Chapter 10
Material Properties of Plant

微視的に見た植物体のマテリアル利用

From Microscopic Views

Yukie Saito

1 Classification of plants Wood , Herb 木本と草本

2 Assembly of Microscopic and macroscopic structure of wood formation of wood

Thickning growth肥大生長・annual ring年輪・heart wood 心材化・lignification木化

3 Components of plant cell wall as chemical resources

3.1 Cellulose 糖鎖Sugar chain ・水素結合hydrogen bondings

3.2 Hemicellulose

3.3 Lignin

Paper 紙・nano fiber ナノファイバー・saccharification糖化・bioethanolバイオエタノール

4 Plants as a carbon resource

4.1 Peat biodegradation生物分解・coal

4.2 Natural modification of biomass into energy

4.3 Artificial modification of biomass into energy and materials

1 Classification of Plants

植　物　界 Plantae（357,000）

「木材の構造」文永堂出版より

隠花植物（Cryptogamae）

葉状植物 Thallophyta（95,000）

(1) 菌藻植物（Fungi, Algae, Lichens etc.）（72,000）
　細菌類，菌類，藻類，地衣類など

(2) コケ植物門 Bryophyta（23,000）
　苔類（9,000），蘚類（14,000）

維管束植物 Tracheophyta（262,000） Vascular

Dimensional change

(3) シダ植物門 Pteridophyta（11,000）
　マツバラン類（40），ヒカゲノカズラ類（1,200），トクサ類（30）
　シダ類（9,300）など

顕花植物（Phanerogamae）

Hard woods and soft woods are fro
very different origin.

(4) 裸子植物門 Gymnospermae（700）
　ソテツ類 Cycadales（目）（90）
　イチョウ類 Ginkgoales（目）（1）
　針葉樹類 Coniferales（目）（540）　**Soft wood**
　マオウ類 Gnetales（目）（70）

Wood

(5) 被子植物門 Angiospermae（250,000）　**Hard wood**　**Herb**
　双子葉類 Dicotyledoneae（綱）（2 亜綱 48 目）（200,000）
　単子葉類 Monocotyledoneae（綱）（14 目）（50,000）

General difference of herbal plants and woody plants

Higher importance as resource

	Thickening growth	Lignin contents	Durability	Dimension	Mechanical strength
Woody plants	Yes	More ≒25%	High	Large	High
Herbal plants	No	Less ≒14 %	Low	Small	Low

Biological definition

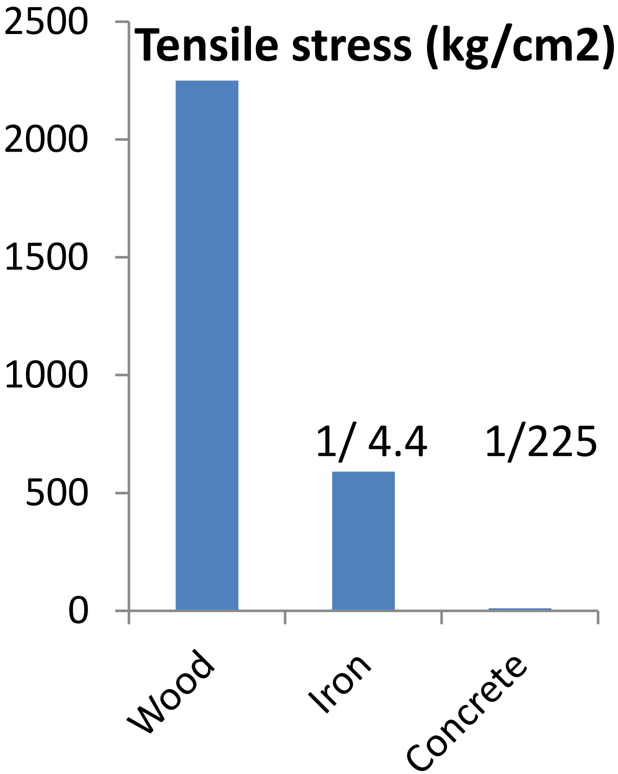
Bamboo, Palm

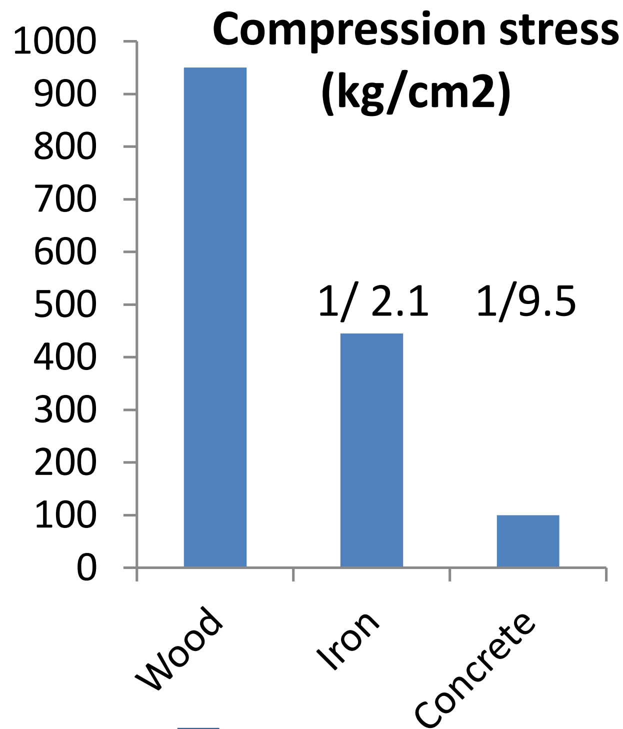
2. Microscopic and macroscopic features of woody plants

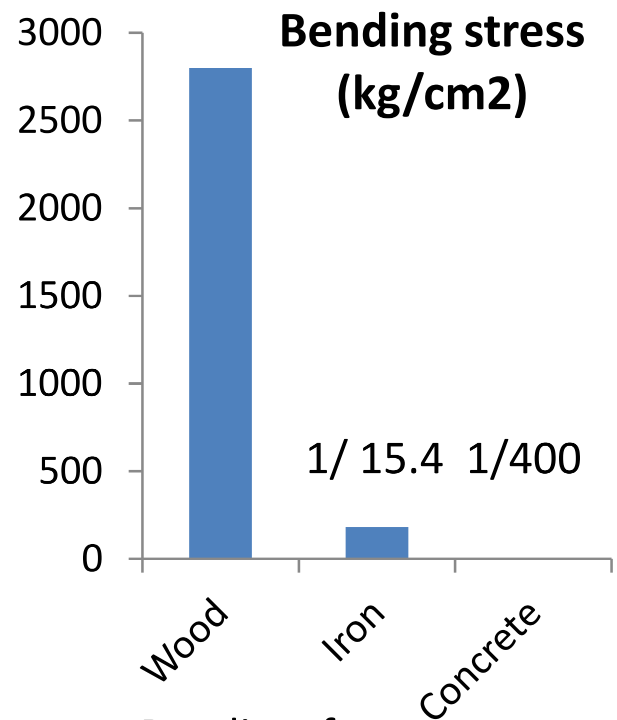

Points to remember:
What differs from artificial materials?
Degradability,
Reproducibility,
High diversity,
Heterogeneity,
Complexity of structure…

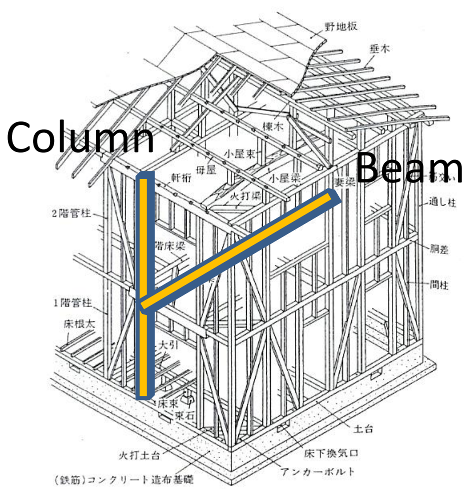
データ出所：日本住宅・木材技術センター「木と日本の住まい」

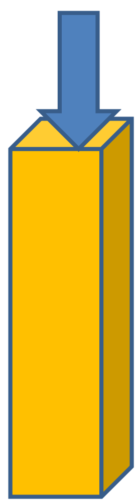
Specific strength (standardized by weight)





