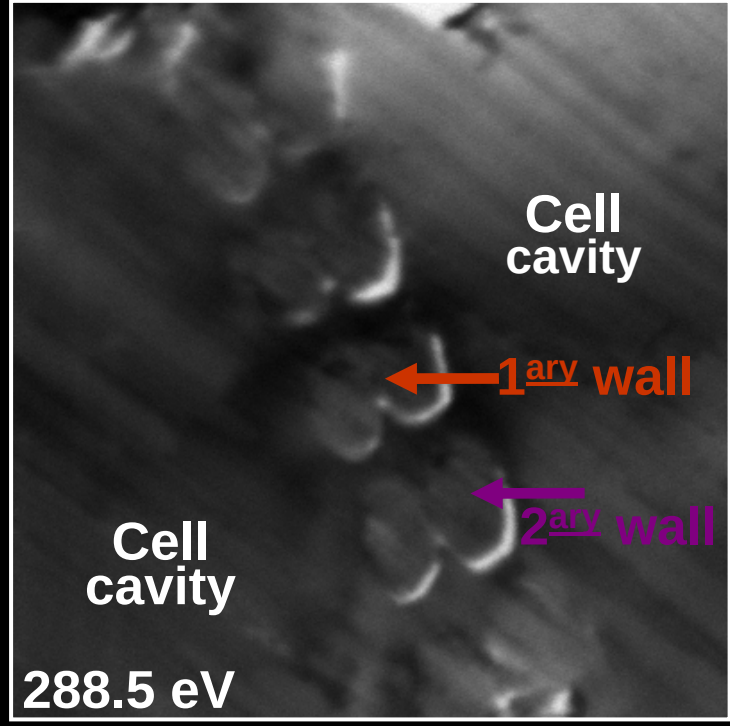


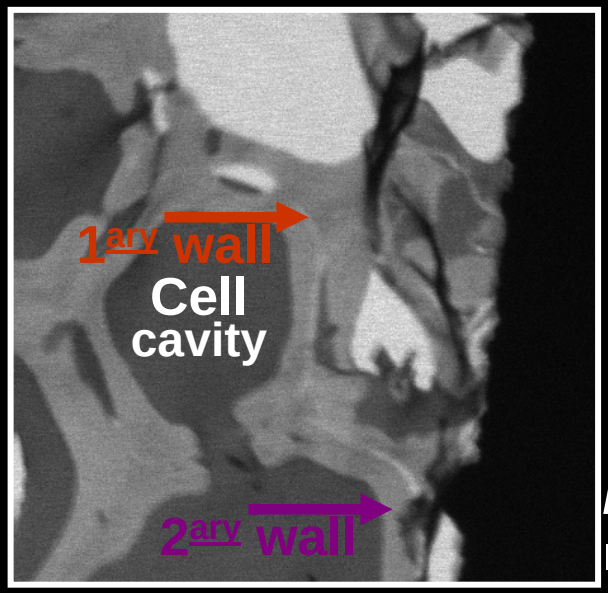

1ary wall
Cell cavity
2ary wall
Selaginella
285.2 eV
8μ
Cell cavity
Cell cavity
1ary wall
2ary wall
Ginkgo
286 eV
8μ
Cell cavity
Cell cavity
1ary wall
2ary wall
Pinus
285.2 eV
3μ
(Boyce et al. PNAS 2004)



Acer

2μ



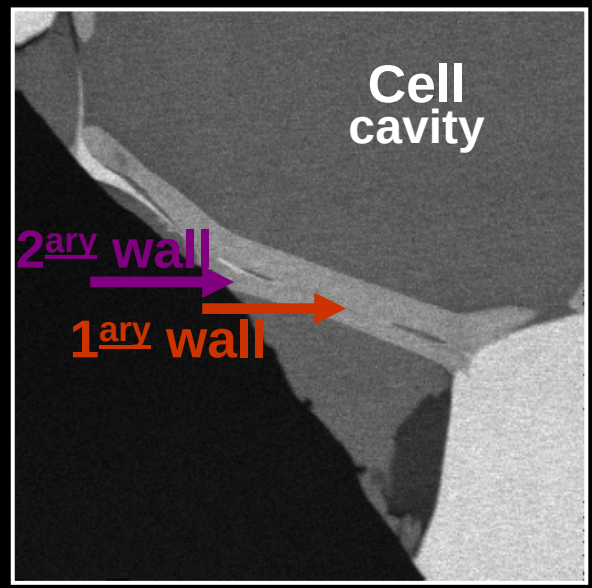


Psilotum

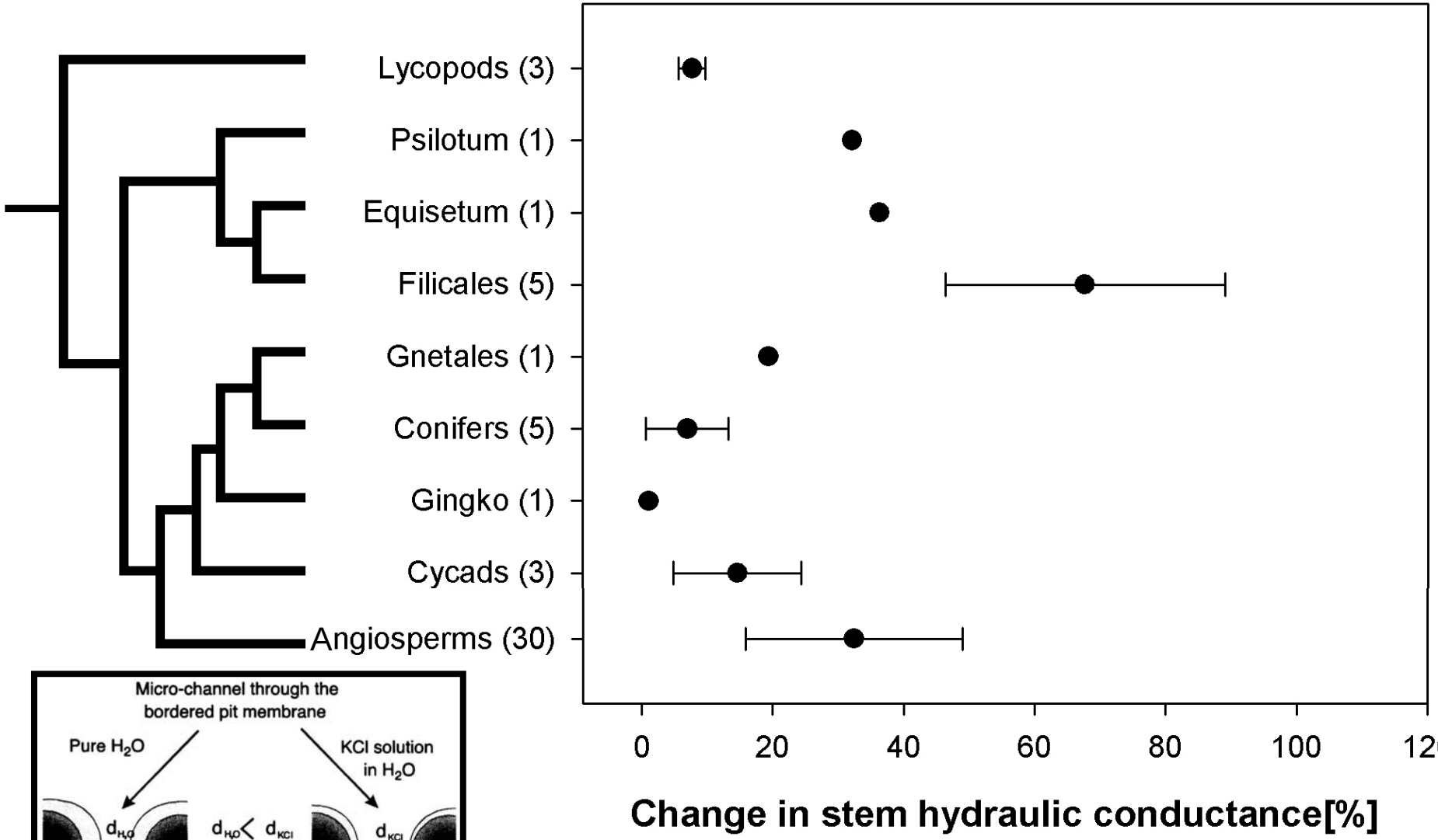
4μ

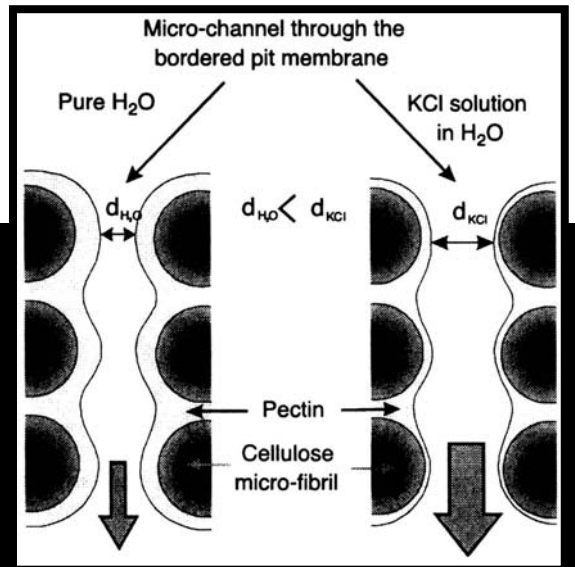
Pteridium

10μ



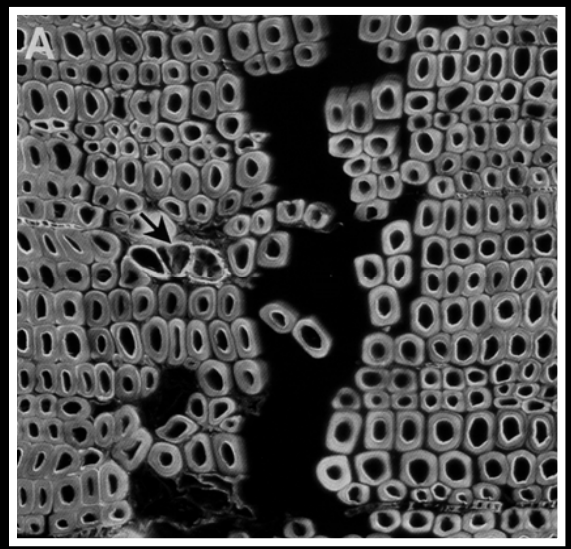
(Boyce et al. PNAS 2004)



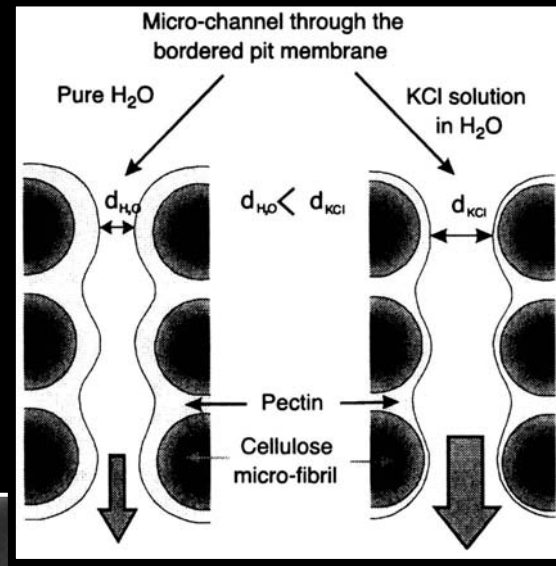


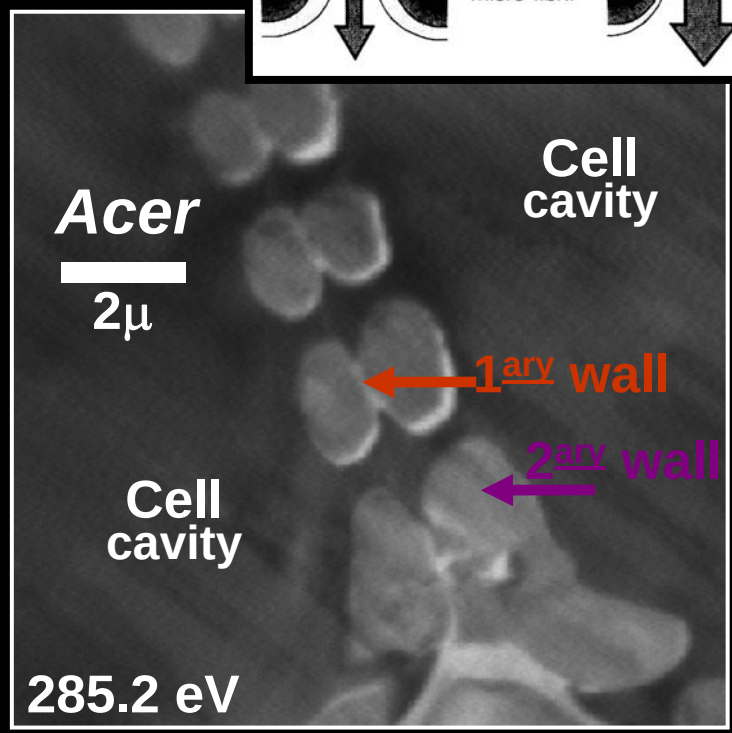
(Boyce et al. PNAS 2004)

Xylem Function	Optimal lignin Placement
Hydraulics	
Short distance distribution	2ary wall
Long distance transport	1ary wall
Refilling after cavitation	2ary wall
Hydrogel transport regulation	2ary wall
Support	
Mechanical strength	1ary wall
Cell-cell adhesion	1ary wall
Withstanding growth stresses	2ary wall



(Donaldson 2002)





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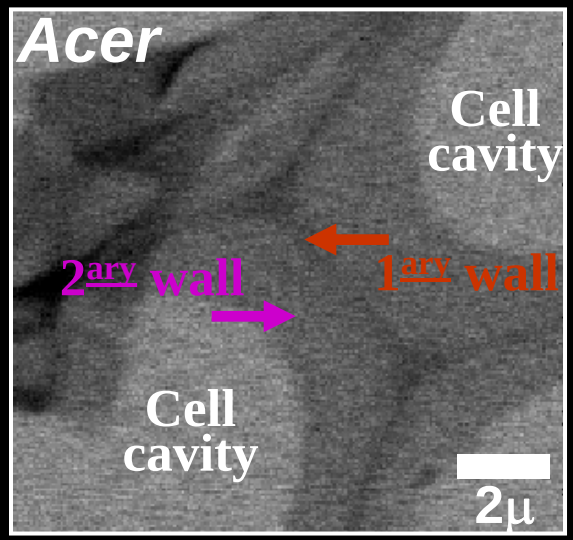
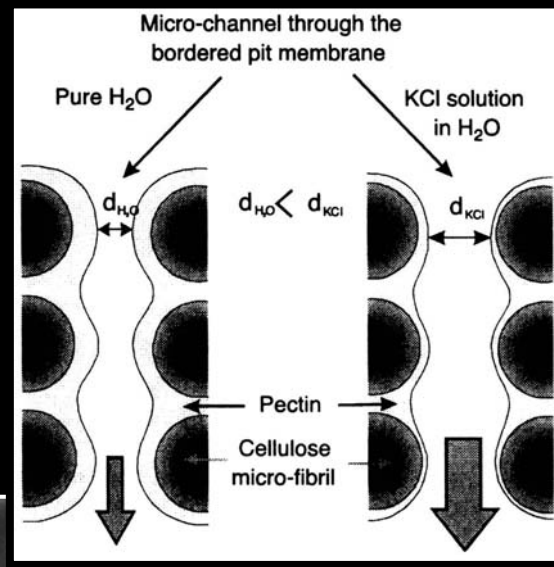
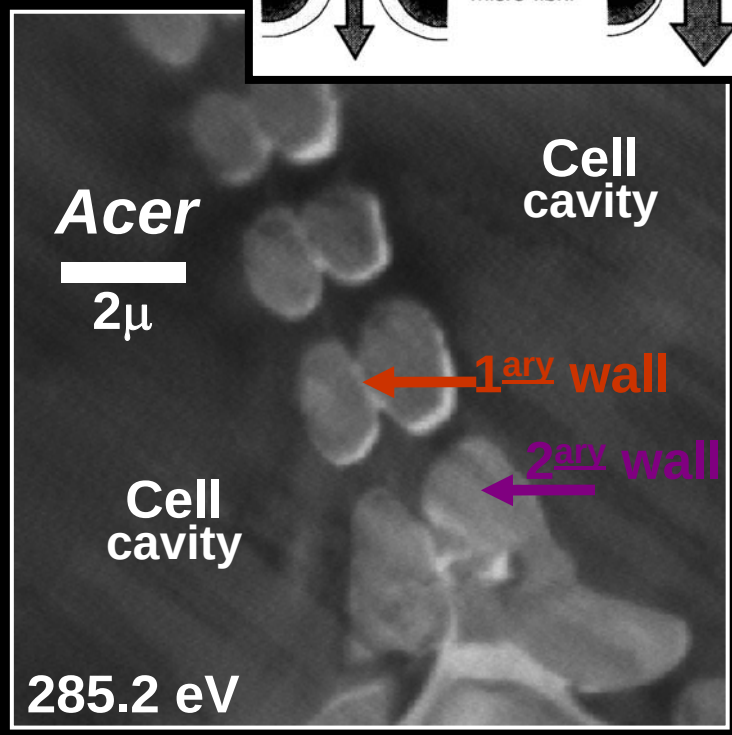
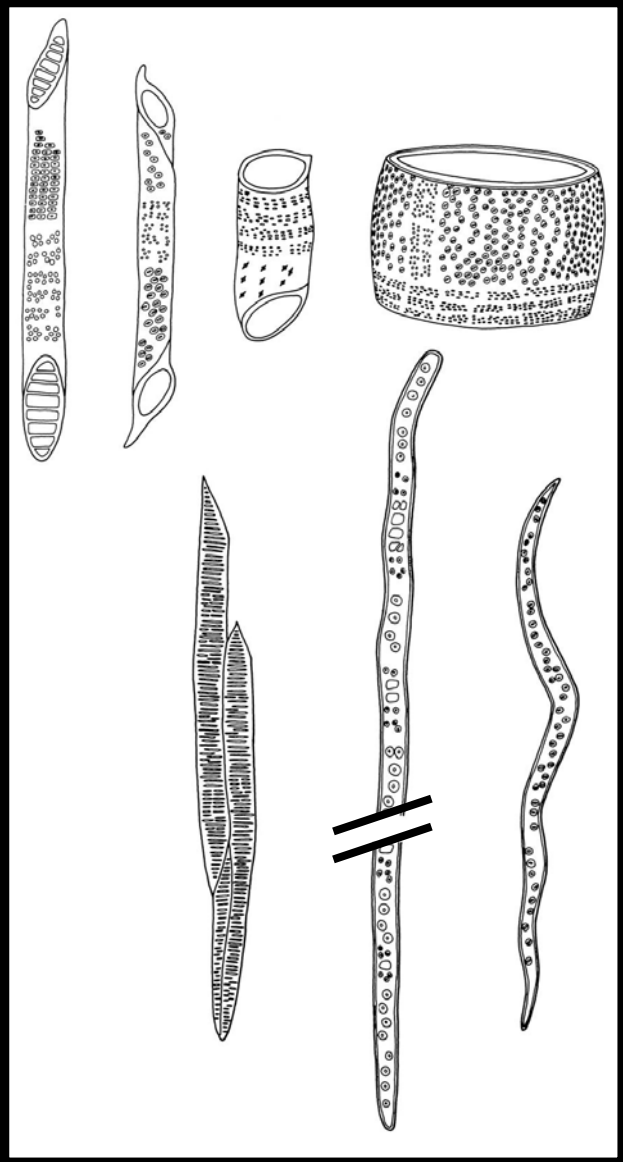