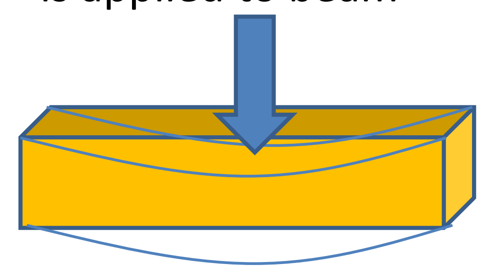




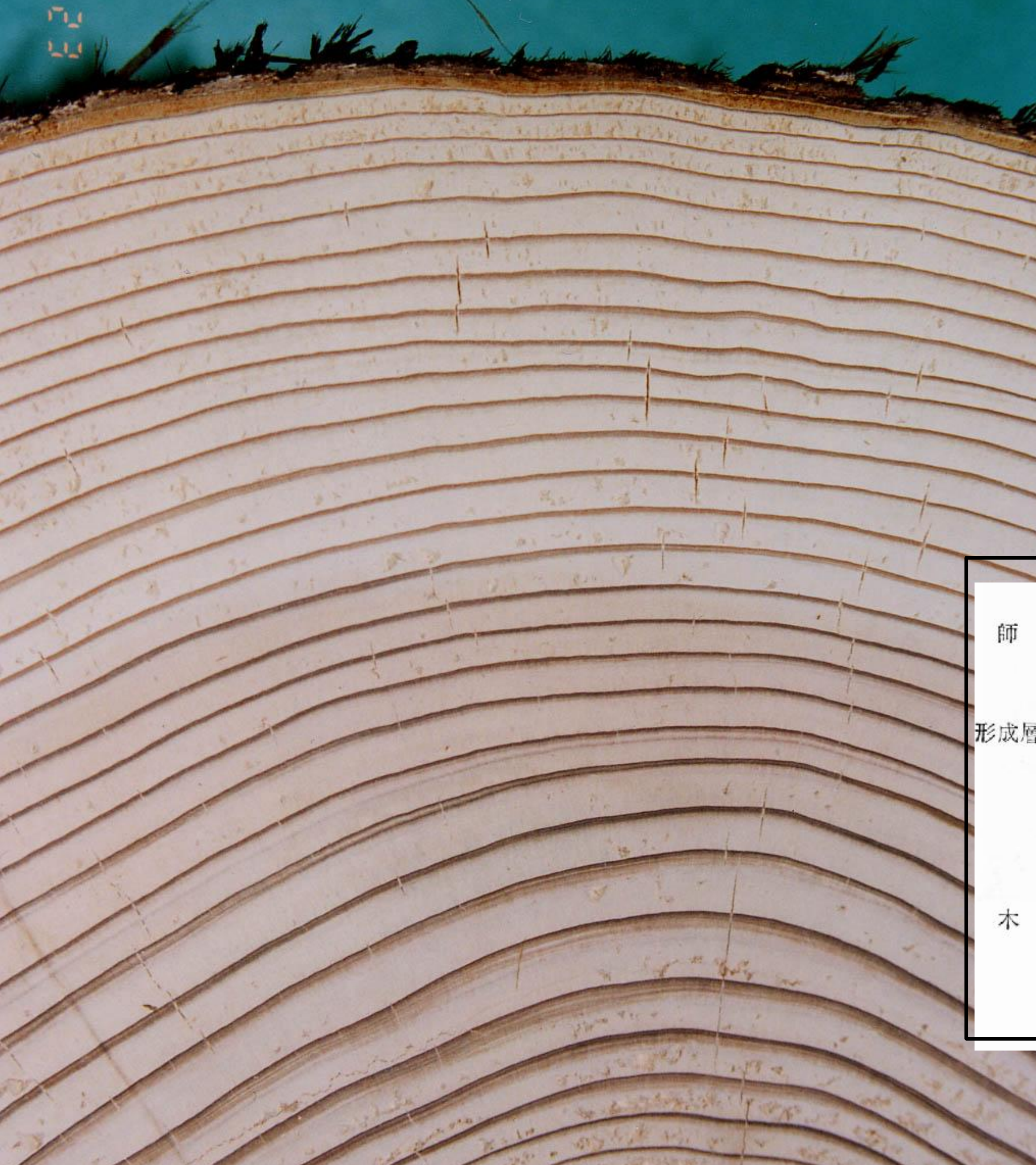


compression force
is applied to column

Bending force
is applied to beam

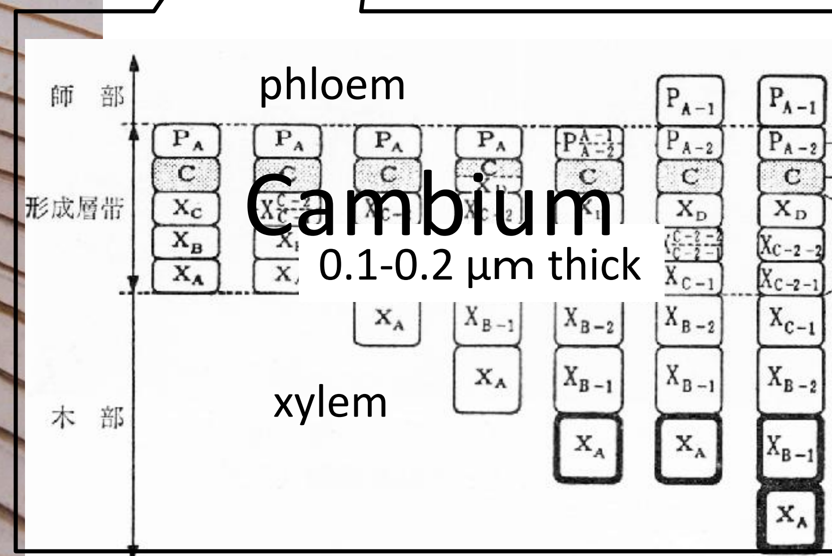


Wood construction

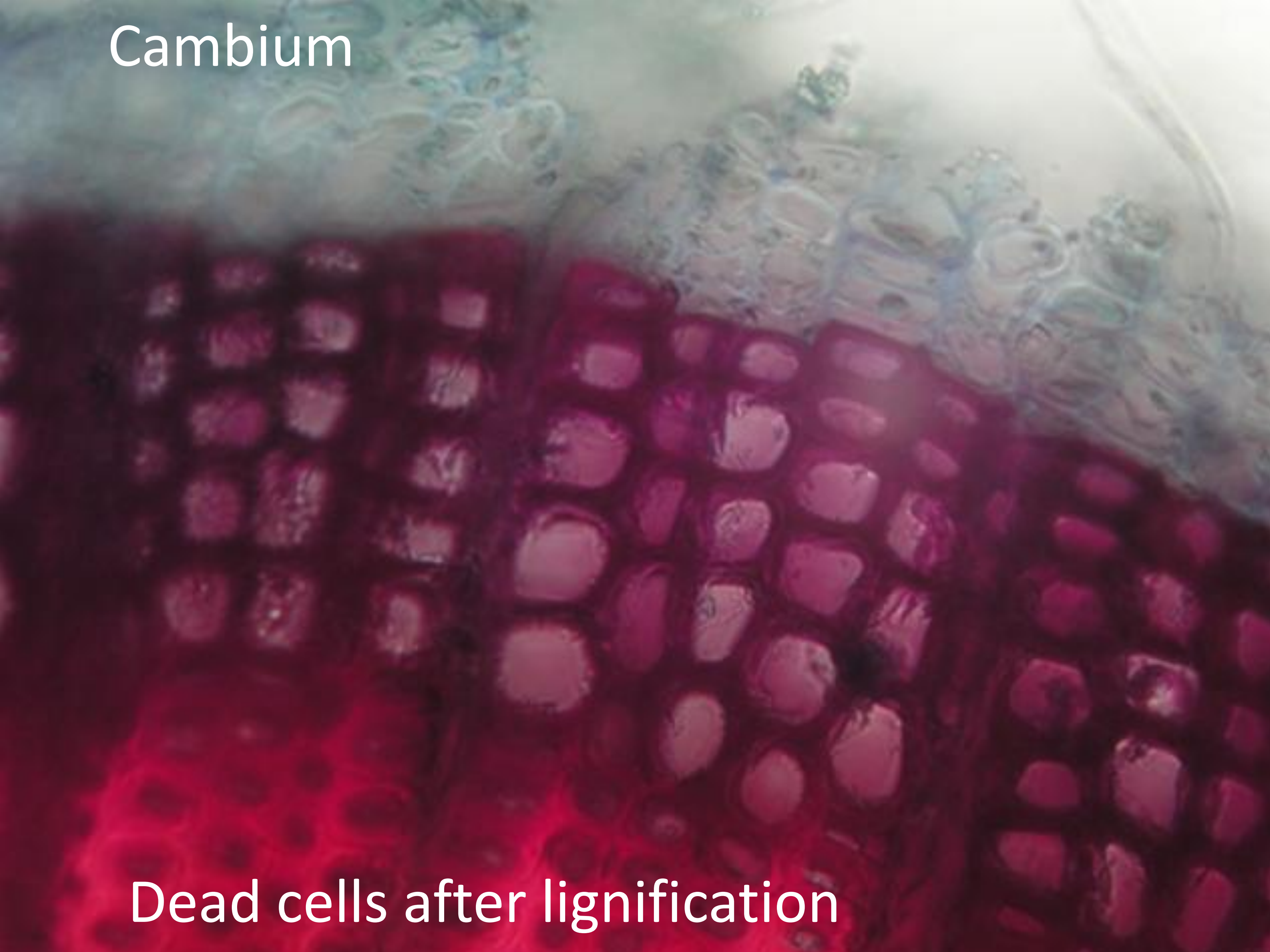


Cross section of *Cryptomeria japonica*

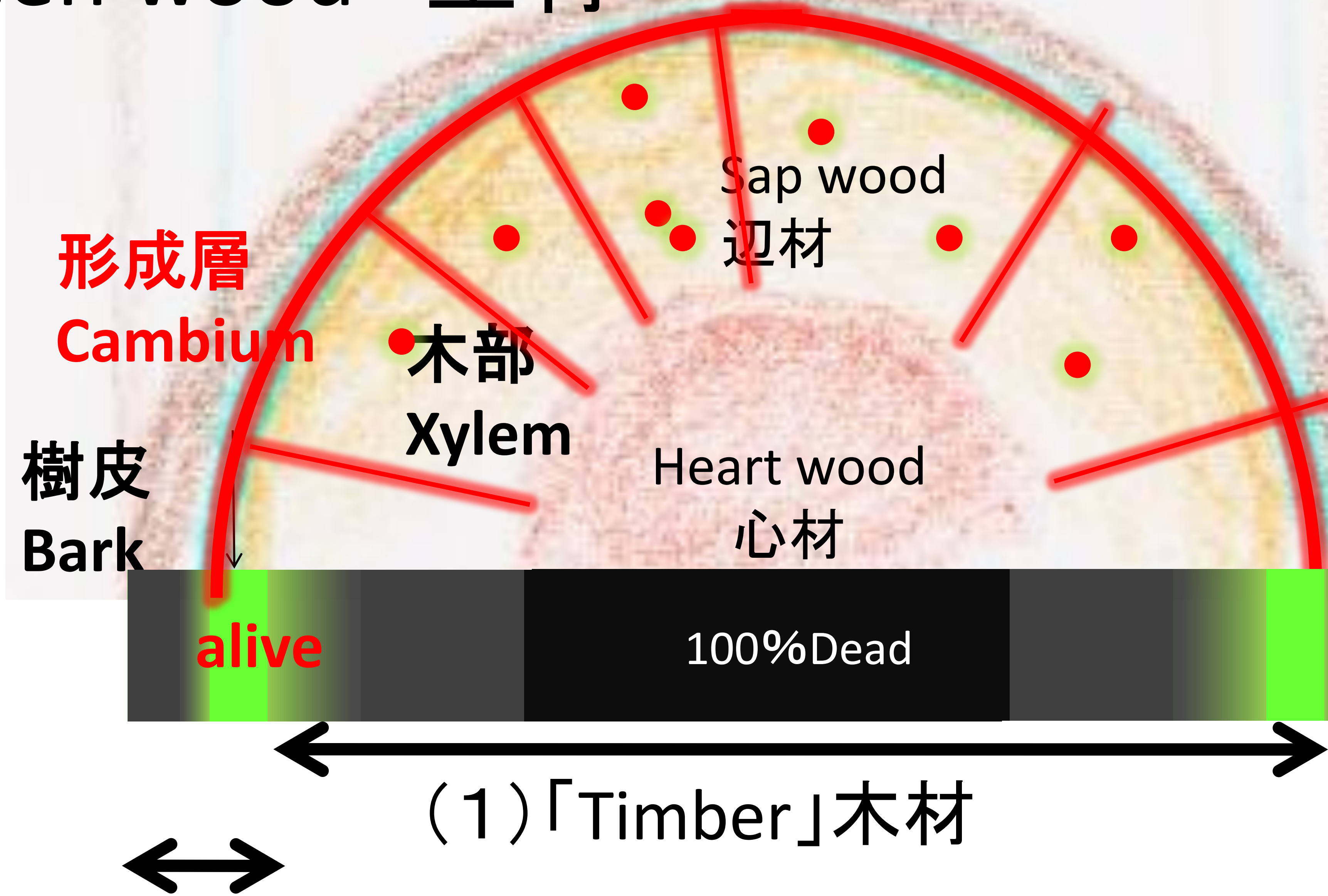
（高部木材保存」



Thickening growth

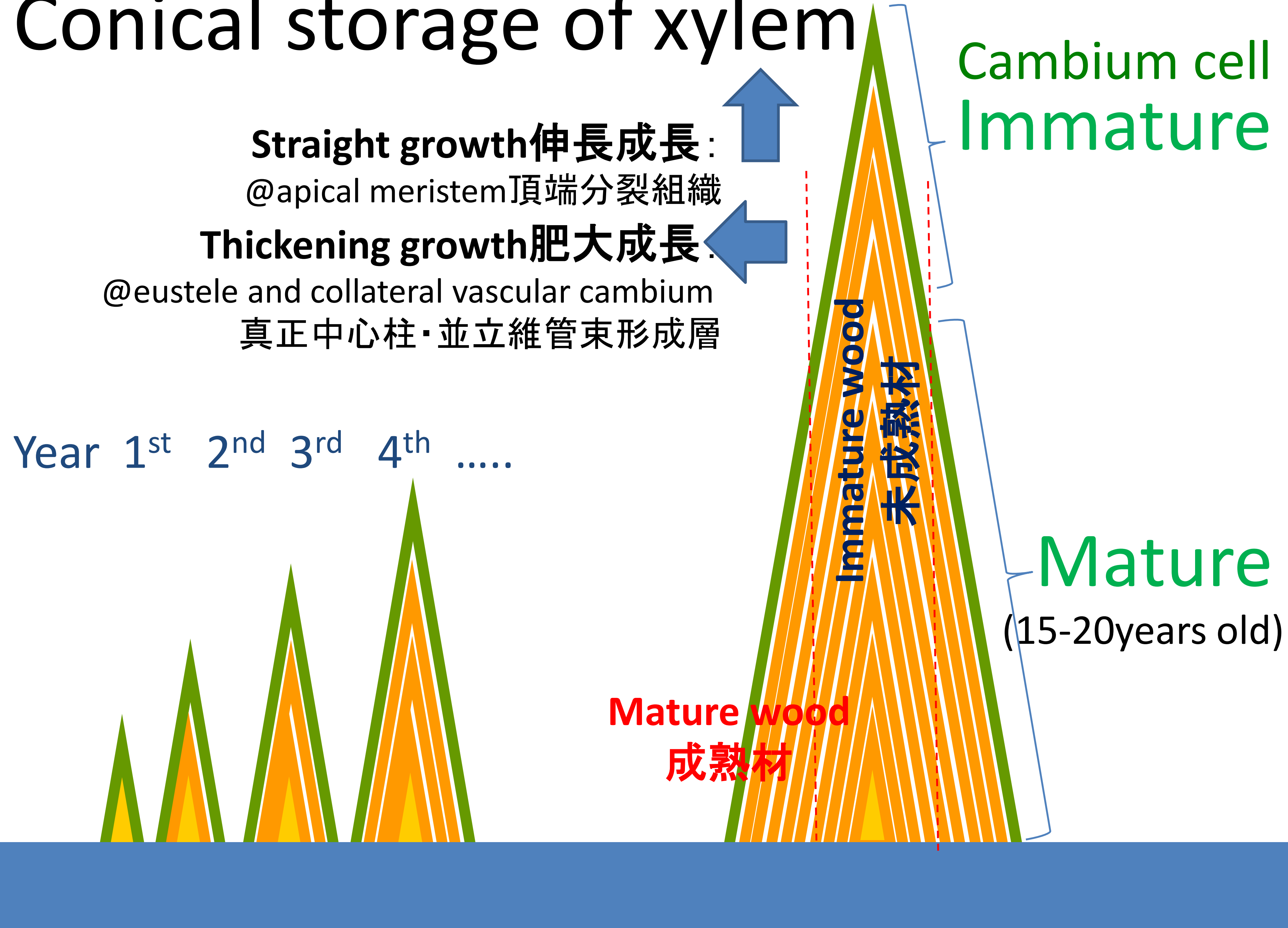

Cambium
Dead cells after lignification

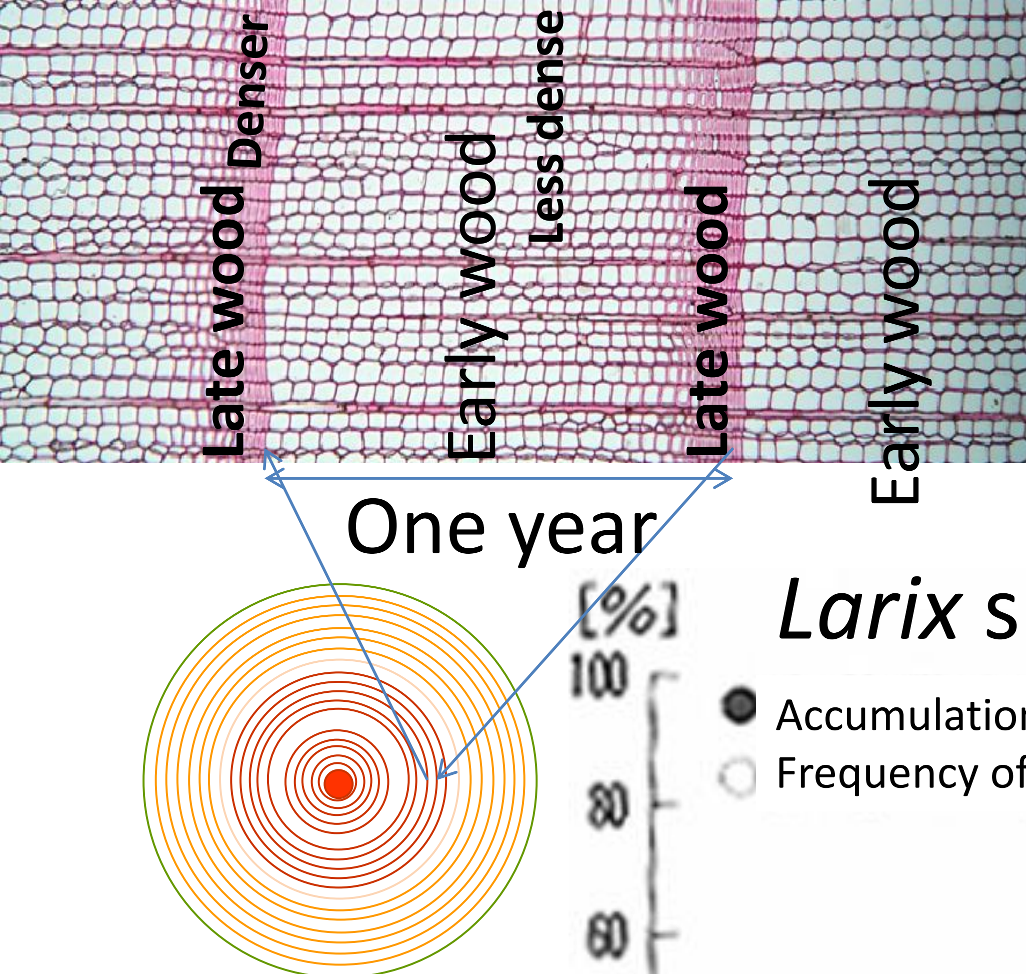
Green wood 生材



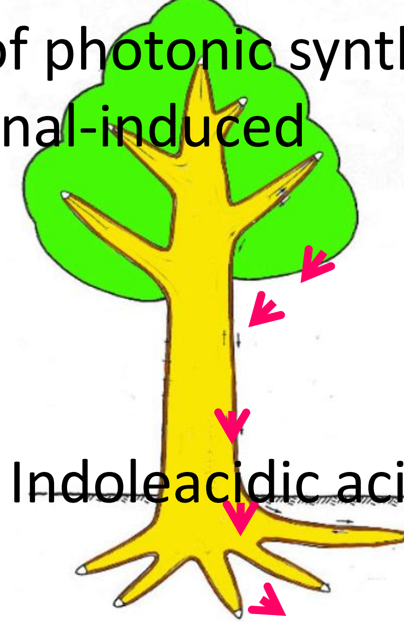
(2)「NonWood Forest Product」非木材林産物

Conical storage of xylem

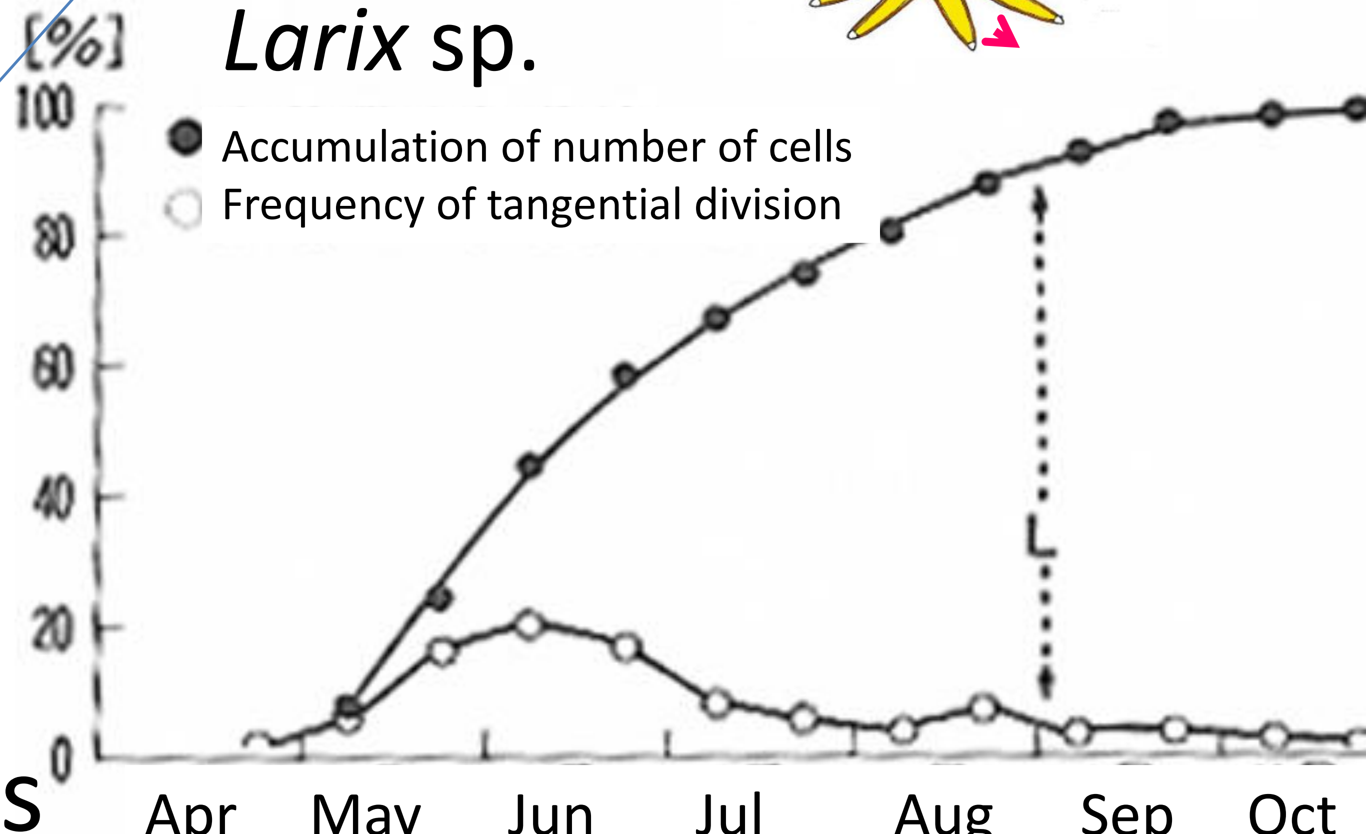




Activity of photonic synthesis
→hormonal-induced



Larix sp.

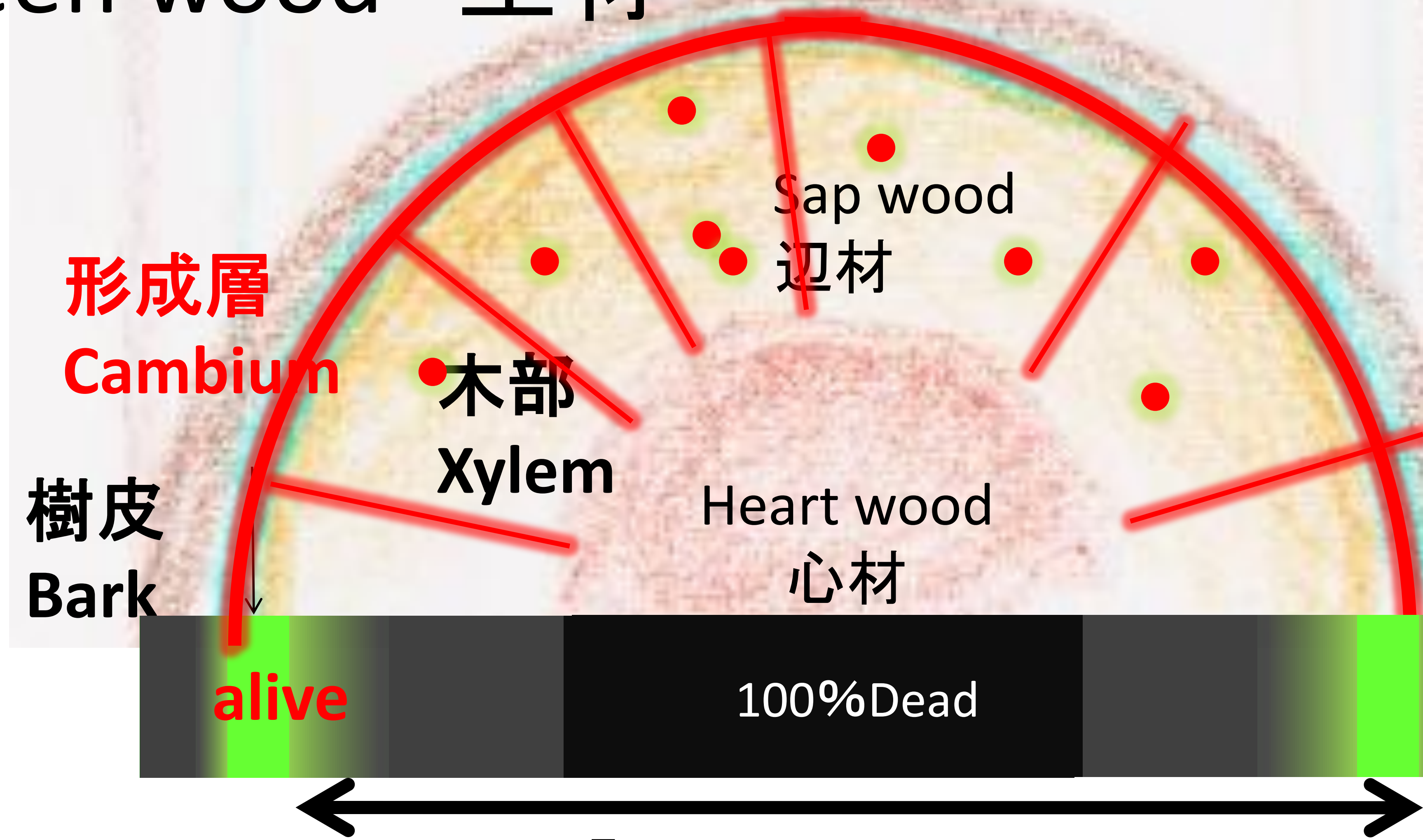


Heterogeneity

Anisotropy

Annual rings

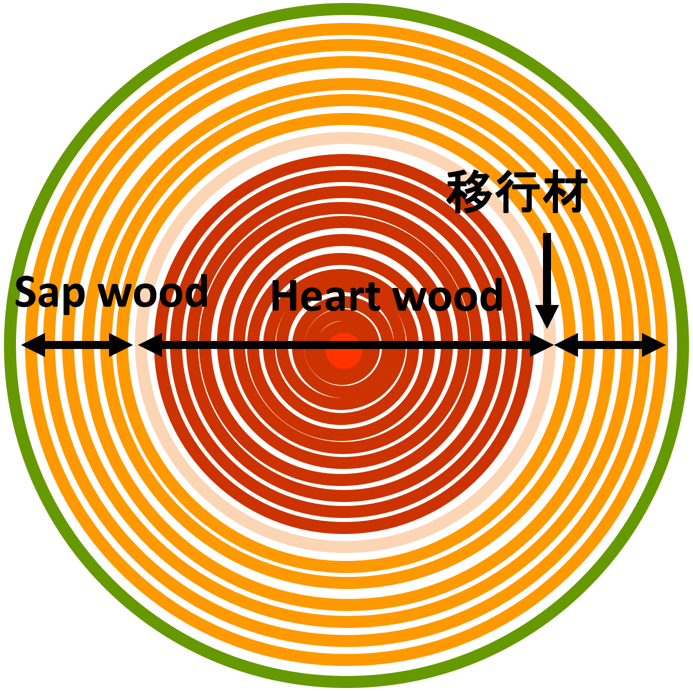
Green wood 生材



（1）「Timber」木材

（2）「NonWood Forest Product」非木材林産物

Heart wood and sap wood



Sap wood 辺材

（whitish）

Some cells (as Parenchyma cells) alive.