Vessel

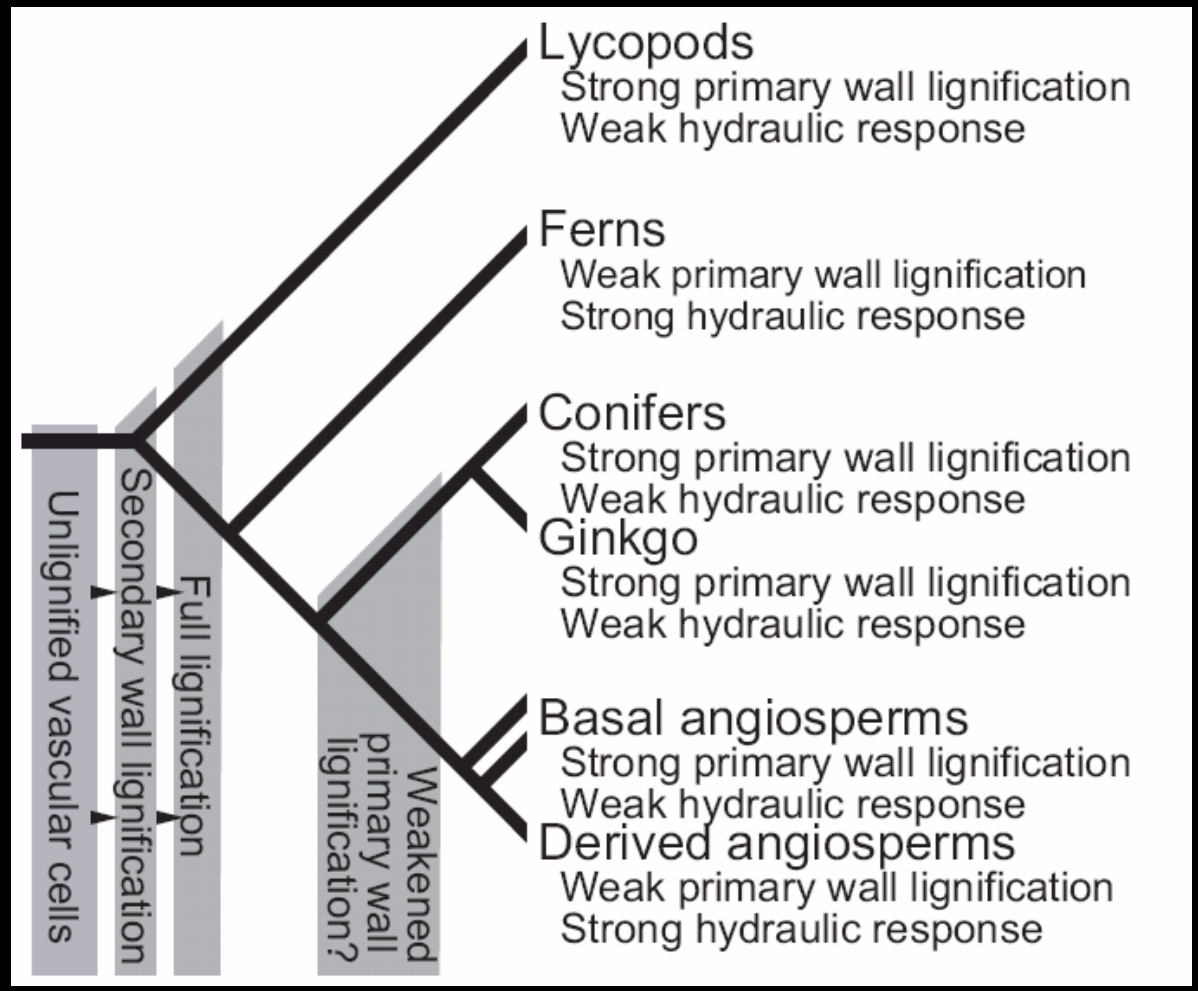
Fiber





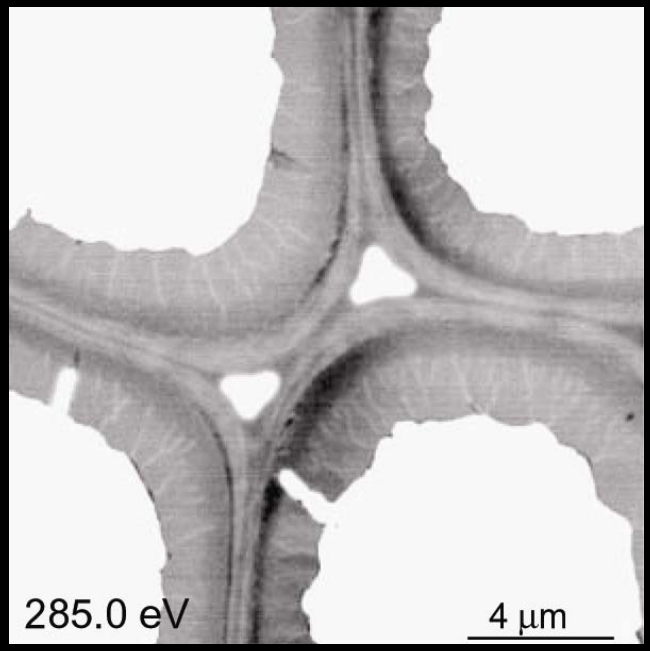


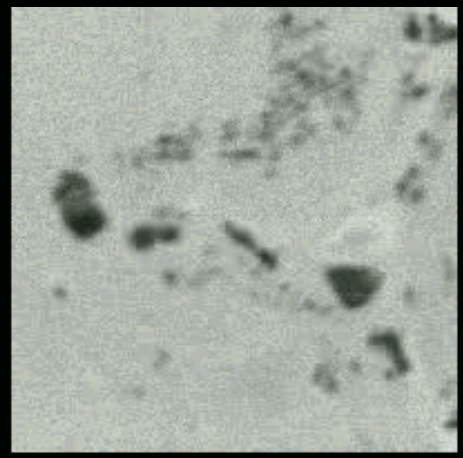
Divergence of xylem lignification patterns



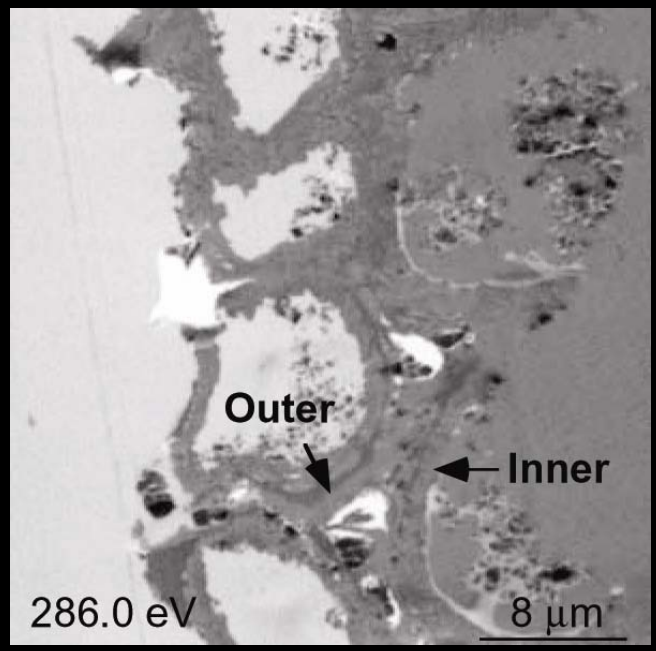
(Boyce et al. PNAS 2004)