Intermediate wood　（移行材「白線帯」）
:Generating polyphenol and flavonoid
High enzyme activity

Heart wood 心材

（darkly colored：characteristic to the species）

All cells dead.

High durability due to the characteristic components.

physiological、water conduction lost

Heterogeneity

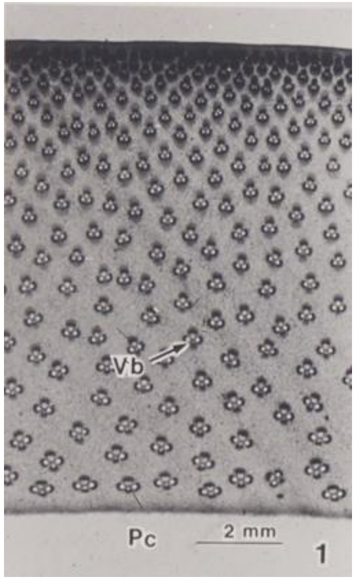
☆　decay durability

☆　difficulty of chemical impregnation

Do trees in tropical forests have annual rings ?

Do herbs, bamboos and palms have annual rings ?

タケ類:単子葉植物イネ目イネ科



生長期間
2か月

伸長速度
37ー120cm・日

寿命
～20年

不斉中心柱(atacrostele)
:並立維管束が不規則に散在する

蛇腹状の節間生長

☆サトウキビ類:イネ目イネ科サトウキビ属

ヤシ類:単子葉植物ヤシ目ヤシ科

What is the difference

between **hard wood** and **soft wood**

広葉樹 針葉樹

in point of view to use as materials ?

Find what is apparent difference between hard wood and soft wood ?

Soft wood針葉樹

ヒノキ japanese cypress
Chamecyparis obtusa

スギ japanese cedar
Cryptomeria japonica

カヤ japanese nutmeg
Torrea Nucifera

ベイスギ Western red cedar
Thuja plicata

ベイマツ Douglas fir
Pseudetsuga menziesii

Special: イチョウ Ginkgo
Gingko biloba

Hard wood広葉樹

クリ chestnut
Castanea crenata

チーク teak
Tectoba spp.

サクラ cherry
Prunus spp.

カシ oak
Quercuss spp.

ケヤキ japanese zelkova
Zelkova serrata

キリ empress tree
Paulownia tomentosa

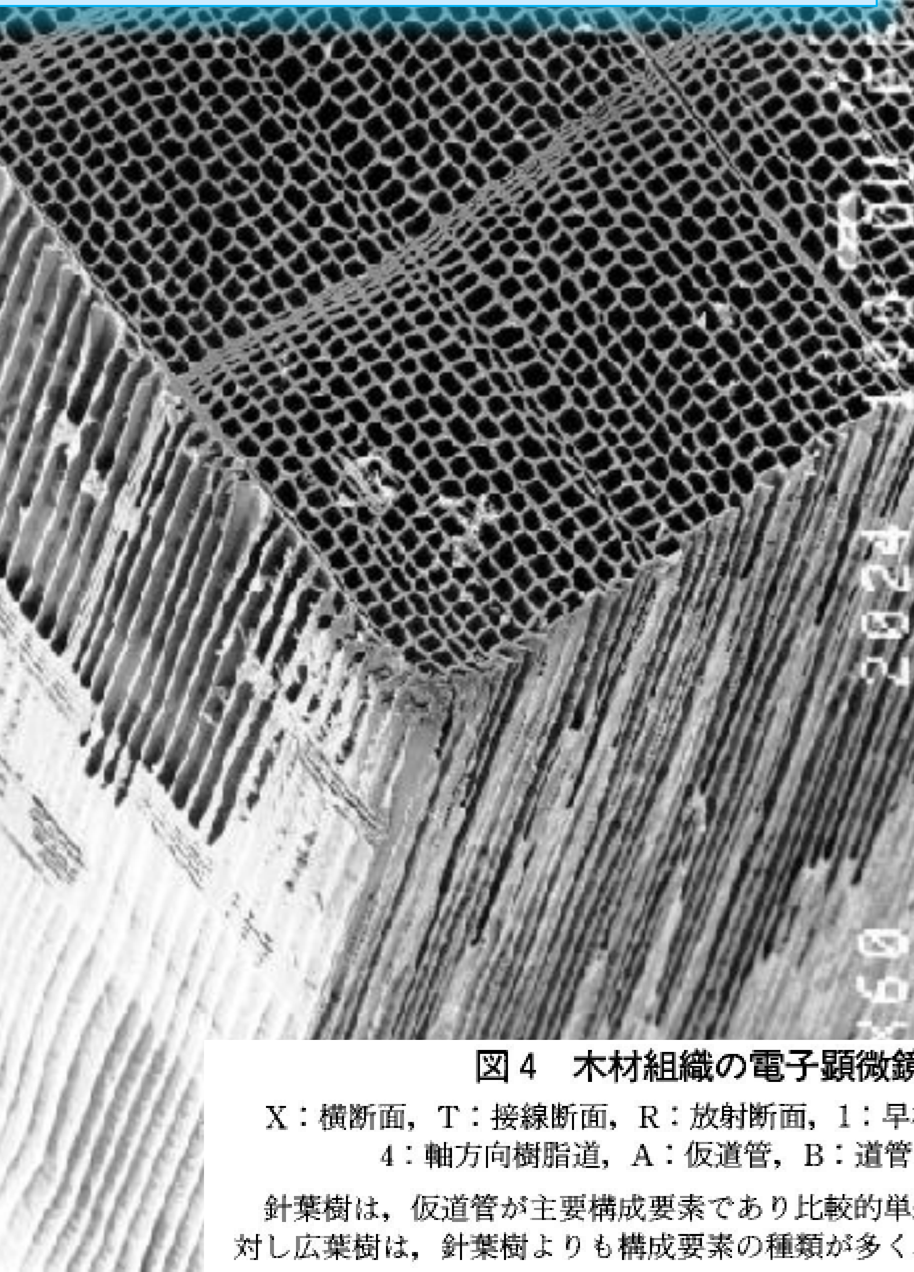
Opitical micrograms of separated cells

Soft wood針葉樹

Hard wood広葉樹

oft wood針葉樹

Hard wood広葉樹



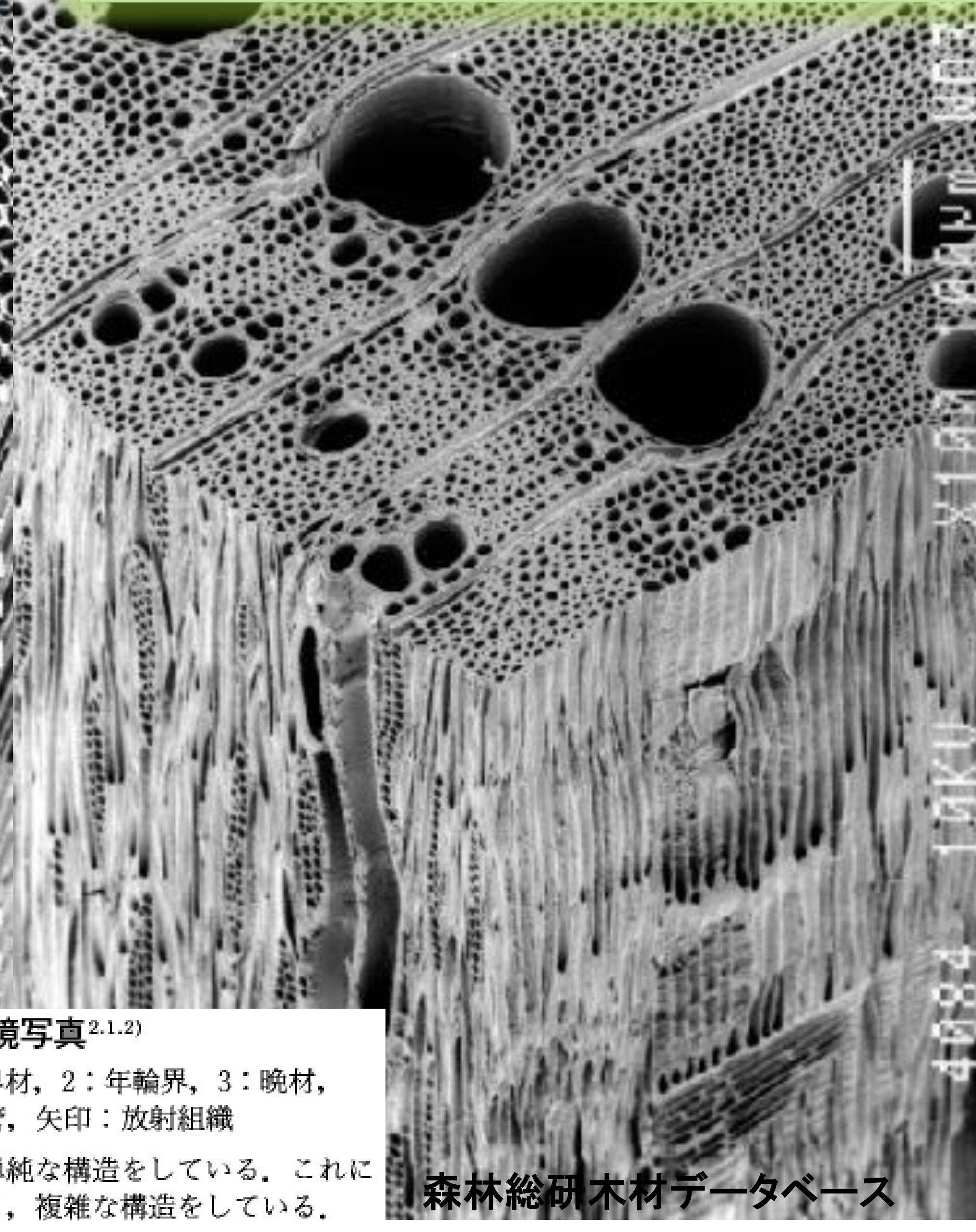


図４　木材組織の電子顕微鏡写真[2.1.2)]

X：横断面，T：接線断面，R：放射断面，1：早材，2：年輪界，3：晩材，4：軸方向樹脂道，A：仮道管，B：道管，矢印：放射組織

針葉樹は，仮道管が主要構成要素であり比較的単純な構造をしている．これに対し広葉樹は，針葉樹よりも構成要素の種類が多く，複雑な構造をしている．

森林総研木材データベース

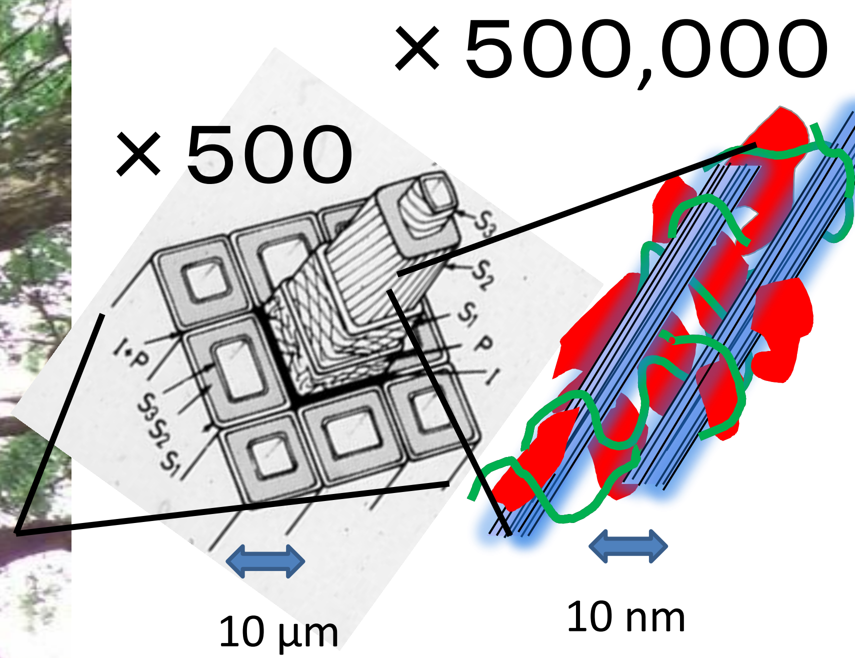
Hagen-Poiseuille law

Viscosity coefficient ↓ (η)

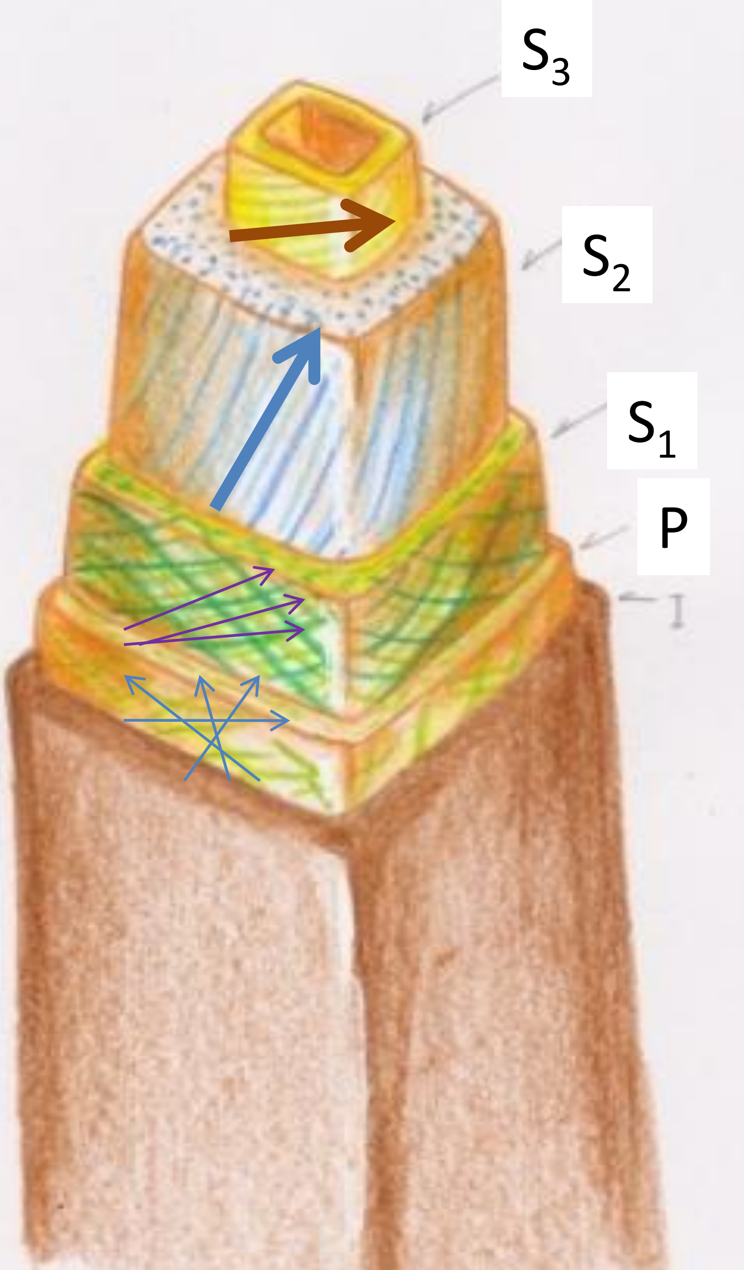
$$Q=(\pi a^4)/8 \cdot (p_1 - p_2)\eta l$$

- Q ↑ Flow rate
- a ↑ Diameter
- $p_1 - p_2$ ↑ Pressure gradiant of the both side of the tube
- l ↑ Length of the tube

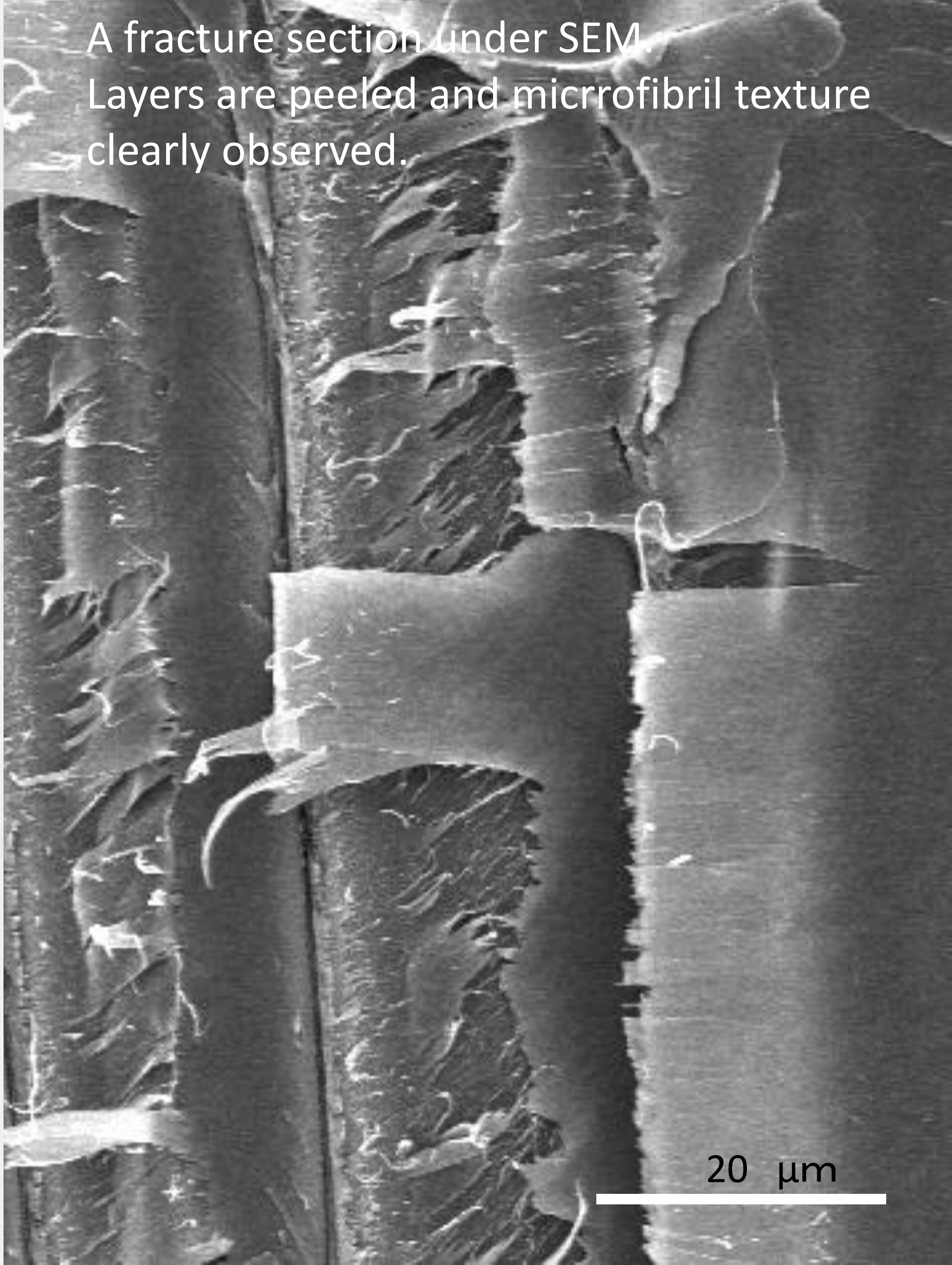
If the diameter becomes twice, the flow rate will be…



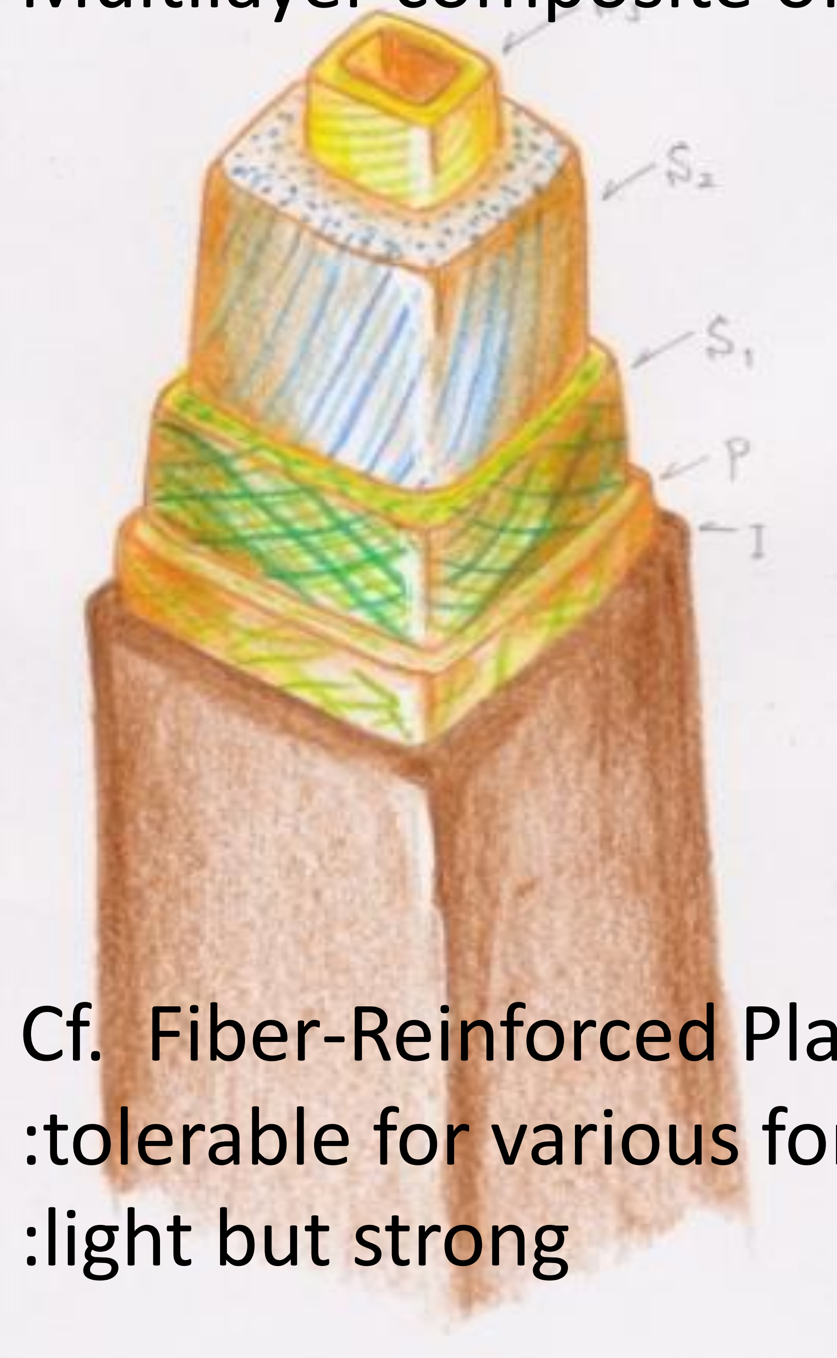
Let’s take a look at tree microscopically

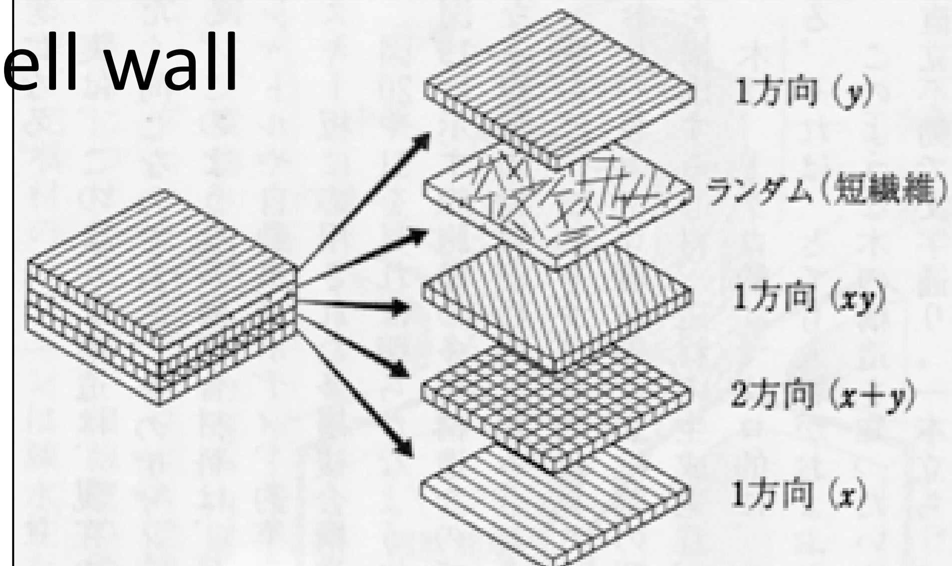


Cell wall structure and cellulose microfibrils

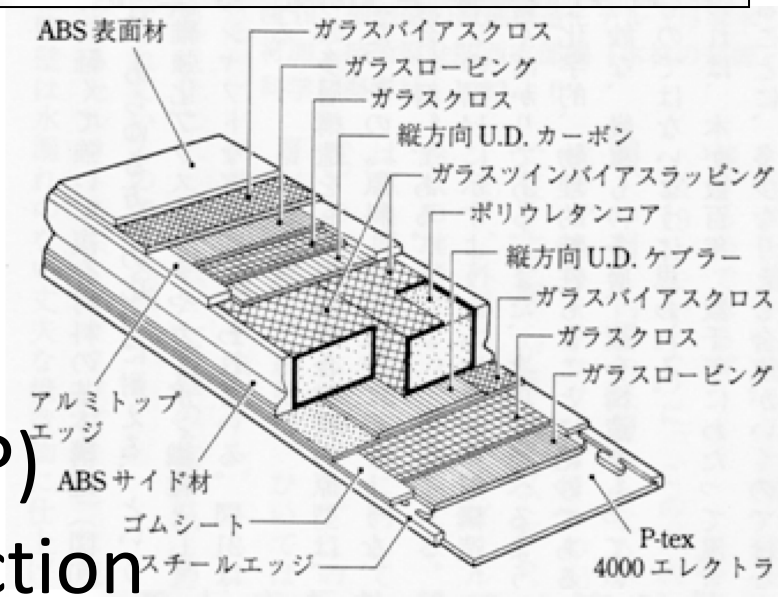


Multilayer composite of cell wall





Basic structure of multilayer composite



多層複合構造の上級者用スキー板（日本機械学会
）

Cf. Fiber-Reinforced Plastic (FRP)

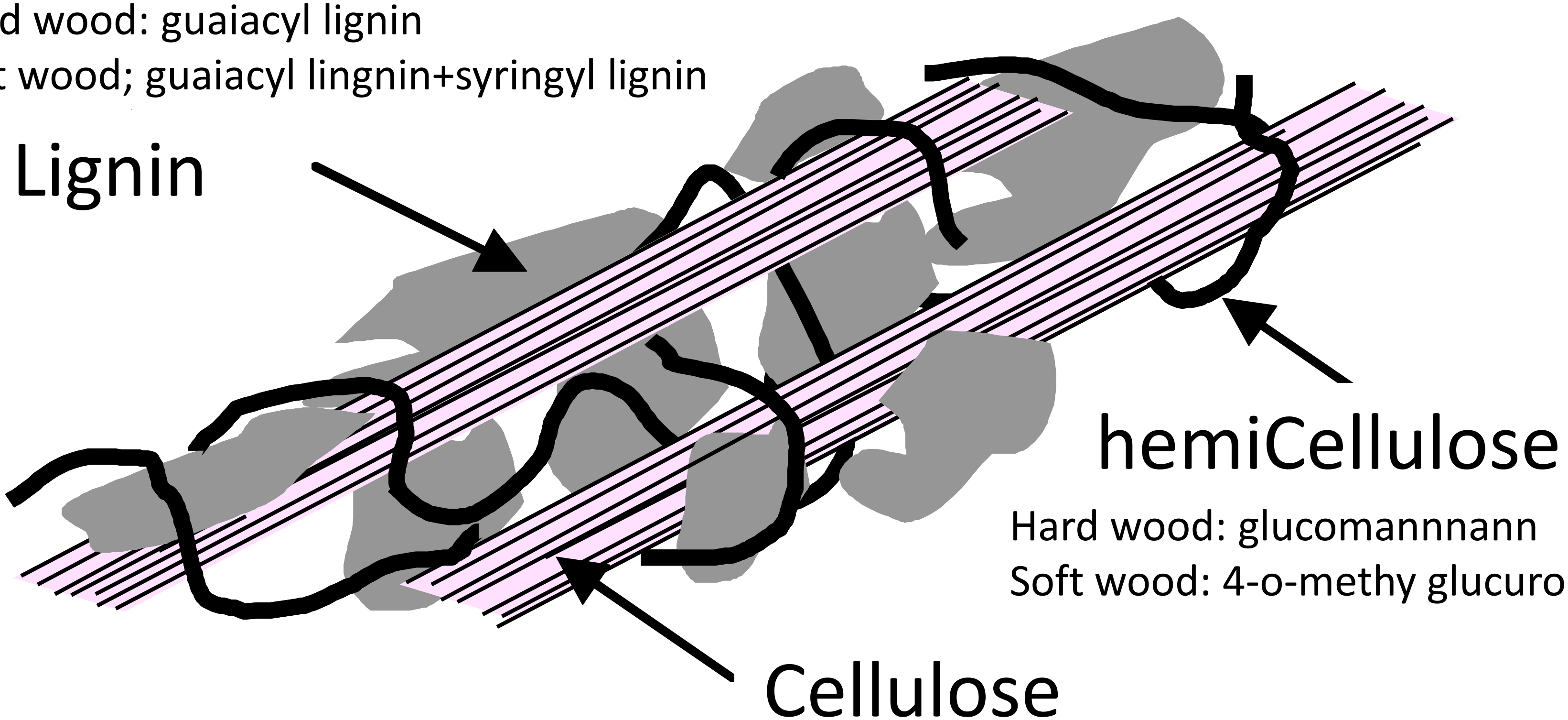
:tolerable for various force direction

:light but strong

Space ship・air plane・automotive body
ski・fishing rod etc.

Cell wall as “reinforced concrete structure” schematical drawing on the molecular level

Hard wood: guaiacyl lignin
Soft wood; guaiacyl lingnin+syringyl lignin



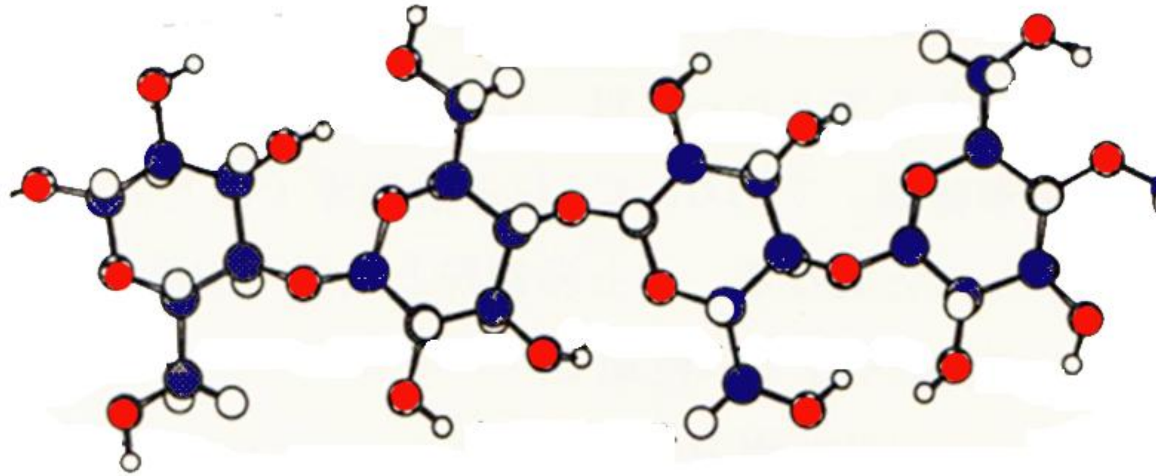
Hard wood: glucomannnann
Soft wood: 4-o-methy glucuronoxylan


×50,000,000
0.1 nm

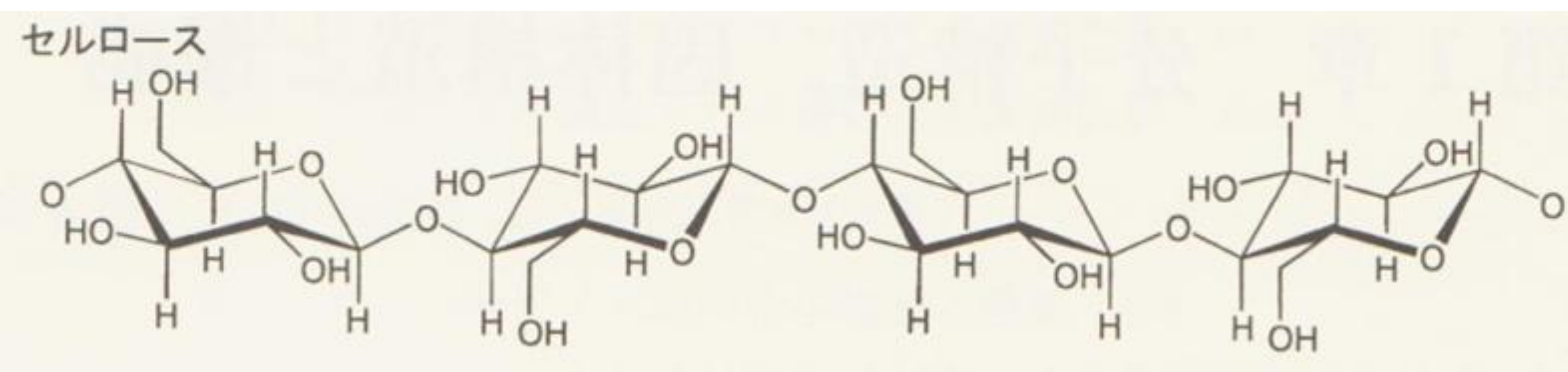
3 Components and structure of plant cell wall and application

3.1 Cellulose
3.2 Hemicellulose
3.3 Lignin

Major 3 components common for almost all of plant cell walls



3.1 Cellulose



Cellulose

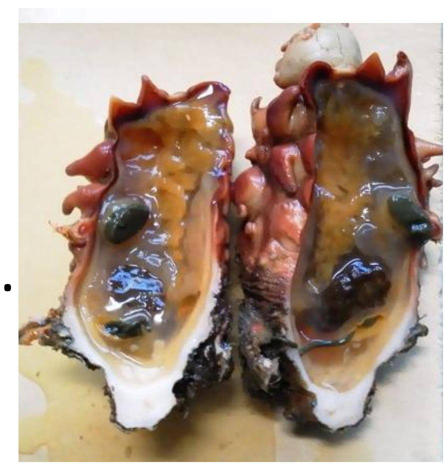
- 40～60% in dried wood cell wall

▪structural biopolymer

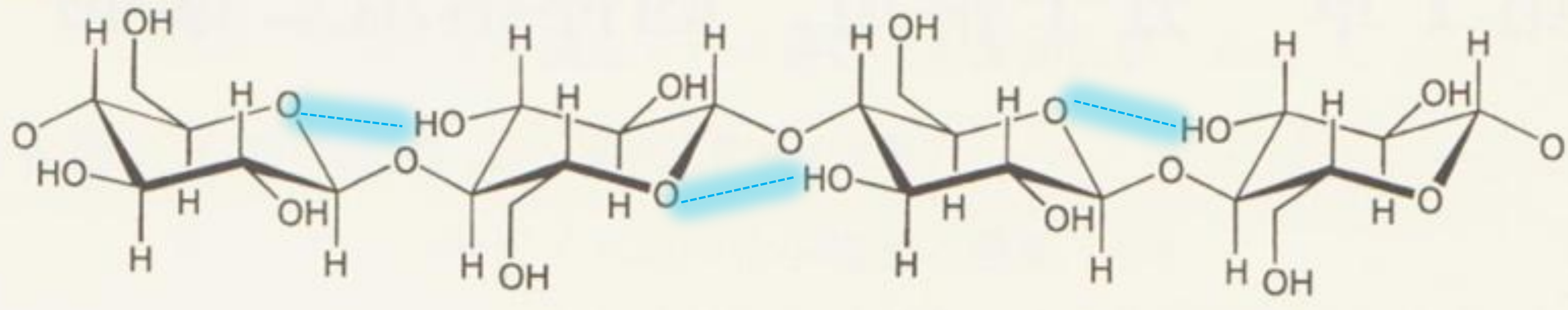
▪most abundant and reproducible

▪ produced by almost of all plants and a certain animals.