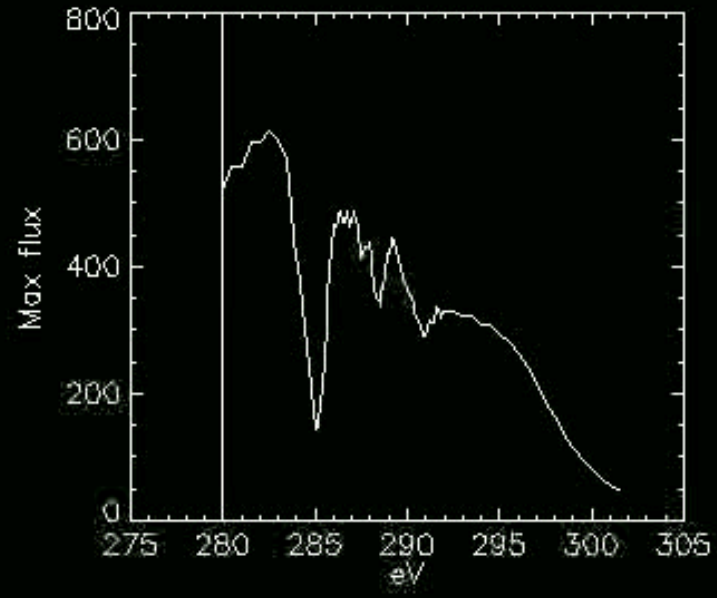
Extant wood



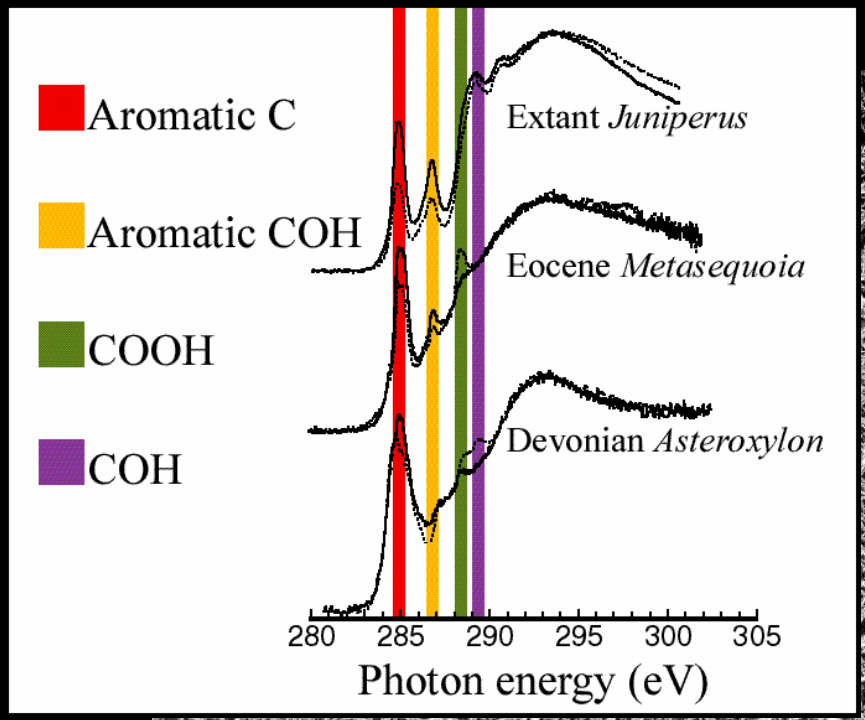


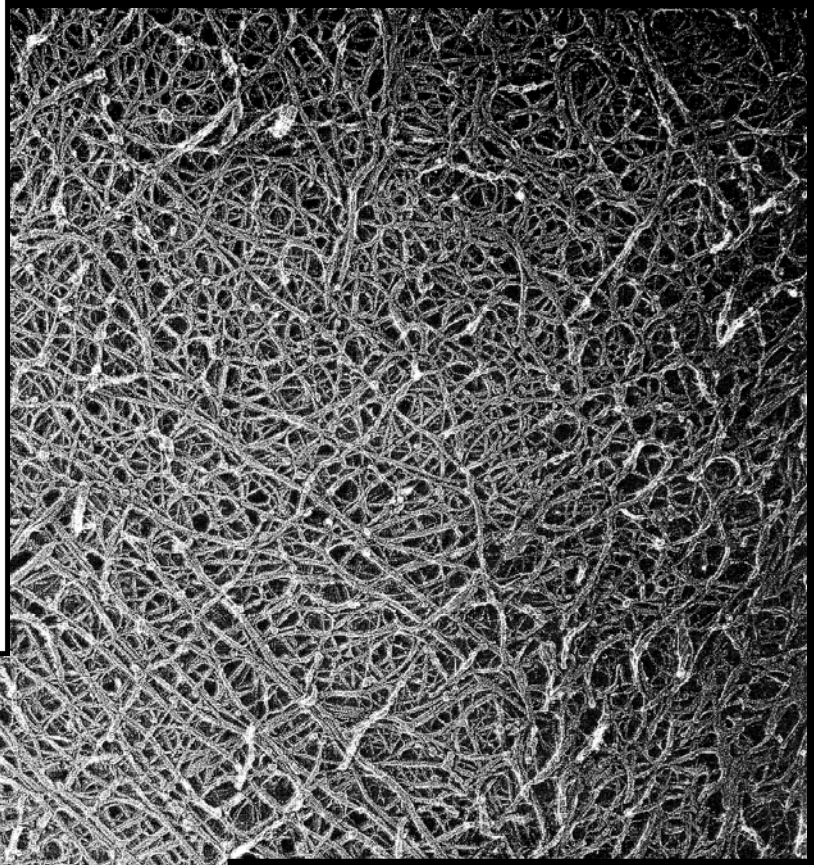
Fossil wood

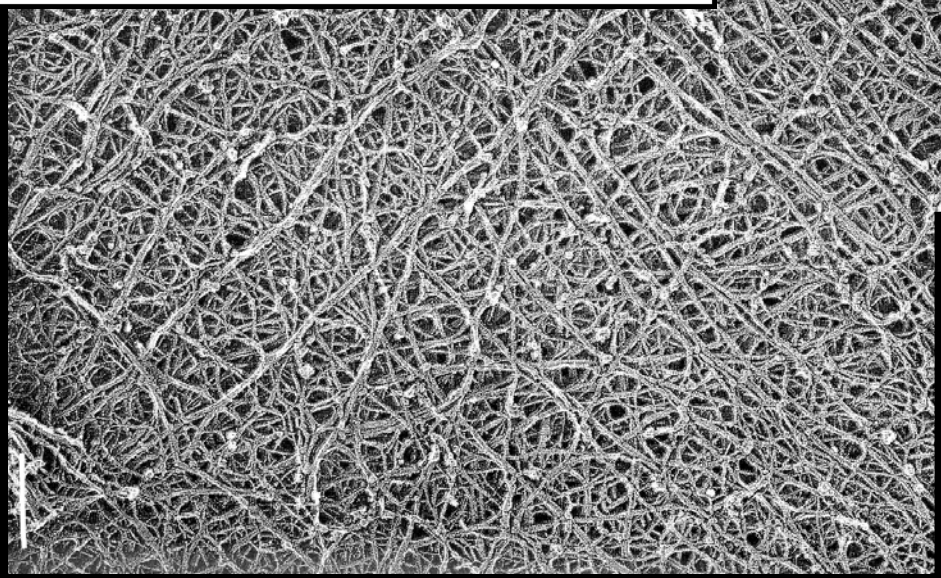


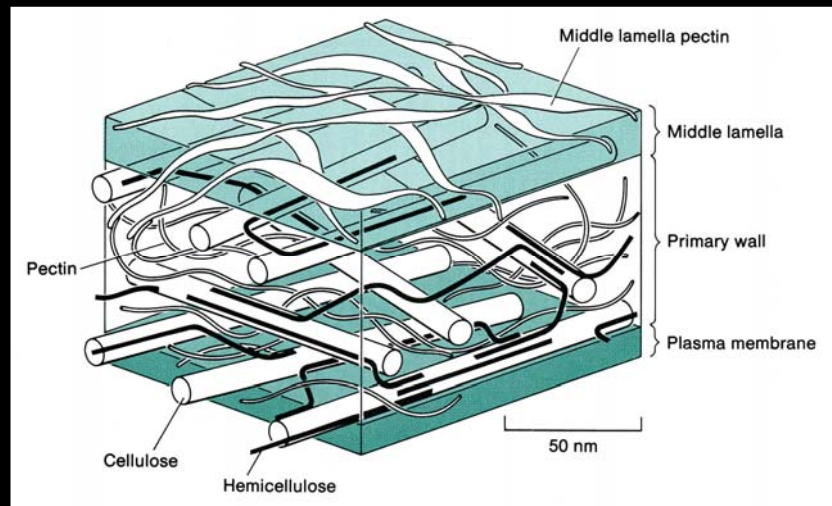


(Boyce et al. Geology 2002)









Bound lignin can protect polysaccharides from degradation for thousands of years

Where does coal come from?

Lignin to lignite

↓

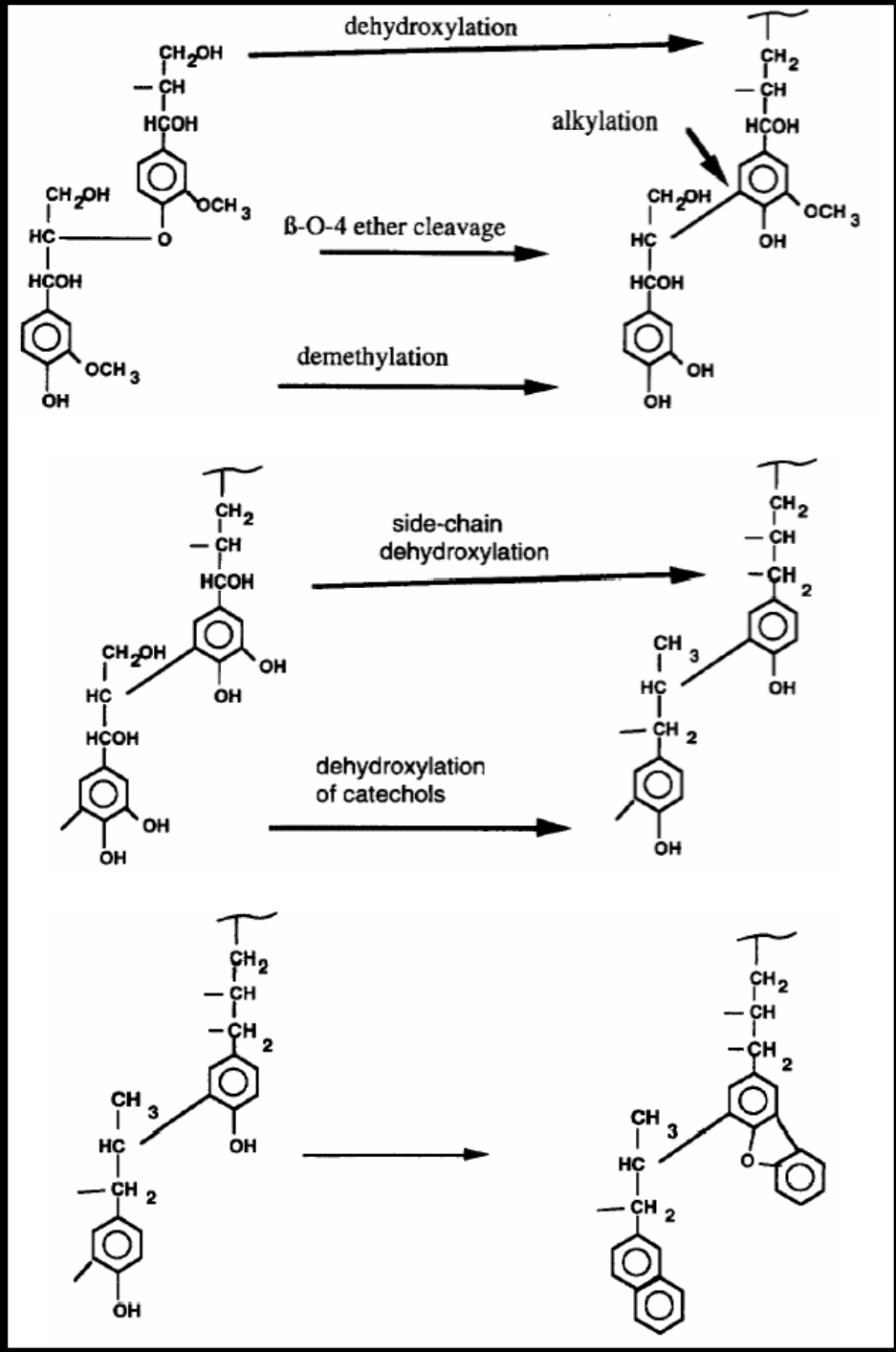
Lignite to subbituminous coal

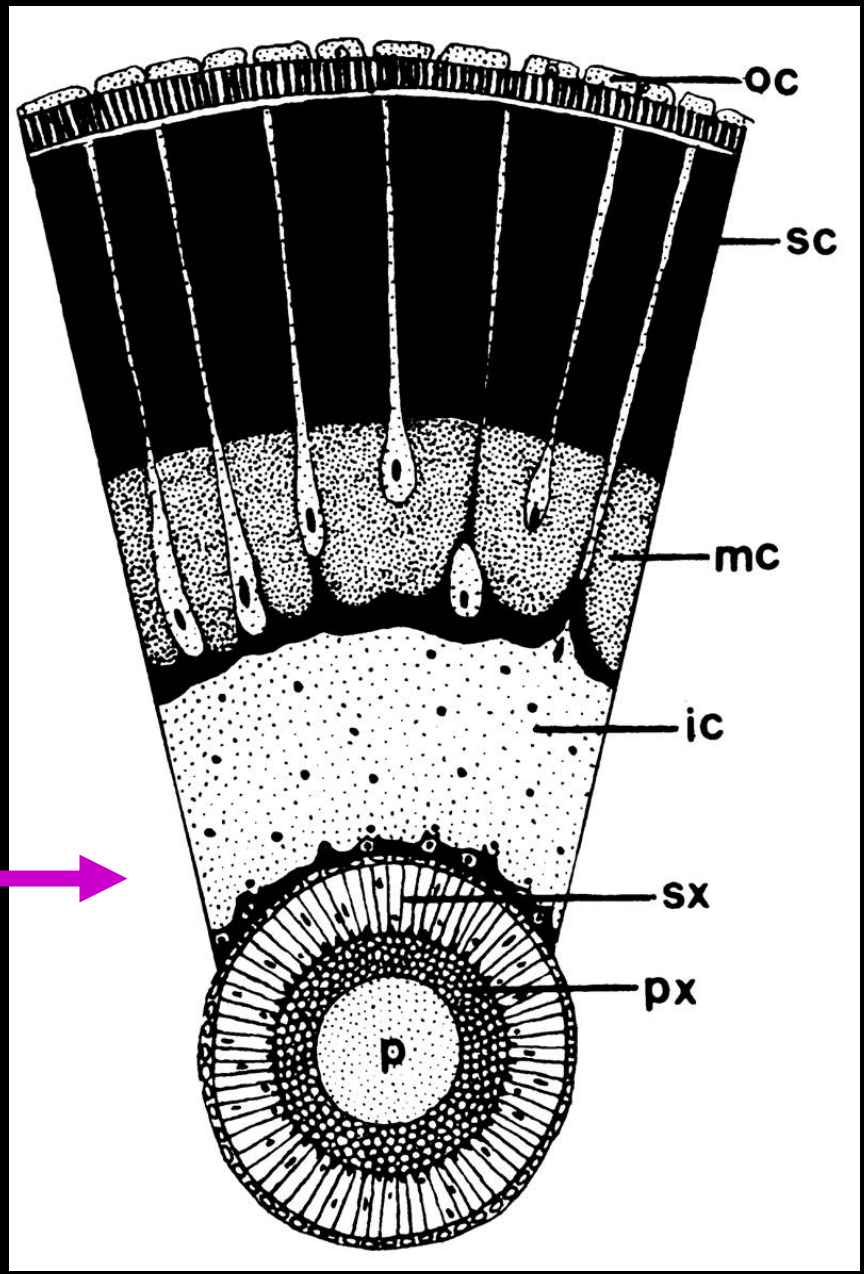
↓

Subbituminous to bituminous coal

Coal comes from lignin.