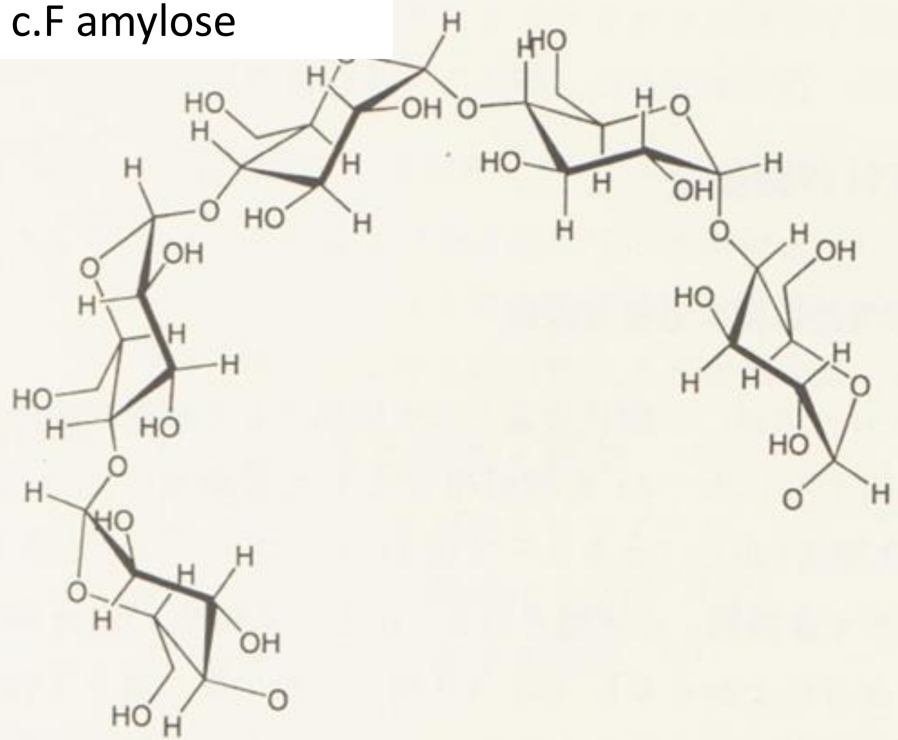
Ascidian ホヤ *Halocynthia* sp.



Acetic bacteriums酢酸菌 *Acetobacter xylinum* cellulose



c.F amylose



D-glucose residue

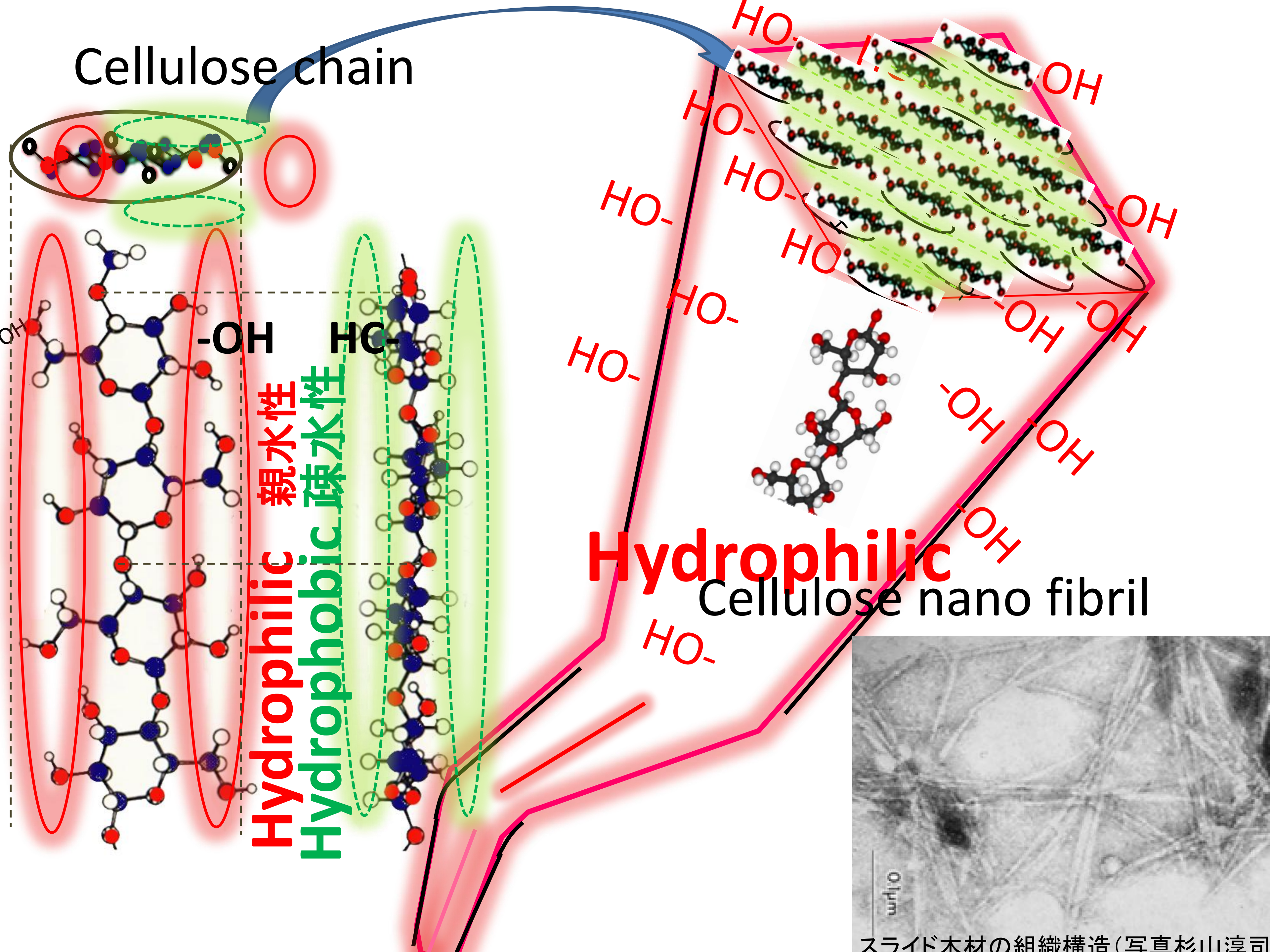
β-1,4-glucoside bond

Linear →crystal structure

no-branch

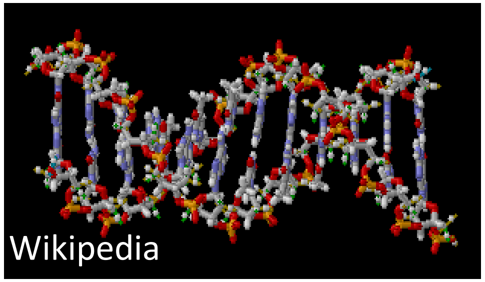
Hydrophilic & Hydrophobic

hydrogen bonding


Cellulose chain
-OH
HC-
親水性
疎水性
Hydrophilic
Hydrophobic
HO-
HO-
HO-
HO-
HO-
HO-
HO-
HO-
-OH
-OH
-OH
-OH
-OH
-OH
-OH
Hydrophilic
Cellulose nano fibril
0.1μm
スライド木材の組織構造（写真杉山淳司

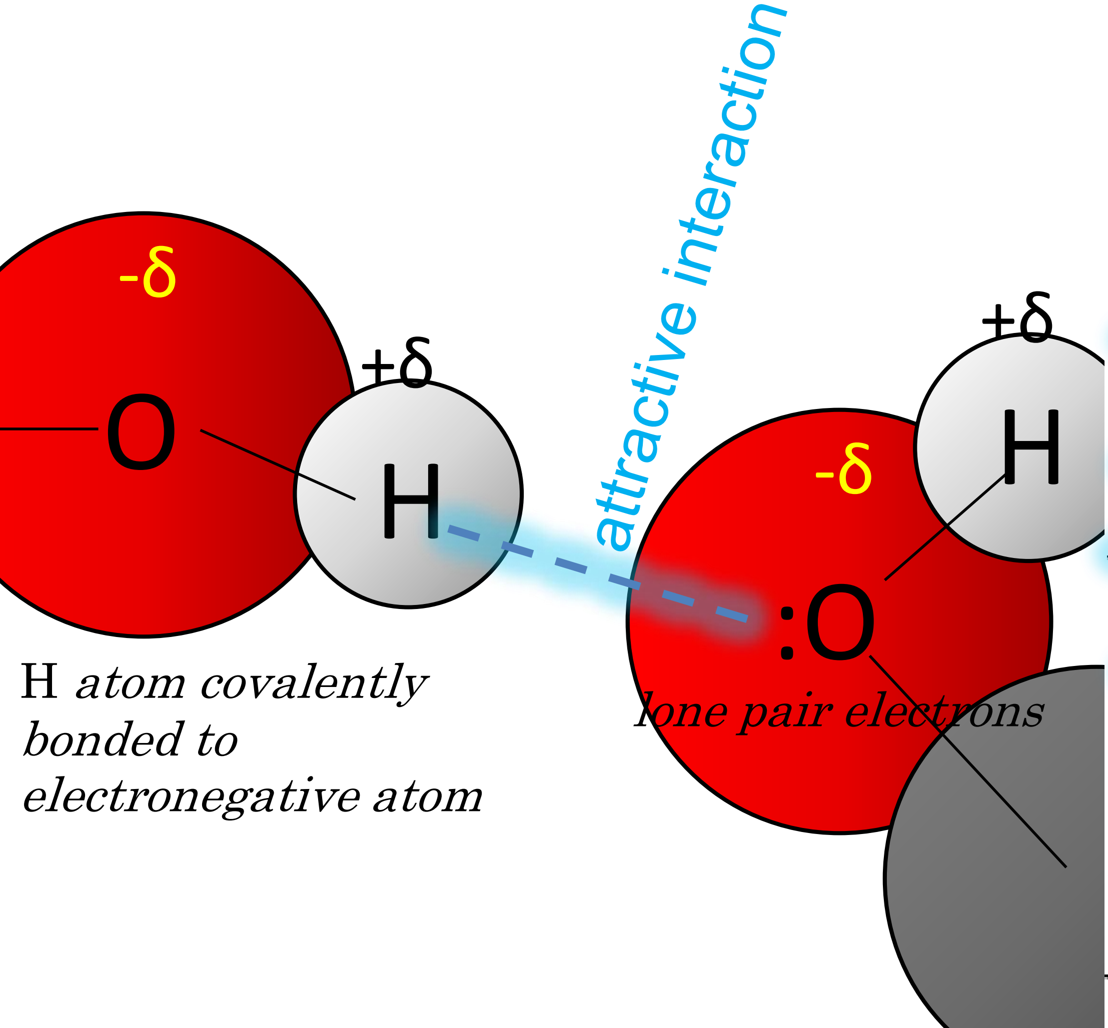
Hydrogen-bonding stabilizing crystal structure of cellulose

Double helical structure of DNA due largely to hydrogen bondings.

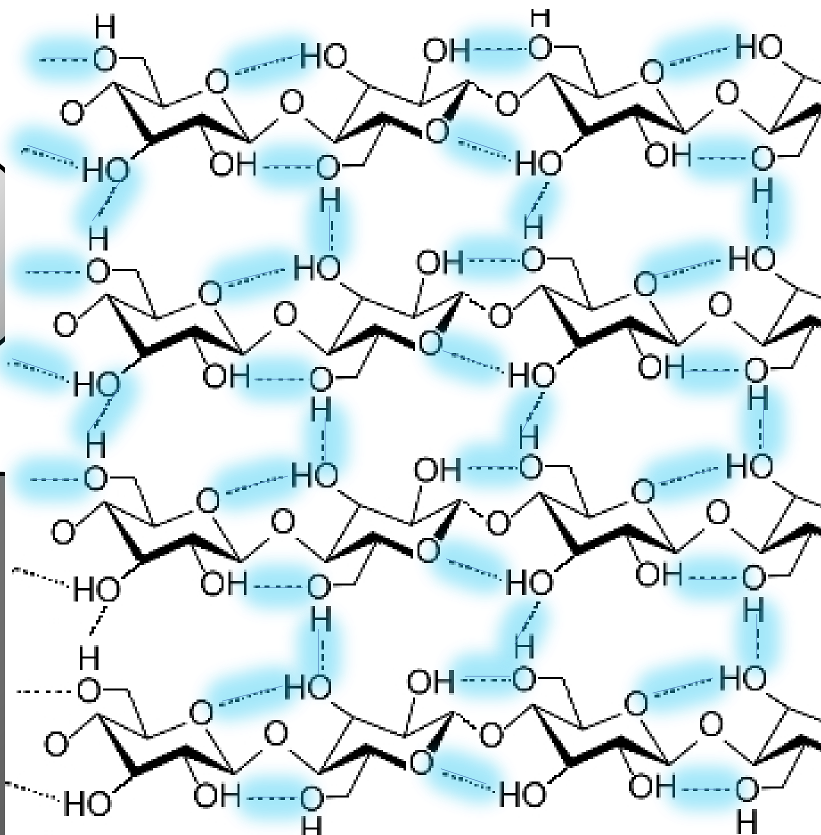


Plant material → -OH･･･O-

A kind of molecular attractions.



Hydrogen-bonding stabilizing crystal structure of cellulose



Cellulo-chemicals

Paper/Pulp

Nanofiber

Fermentative products

cello-oligo-sugers and the derivatives

Functional derivertives from cellulose

paper/pulp

Pulp : refined plant fiber for paper.

Hydrogen bondings

Mechanical pulp (MP)

Chemical pulp (CP)

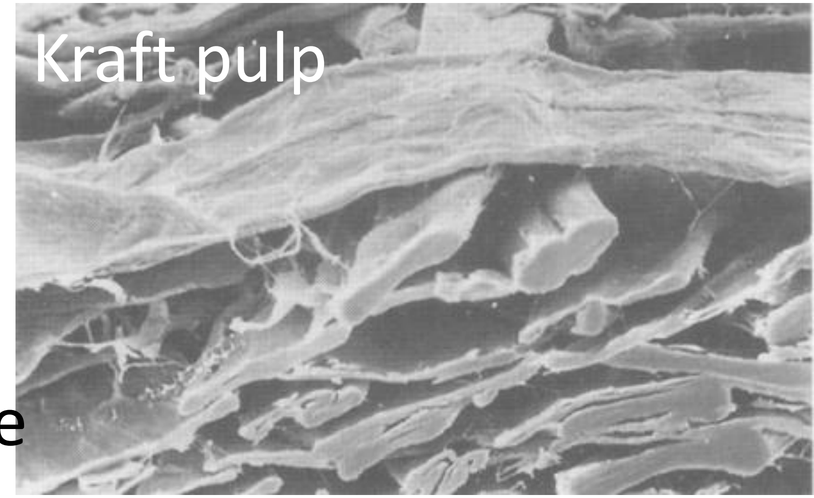
Removing lignin →Beating

Kraft Pulp
Sulfide Pulp
Alkaline Pulp

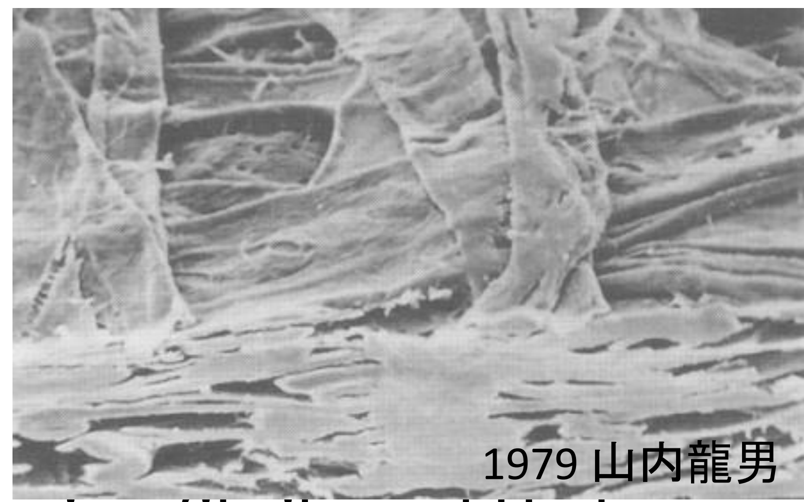
} **Breach**

High strength paper ←only cellulose
“black liquor”= lignin, resin+ added chemicals

Before

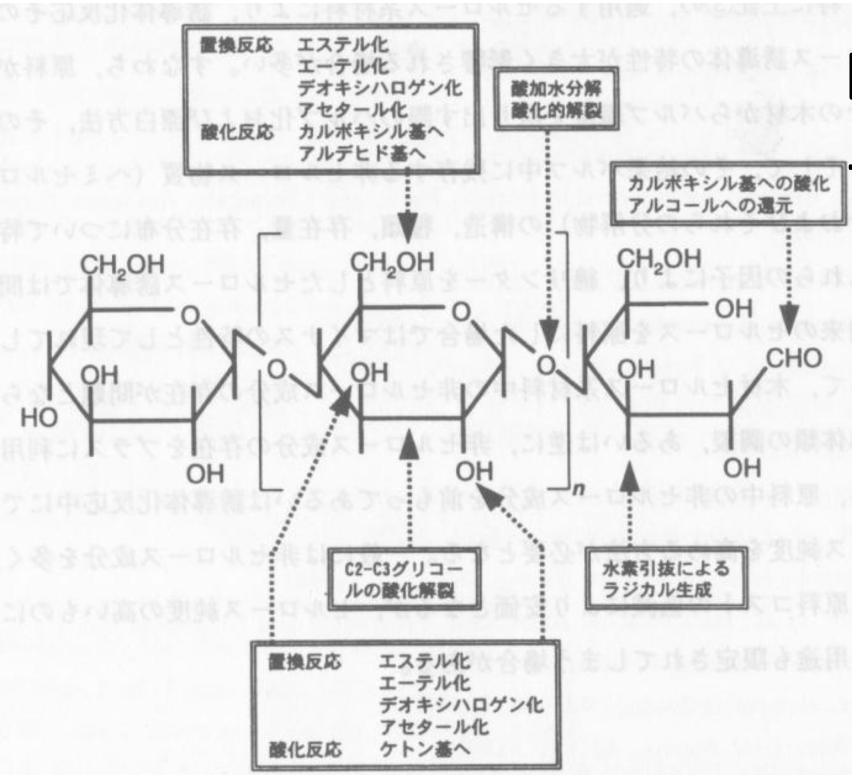


After



Raveled out and interwoven microfibrils and Hydrogen bondings between them forms a sheet of a paper.

Functional derivatives from cellulose



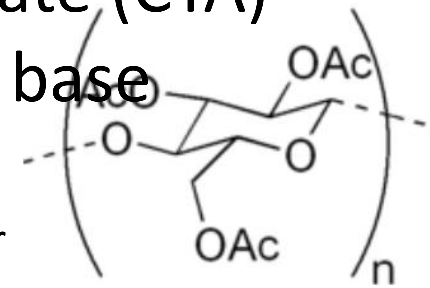
Various derivatives from cellullose

ウッドケミカルス（磯貝）

Esterification

→cellulose-tri-acetate (CTA)

fibres and film base



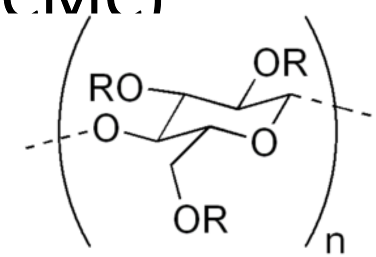
TCA: Tobacco filter

Etherification

→carboxyl methyl cellulose

(cellulose gum, CMC)

food science



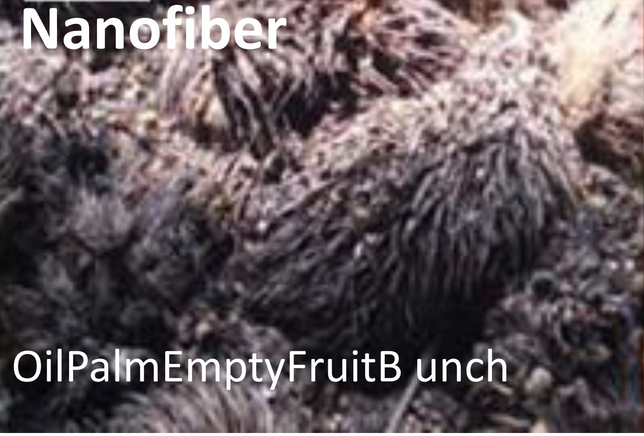
viscosity modifier

thikener

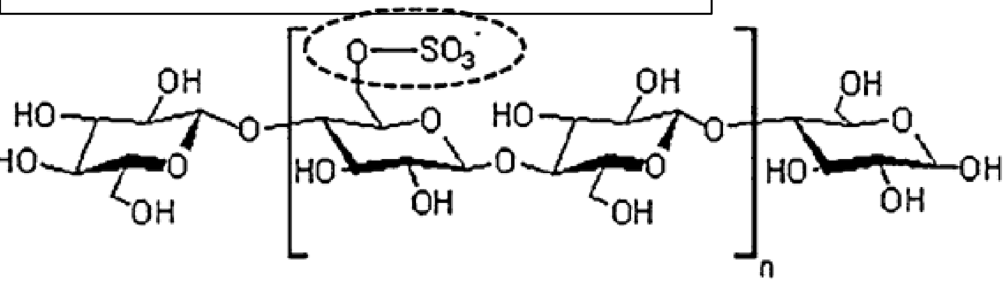
stabilize emulsions

R = H or CH_2CO_2H

Nanofiber



How to nano-disperse

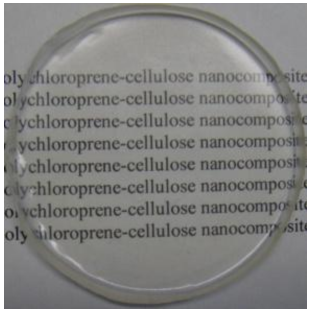


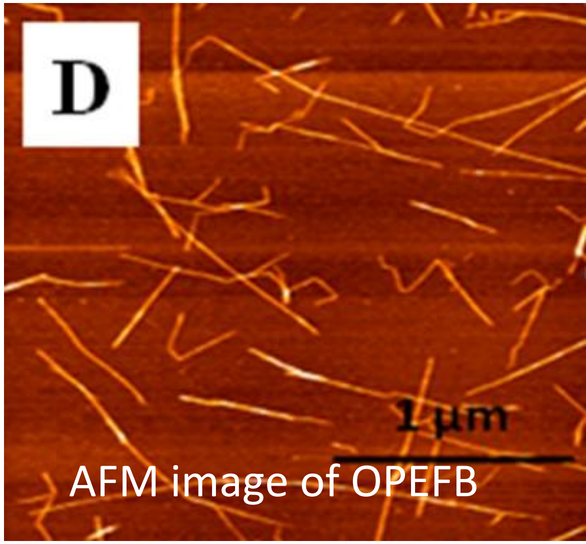
charged surface was formed by sulfate ester group. This enabled the nano-dispersion.

Fahma Farah (2011)

Cellulose **single** nanofiber

Application: automobile, construction, electronics, package etc.





Elastic modulus 138GPa

Tensile strength 3 Gpa →5 times of steel

Linear thermal expansion coefficient

0.1 ppm/K →<1／50 of glass

Transparent

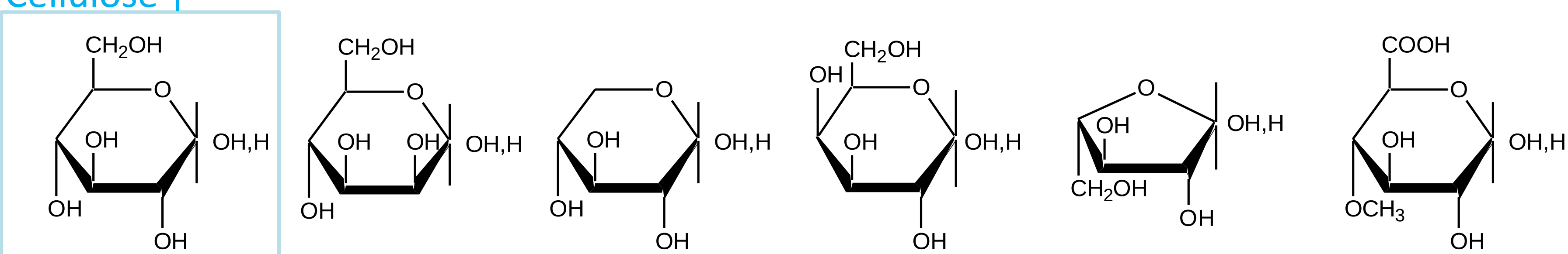
3.2 Hemicellulose

Hemicellulose

- Collective term for polysaccharides included in wood except for cellulose
- Soft wood 20～30%、hard wood 15～25%
- Intermediary between cellulose and lignin

Main constituent monomers

Cellulose↑

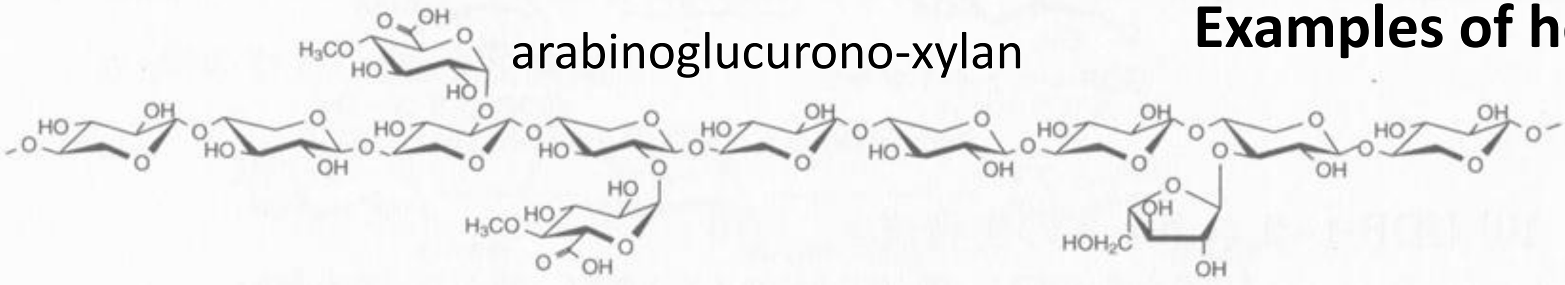


D-glucose D- mannose D-xylose D-galactose L-arabinose, 4-o-methyl-D-glucuronic acid

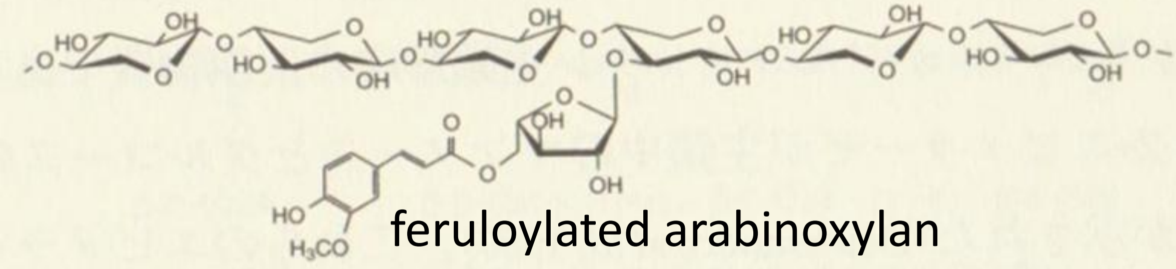
図出典「木質の形成」(海青社)

Examples of hemicellulose

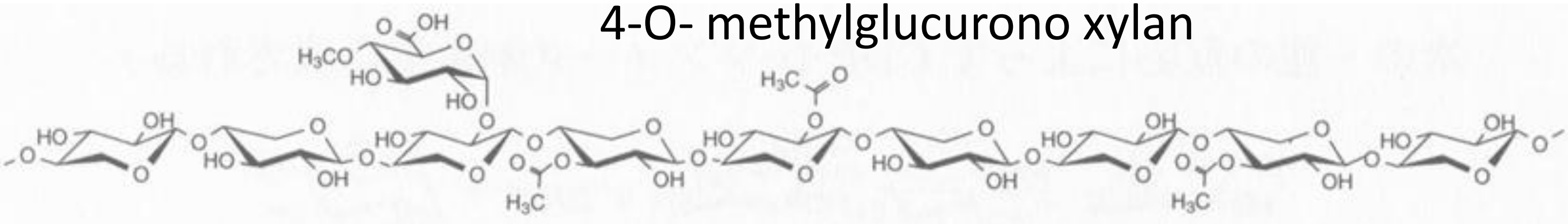
☆Hetero polysaccharide
☆branching



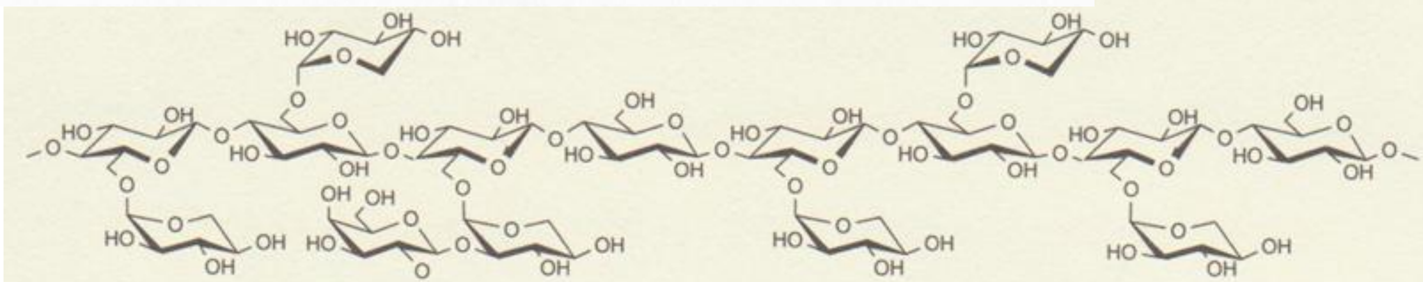
arabinoglucurono-xylan



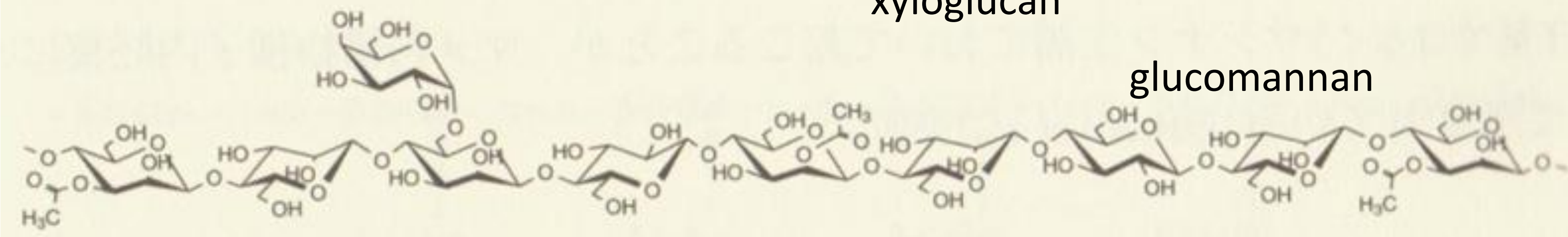
feruloylated arabinoxylan



4-O- methylglucurono xylan



xyloglucan

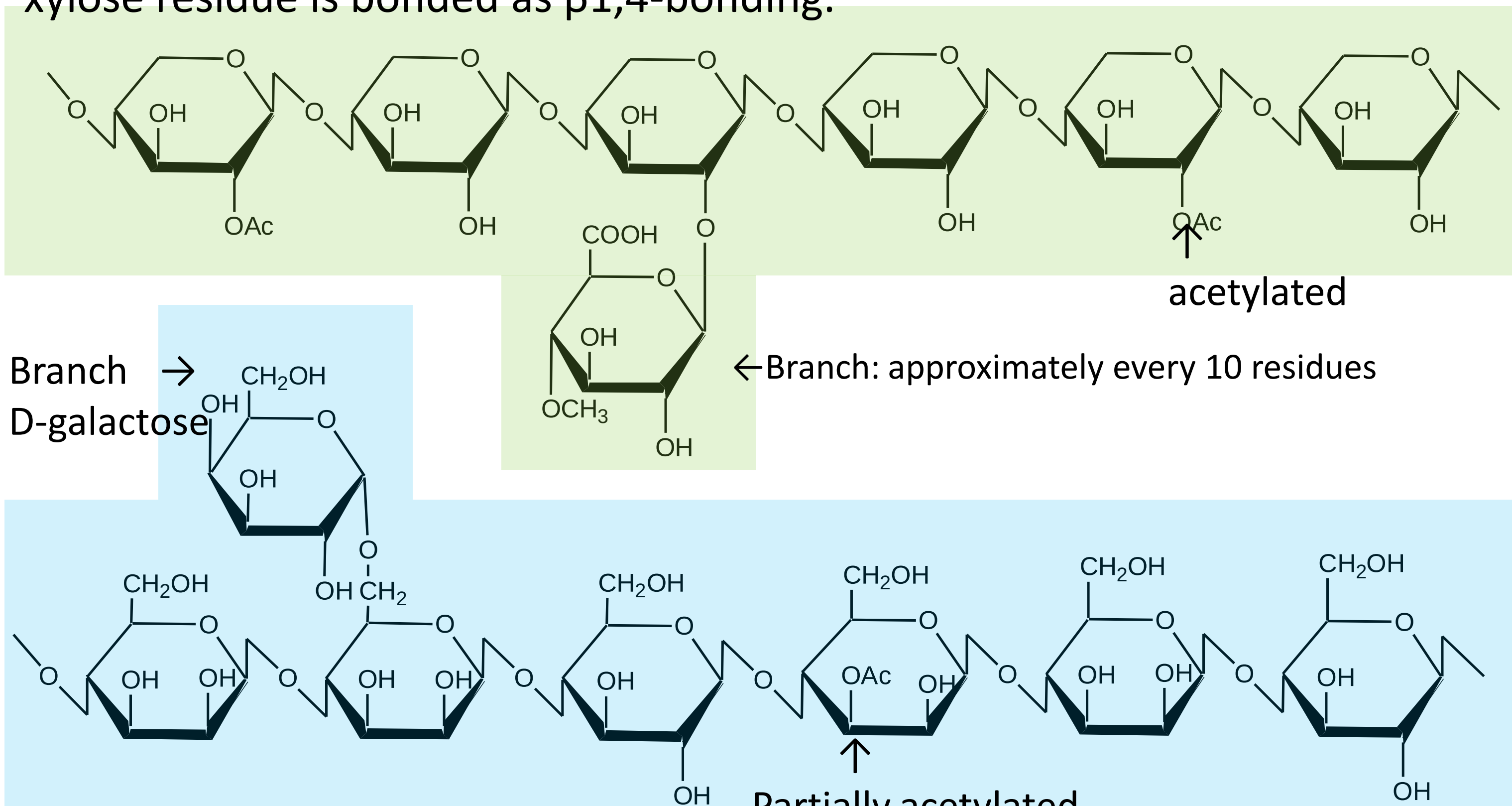


glucomannan

Chemical structure of typical hemicelluloses

xylose residue is bonded as β1,4-bonding.

Xylan
Hard wood



Gluco-
mannnan
Soft wood

D-mannose: D-glucose　3〜4 : 1

Difference of hemicellulose

History of evolving

Affects on properties (biological durability)

Structural properties of hemicellulose

- Hetero polysaccharide
- Branching / acetylation

↓

- Amorphous
- Hydrophilic
- Degradable chemically and billogically

Application

- Hardwood xylan

→furfural

---usable as raw material for 6,6 nylon and fran-resin

→xylose

--- sweetener, artificial color by Maillard reaction

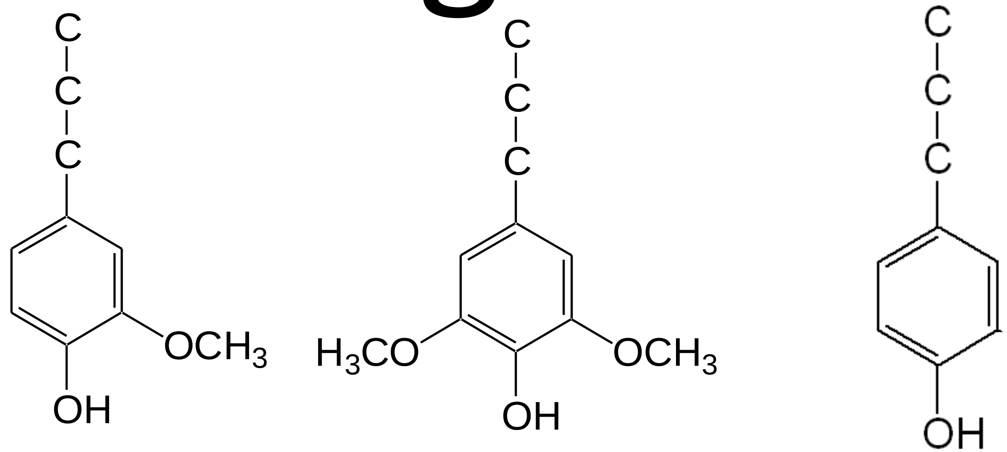
- Biological active agents（antitumor、dietaly fiber）

Reproductive, abundant next to cellulose, but scarcely extracted nor used.

Exceptional case:
Xylitol is produced by sulfuric acid-hydlysis of white birch .