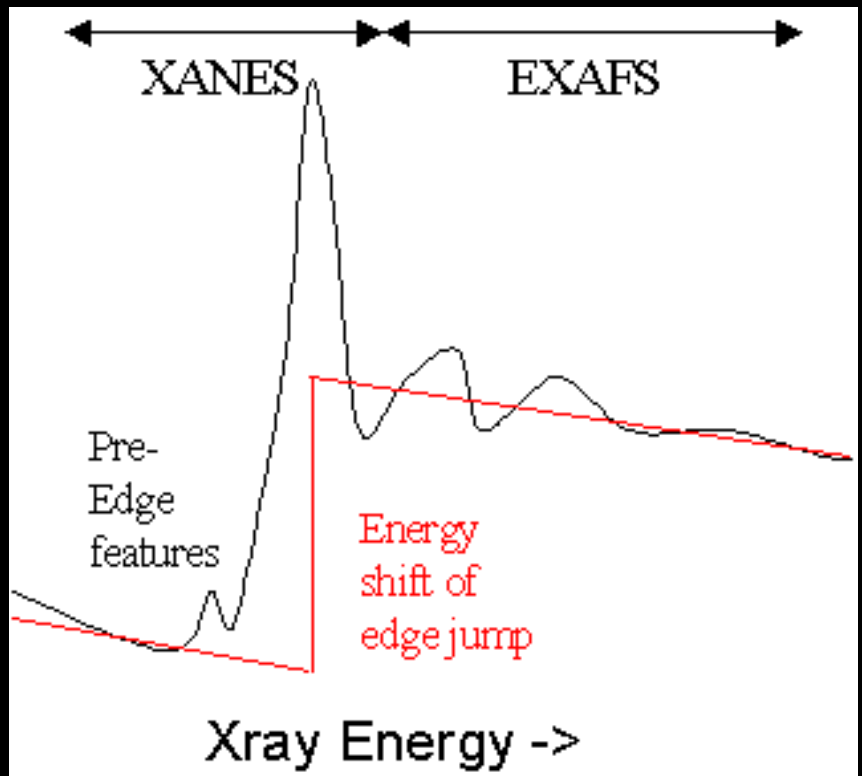
(Hatcher & Clifford 1997)

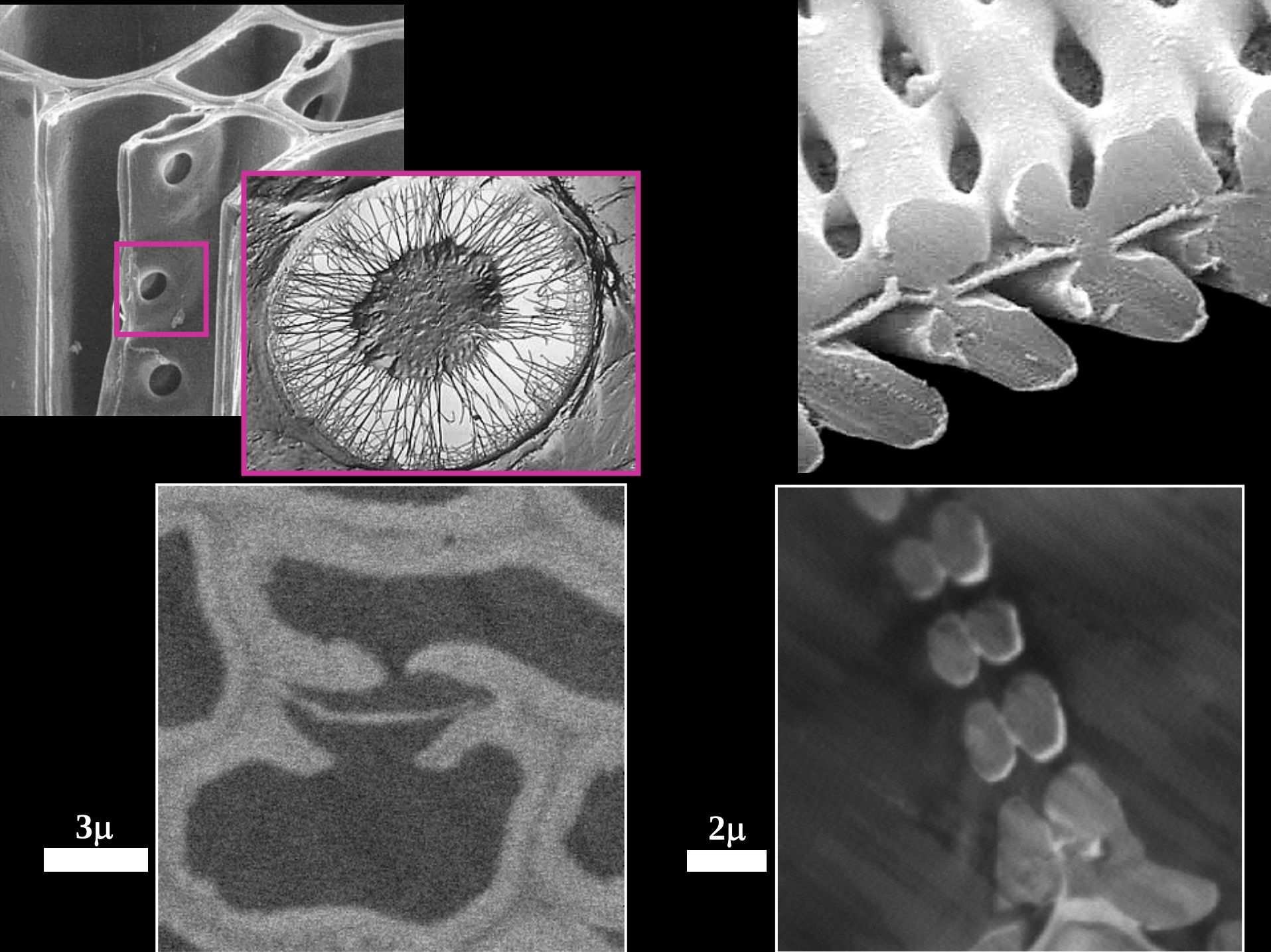


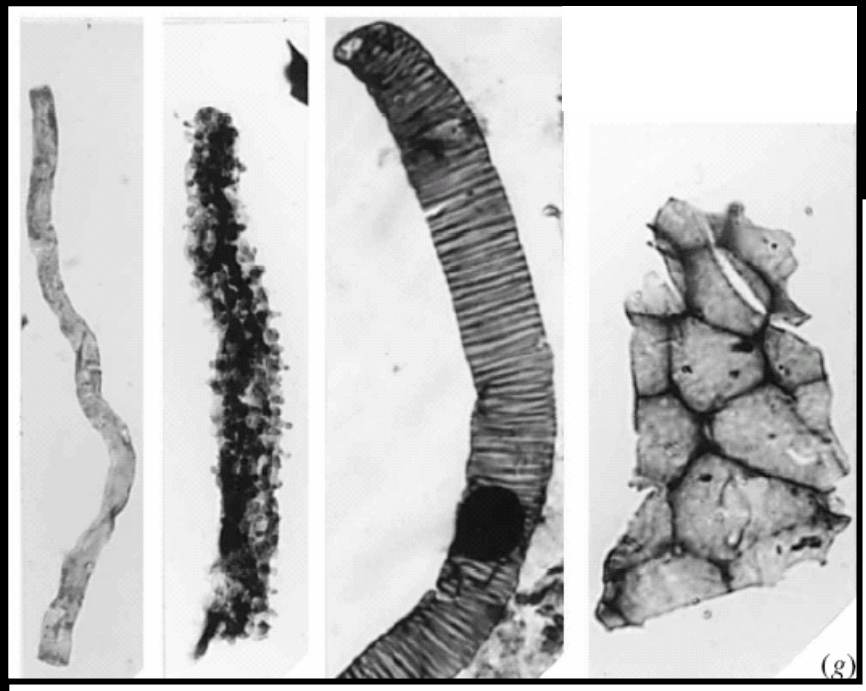

oc
sc
mc
ic
sx
px
p

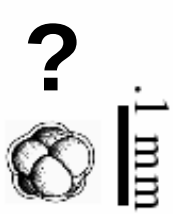
So where does coal come from?

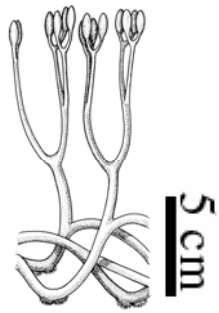
- Distribution of lignin in vascular cell walls
- Devonian evolution of lignified vascular cells
- Derivation of coal from lignin