3.3 Lignin

lignin



guaiacyl　　syringyl　　P-hydroxyphenyl

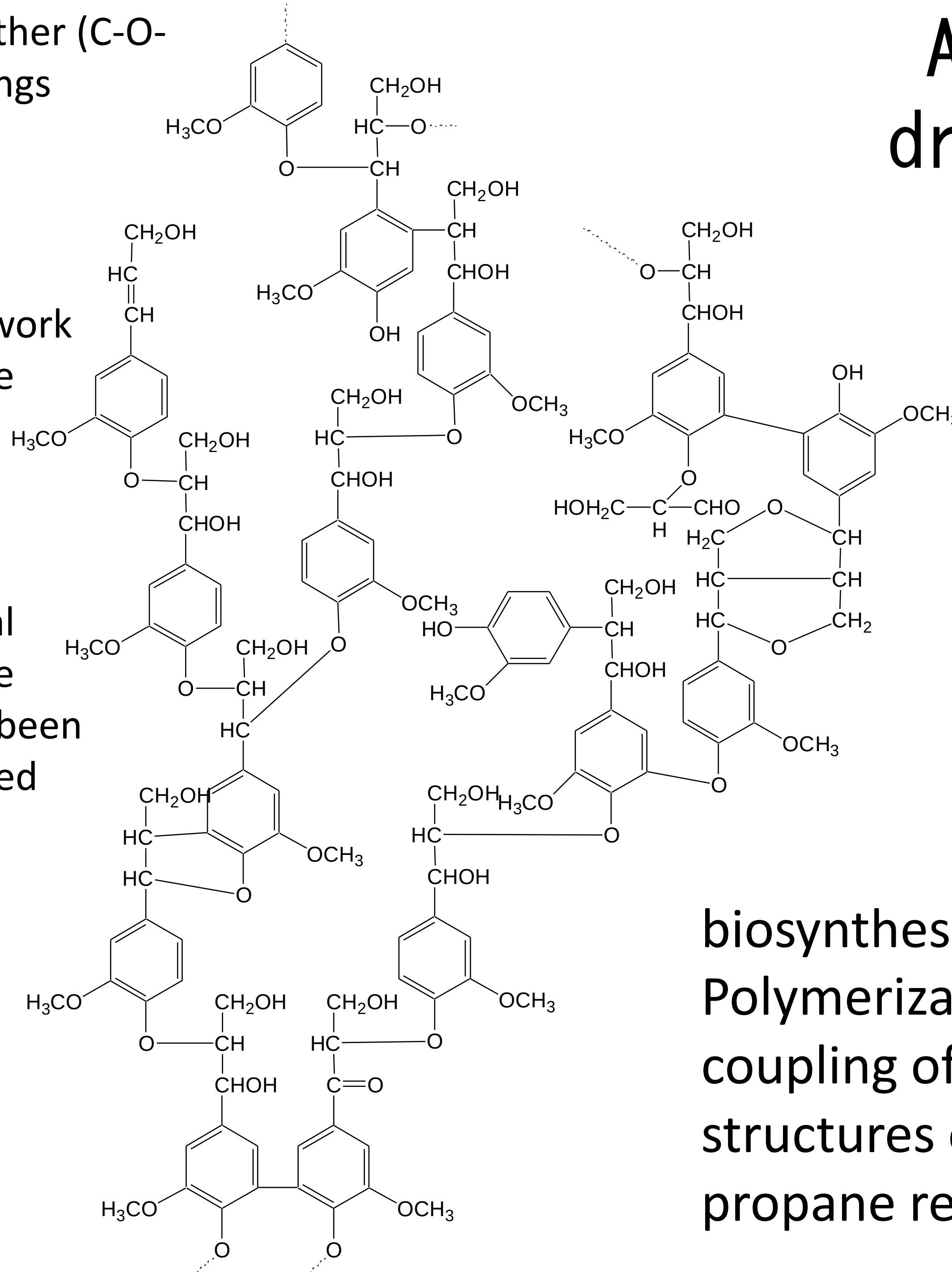
- Structural unit: phenylpropane（C_6-C_3）
- Hard wood: guaiacyl lignin
- Soft wood; guaiacyl lingnin+syringyl lignin
- 25～35％ in soft wood 、20～25％ in hard wood

A schematical drawing of soft wood lignin

C-C or ether (C-O-C)bondings

3D-net work structure

Chemical structure has not been elucidated



biosynthesis：
Polymerization of random radical coupling of various resonant-structures of radicalized phenyl propane residues

Properties

- hydrophobic
- various type of bondings → High bio-resistance

Industrial Application

- monomerization alkilphenol derivatives etc.
- Functionalization

  Water reducing admixture (for concrete construction)

  ～lignin sulphonic acid ///despersion、air-entrainment

  Used with lead battery electrode

- Resin miscible in phenol → addhesives
- Carbon fiber (1960-)

Practical utilization is difficult so far:
Lignin sulfonic acid is from Sulfate Pulp production←SP is not produced so much due to its cost.
Kraft lignin ←Black liquor is mainly used for fuel.

Refining technology of biomass

1　chemical pulp

2　Biomass saccharification (chemically)

3　Biomass saccharification (enzymatically)

4　High pressure high temperature treatment

5　low-boiling solvent

6　high-boiling solvent

Wood cell wall

- Constituent element　C:H:O

  weight ratio　５０：６：４４　（N0.05～0.4）

  mol ratio　３２：４６：２２

- major component

  cellulose:hemicellulose:lignin

  weight ratio　５０：２５：２５

4. Plants as a carbon resource

Organism as a carbon concentrating system on the planet

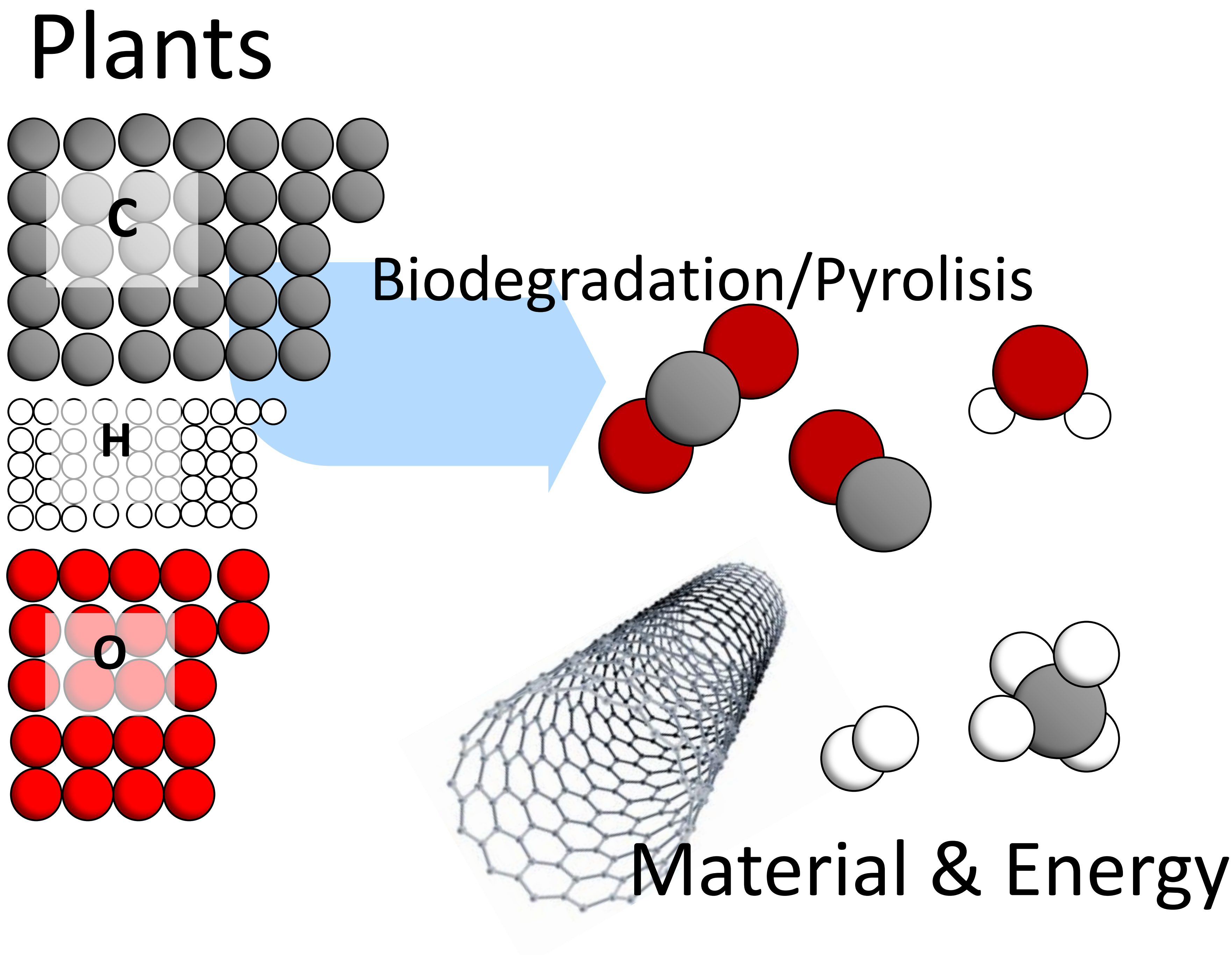
4.1 Peat

4.2 Natural modification of biomass into energy

(Peat → Fossile fule?)

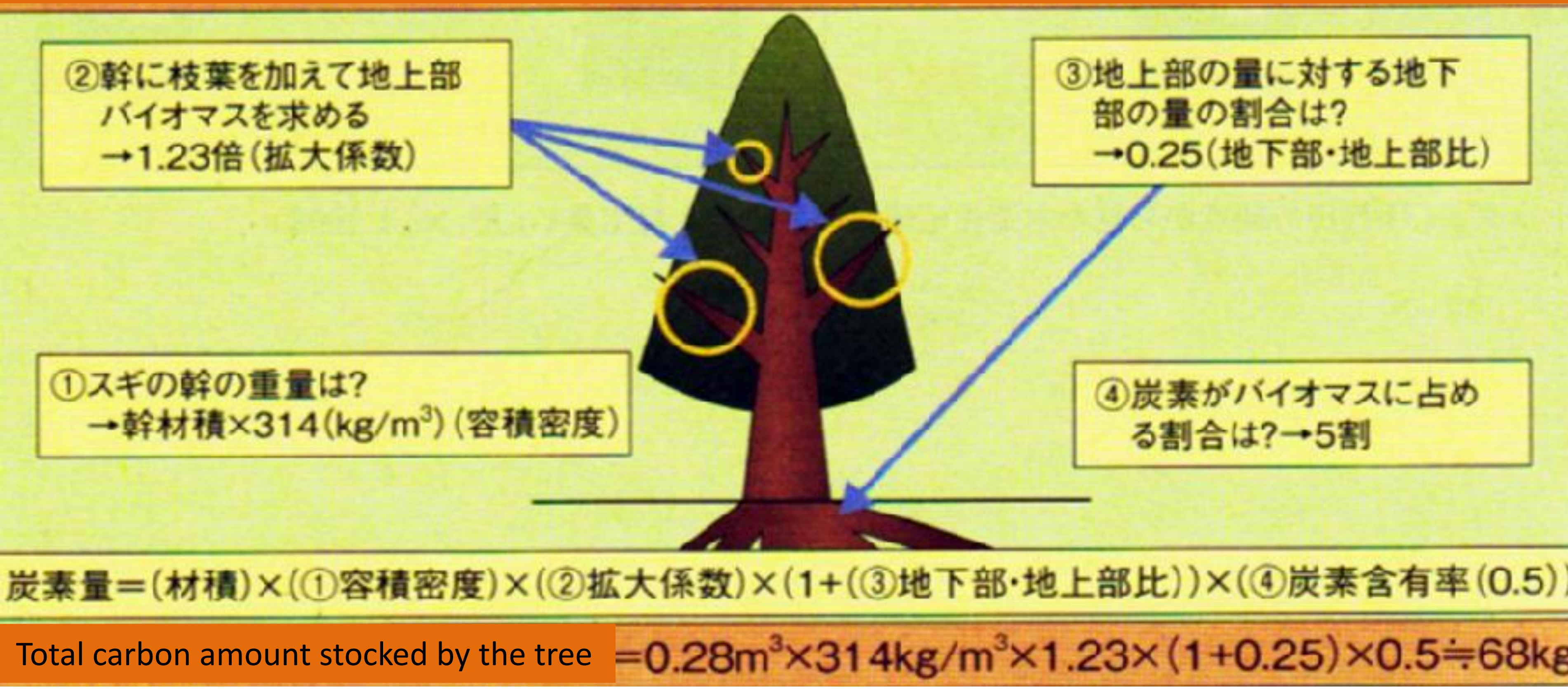
4.3 Artificial modification of biomass into energy and material

(Biomass → Artificial fossile fule & Carbon materials)


Plants
C
H
O
Biodegradation/Pyrolisis
Material & Energy

Amount of Carbon stocked by a tree

Tree in japanese cedar forest (diameter 20cm, tree hight 18 m, timber volume $0.28m^3$ averagely)



Total carbon amount stocked by the tree

林業白書H21

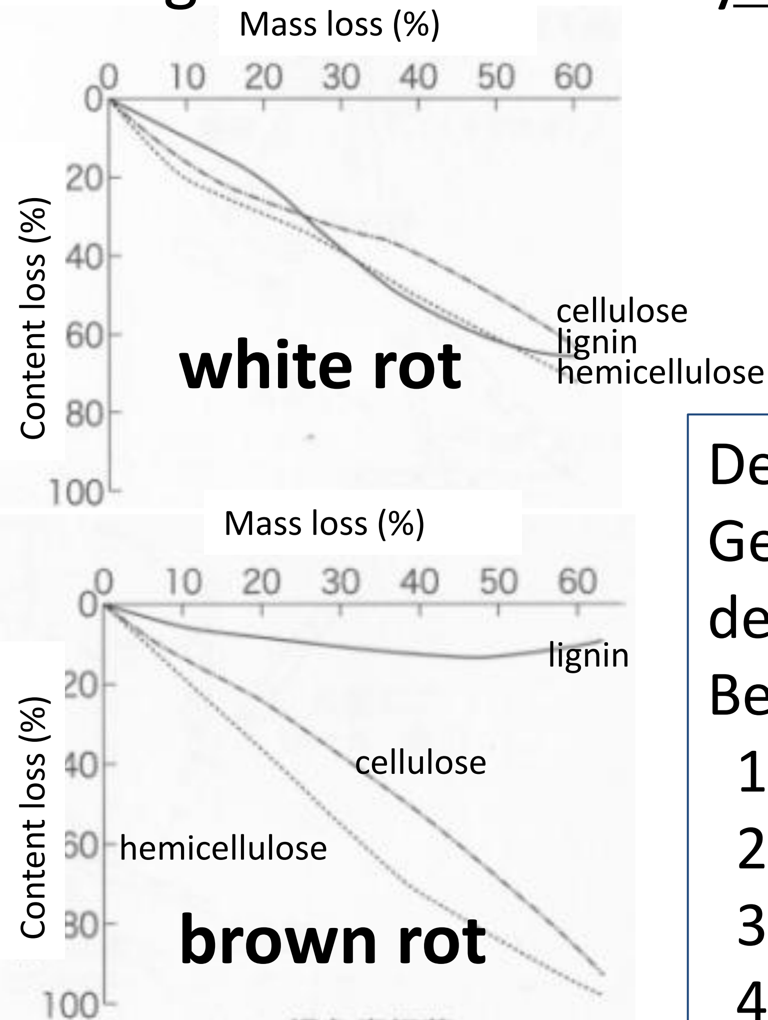
An typical japanese ceder tree stocks 68 kg of carbon.

Biomass conversion in nature (wood degradation)

degradation： mainly by basidiomycete（⊂fungi）

- white rot白色腐朽菌
- brown rot 褐色腐朽菌

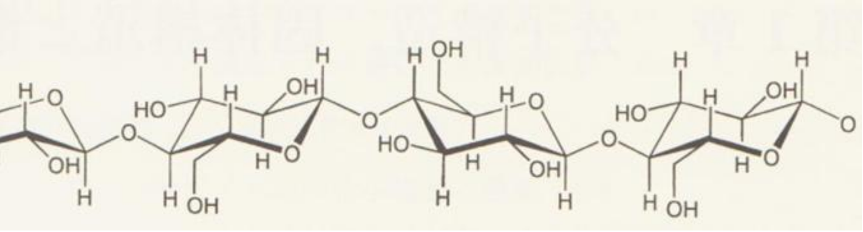
soft rot軟腐腐朽菌

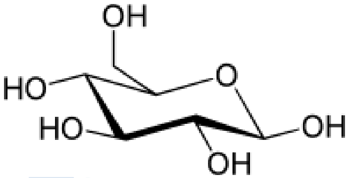


(Kirk, T. K. and Highley, T. L., 1973)

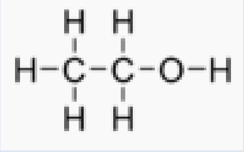
Degradability largely depends on species.
Generally hard woods is more easily degraded than hard woods.
Because of
1 less amount of heart wood extracts
2 syringyl-rich lignin
3 hemicellulose including more pentosan
4 Easier moisture penetration

Degradation of cellulose (Biomass saccharification)





Yeast 酵母
Saccharomyces spp.



(1) Chemical saccharification

Inorganic acid

- Acid hydrolysis and cleavage of glycosidic bond
- Susceptibility depends on kinds of polysaccharide.
- Coexistent lignin does not matter for the reaction.

(2) Biological saccharification

Cellulose decomposer organism

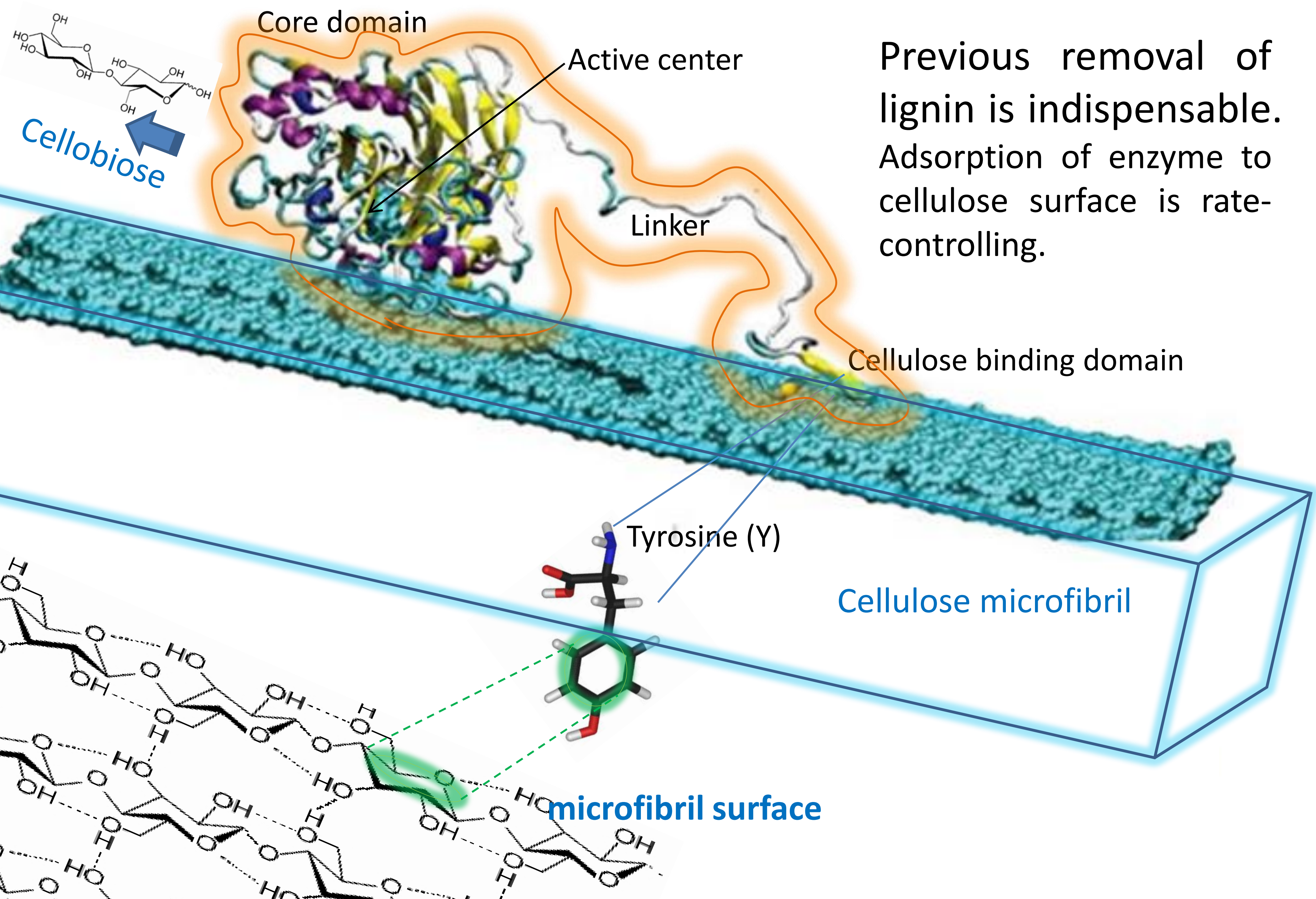
Mainly by yeasts, but other efficient species are being explored among ascomycetes子嚢菌 or digestive tracts消化管 of animals and insects・・・