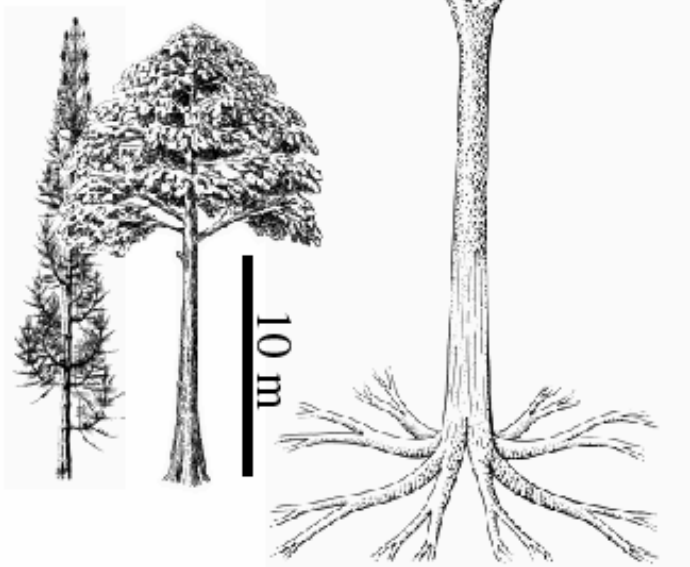



3µ
2µ









490 443 417 354 **Millions of years**

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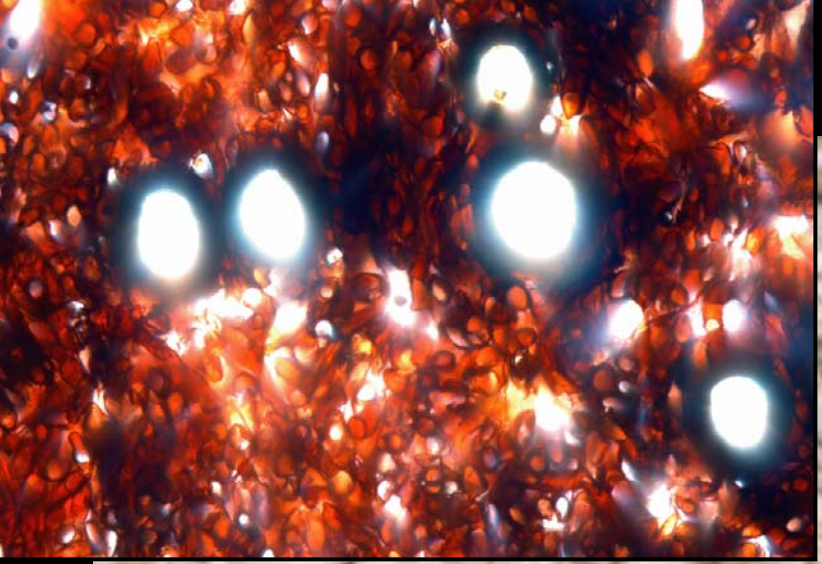
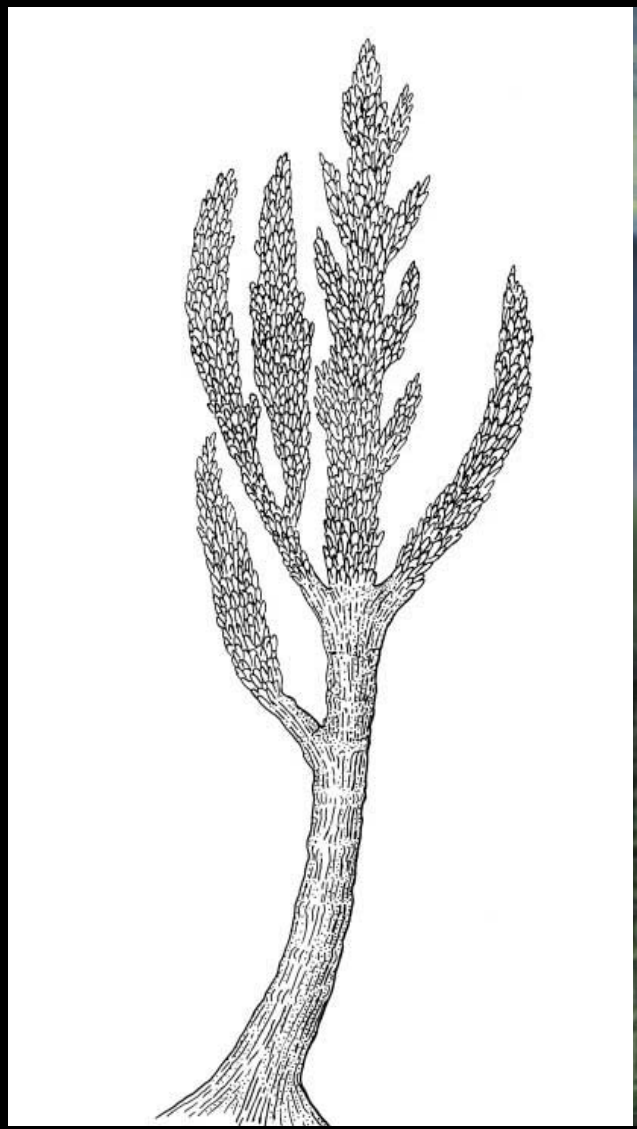
Ordovician Silurian Devonian Carboniferous

Devonian *Prototaxites*?

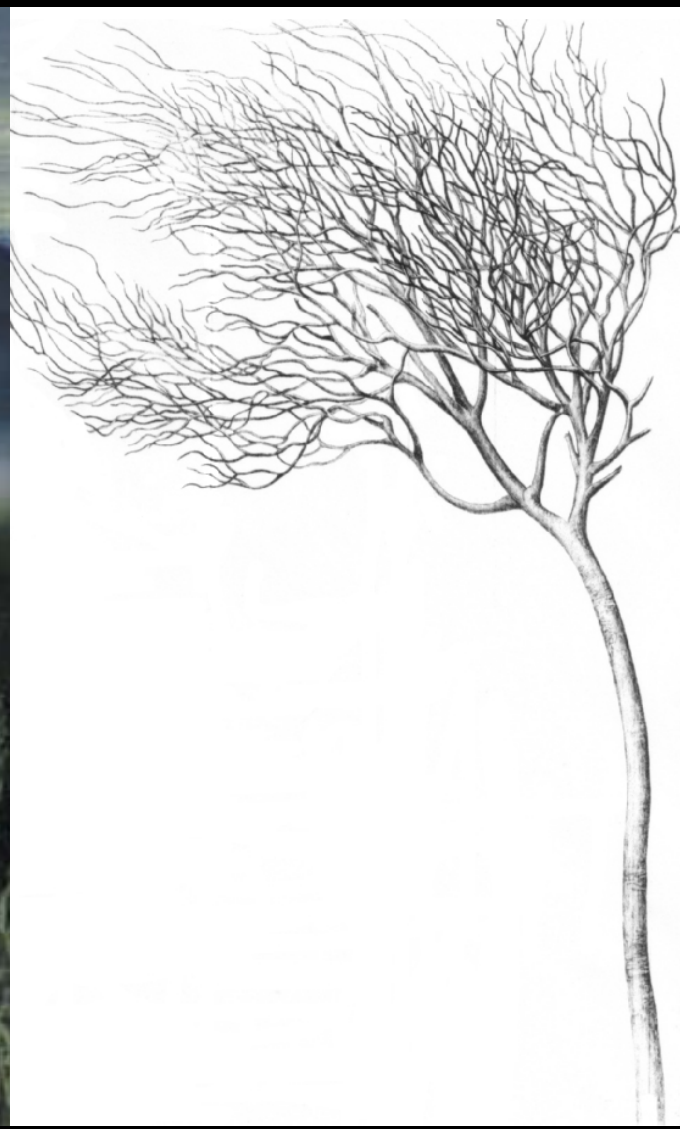


Vascular plant?	Dawson 1859
Lichen?	Caruthers 1872
Green algae?	Caruthers 1872
Brown algae ?	Seward 1898
Fungus?	Church 1919
Red algae?	Jonker 1979

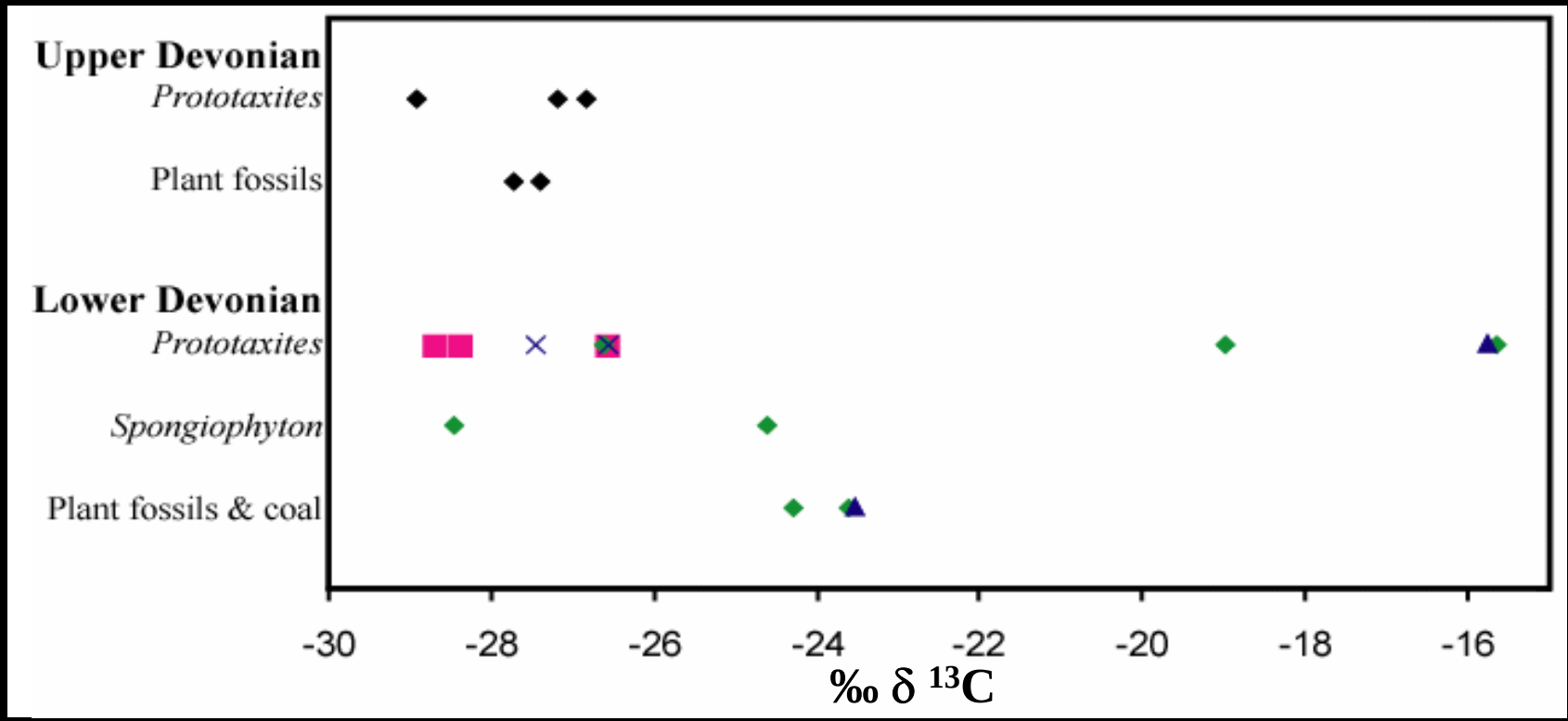


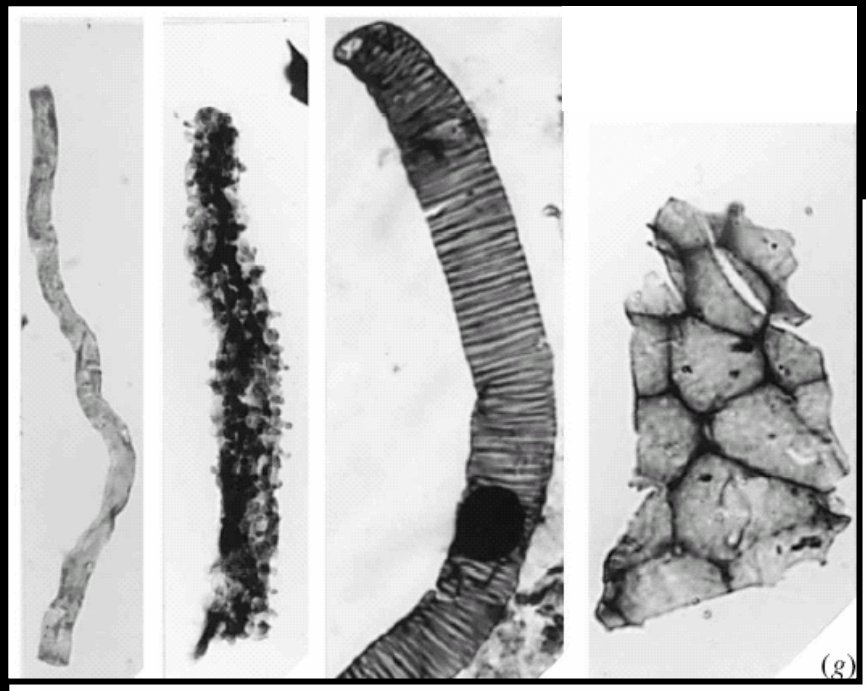
(Dawson 1888)

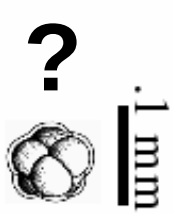
(Hueber 2001)

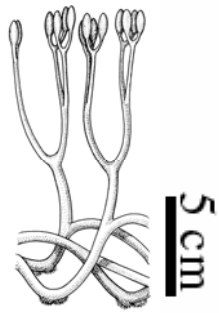


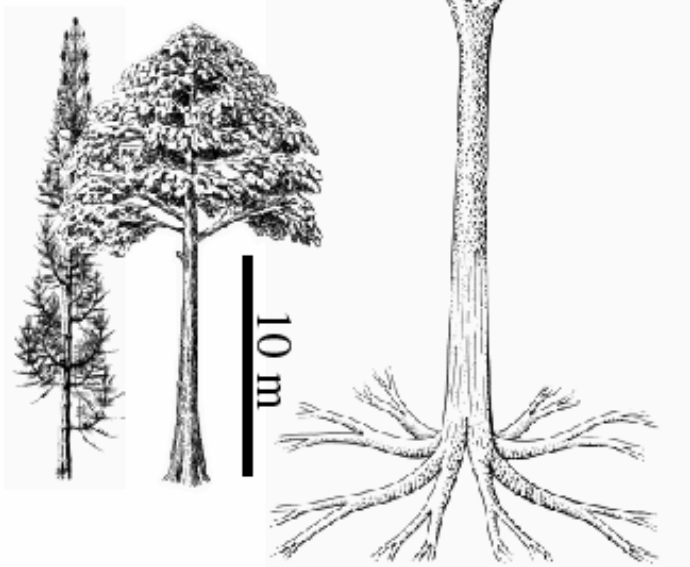
(Schweitzer 1983)


Upper Devonian
Prototaxites
Plant fossils
Lower Devonian
Prototaxites
Spongiophyton
Plant fossils & coal
-30
-28
-26
-24
-22
-20
-18
-16
‰ δ 13C





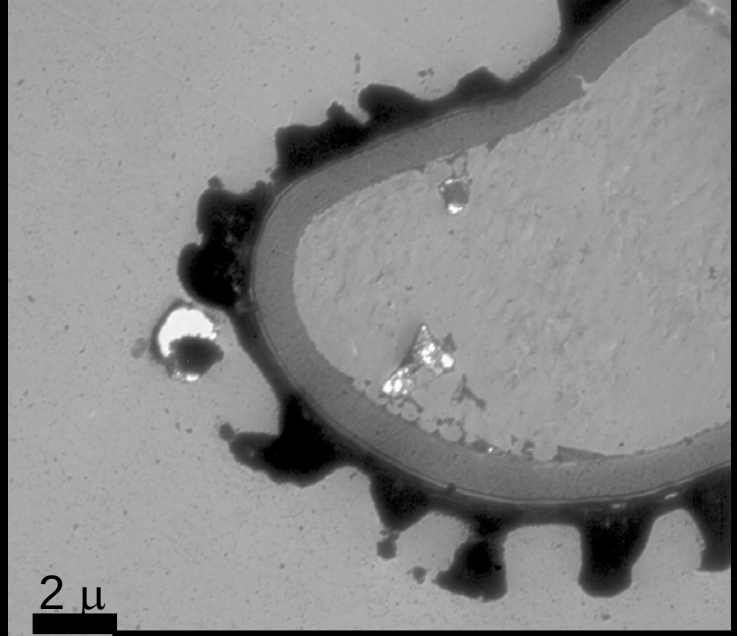


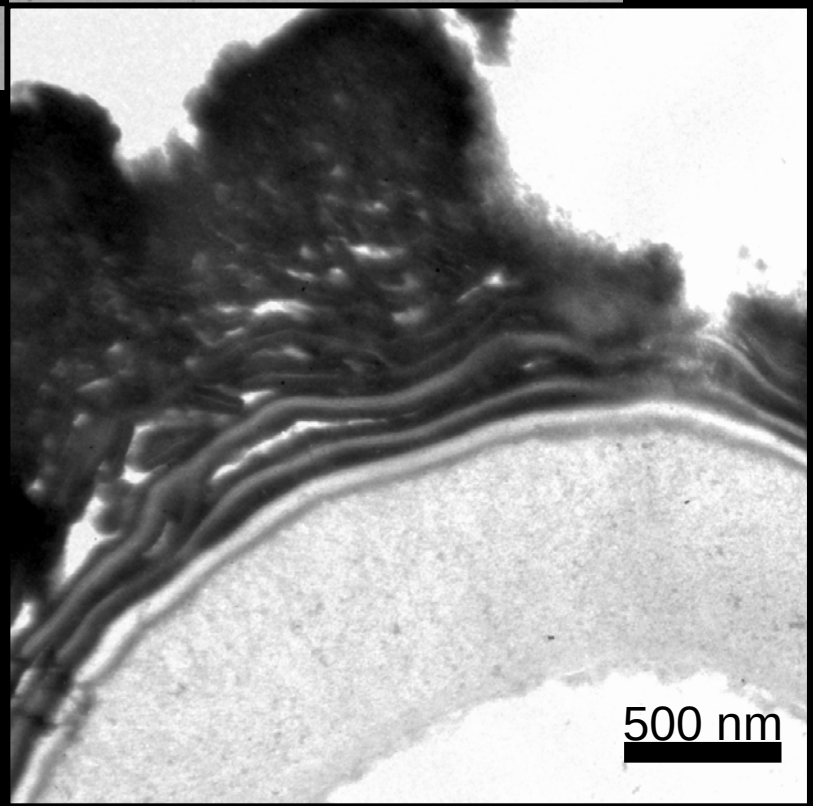


490 443 417 354 **Millions of years**

E M L E L E M L E L

Ordovician Silurian Devonian Carboniferous





Pollen & spores