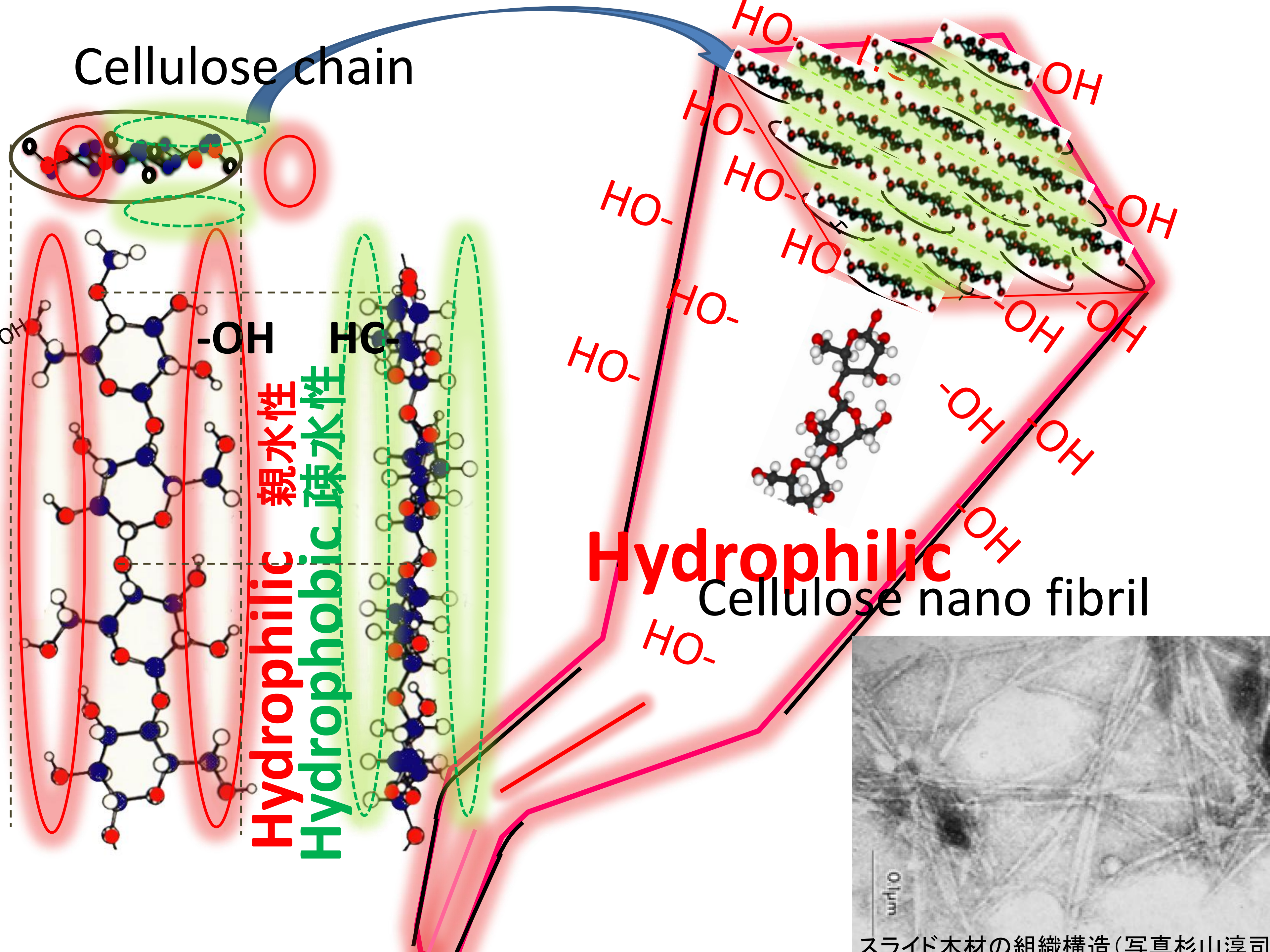
- Biodegradation by cellulase (enzyme)
- Around room temperature
- Previous treatment for removal of lignin is indispensable.

Cellobiohydrolase Cel7A (CBH I) Improving High-Performance Molecular Dynamics Codes For Biology, Renewable Energy: Bioethanol, Michael Crowley et. al.

Previous removal of lignin is indispensable.

Adsorption of enzyme to cellulose surface is rate-controlling.




Cellulose chain
-OH
HC-
親水性
疎水性
Hydrophilic
Hydrophobic
HO-
-OH
Hydrophilic
Cellulose nano fibril
スライド木材の組織構造（写真杉山淳司

4.1 Peat 泥炭

Peat

—an accumulation of partially decayed vegetation.
commonly moss or plants contributes.

Variety of peats – species, carbonization…

Provides records of past vegetation and climates of thousands of years, sometimes.

Cultivation soil for orchids蘭、peat-smell of scotch whisky, “peat-layer” in construction field

Peat soil formation and the distribution

Necessary condition：

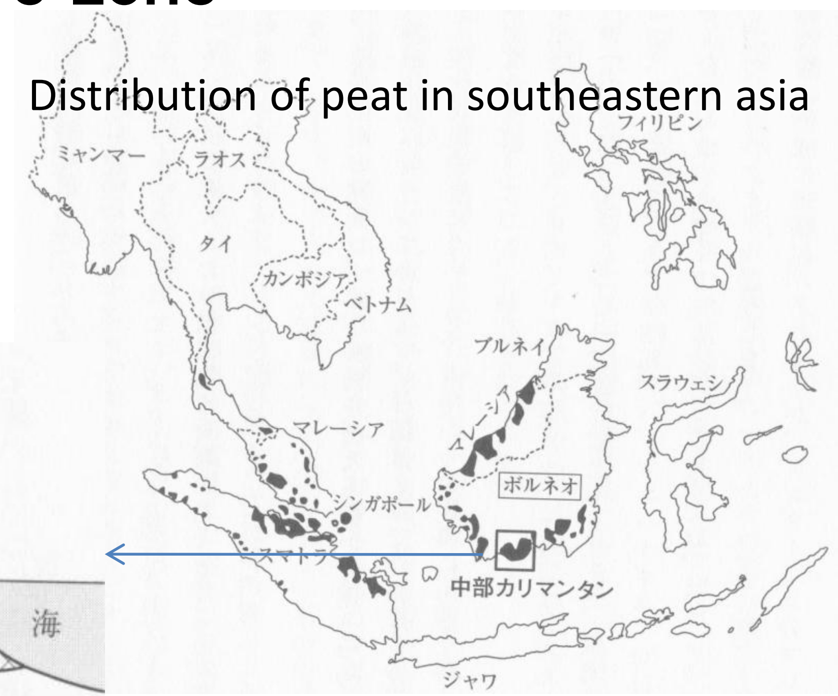
Favorable geography for accumulation of water and plant residue

Proper decomposition rate by microbes

・peat generated cool/temperature zone

・tropical peat

Distribution of peat in southeastern asia



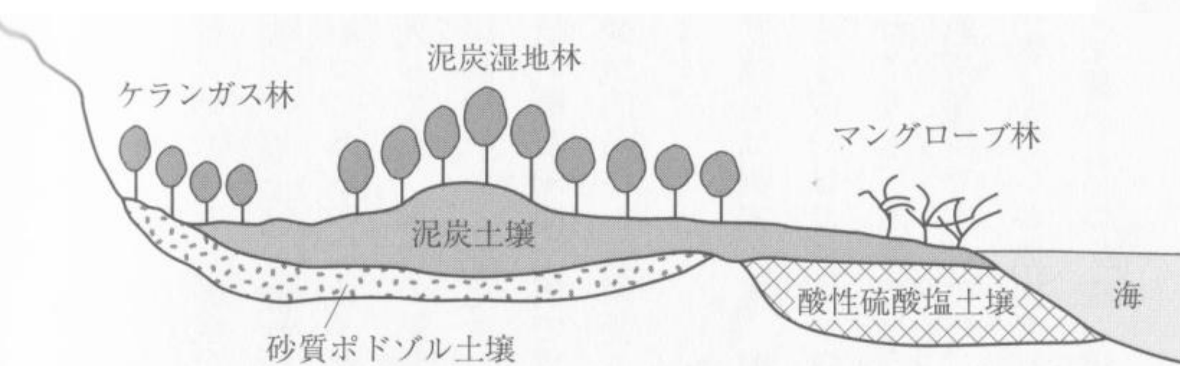
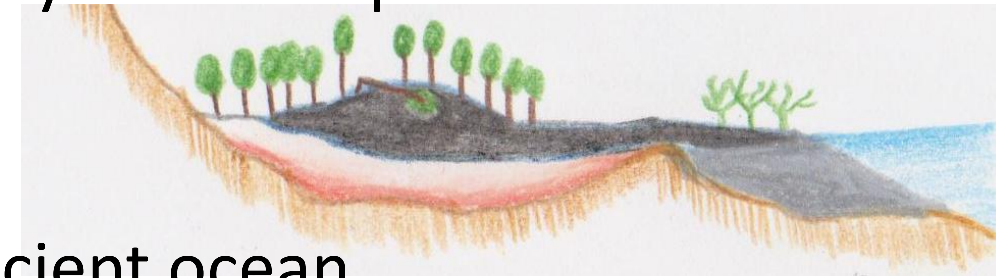


図　大崎満・岩熊敏夫編著「ボルネオ—燃える大地から水の森へ」

Peat …→ coal, petrol and natural gas ?

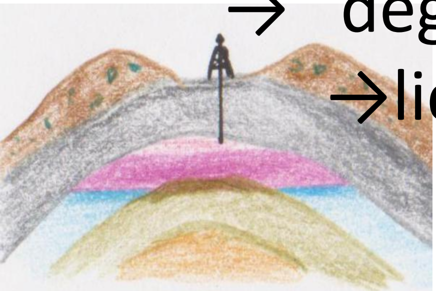
Formation of coal

400 million years ago, Paleozoic era, Carboniferous 古生代「石炭紀」
exuberant forests accumulated C from primitive atmosphere
→converted to peat by anaerobic bacteria
→converted to coal by heat and pressur



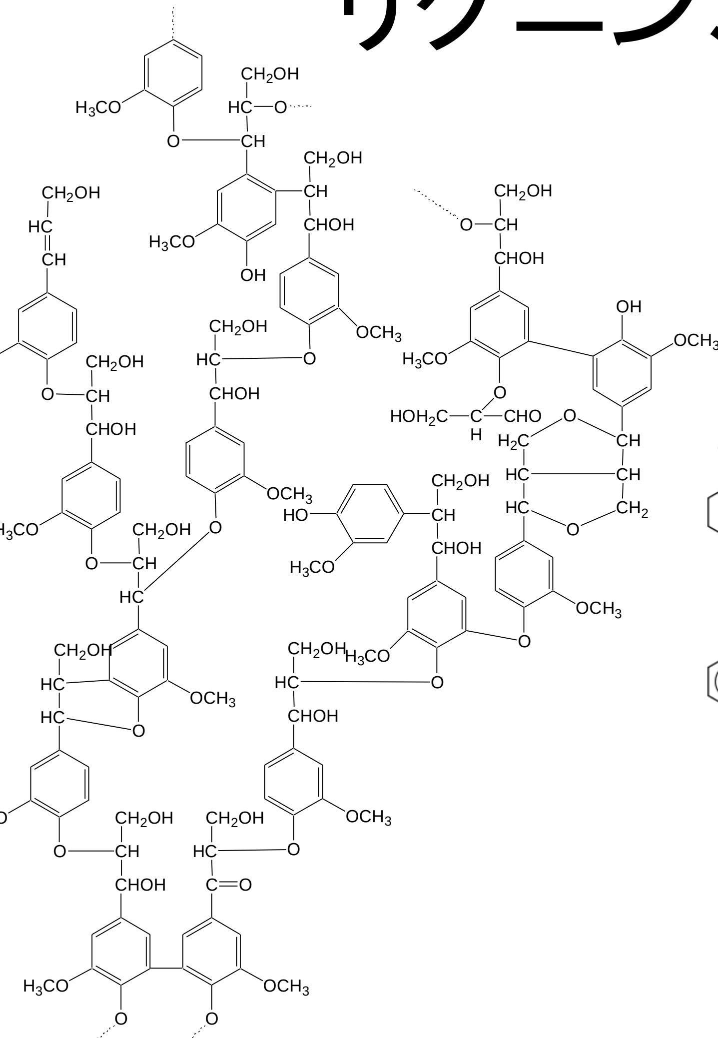
Petrol and natural gas

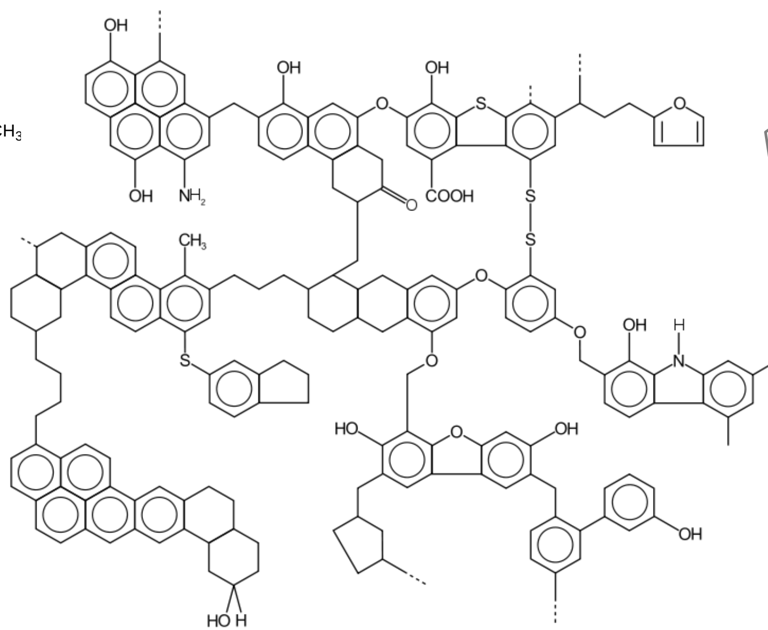
?00 million years ago, at ancient ocean
accumulated organic remains
→ degraded by bacteria
→liquid/gaseous hydrocarbons by heat and pressure
→long-range migration via spongy layers

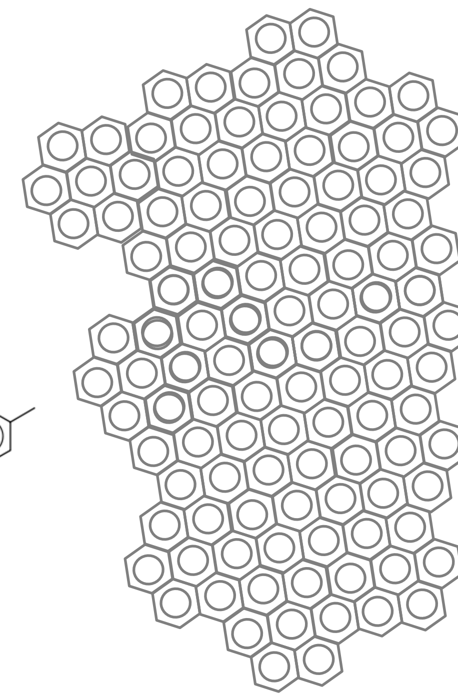


Both of them are from Biomass, originated from solar energy.

Lignin, coal, graphitic carbon
リグニン、石炭、黒鉛質炭素





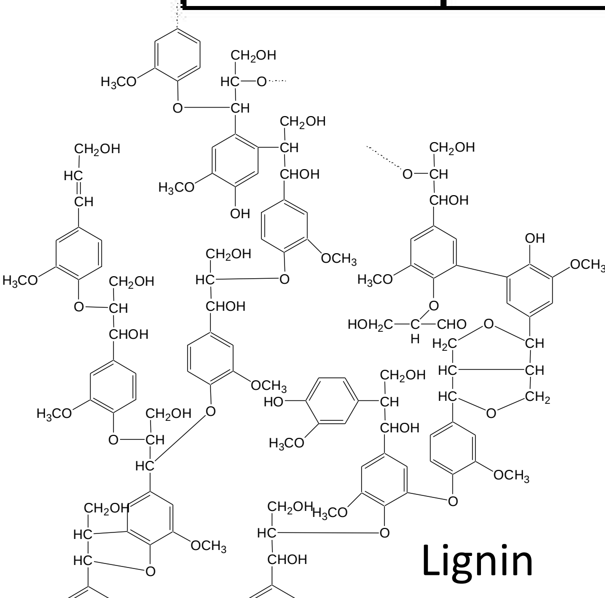


4.2 Natural modification of biomass into energy

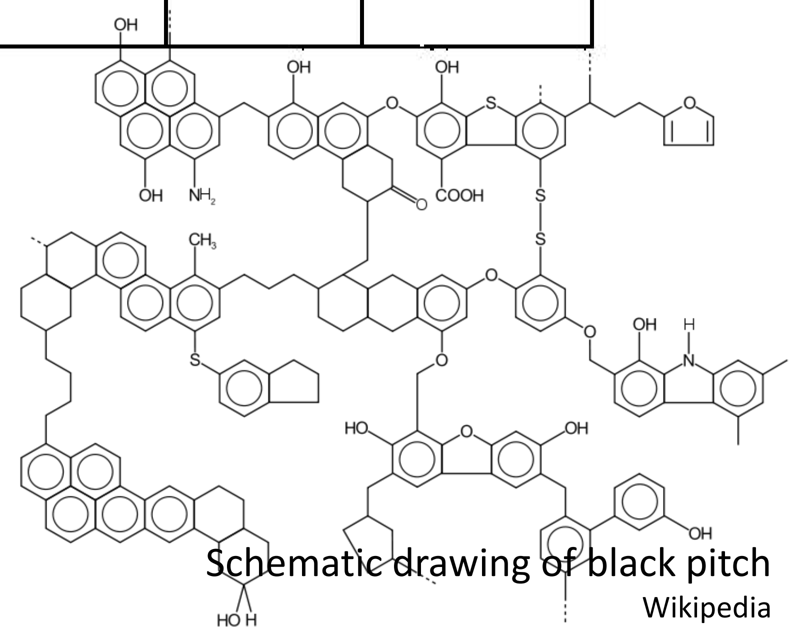
Characteristic of fuels

Ramage and Scurlock, 1996

fuel	Atomic ratio C	Atomic ratio H	Atomic ratio O	Weight (%) C	Weight (%) H	Weight (%) O	Amount of heat GJ/t	CO2 generation kg/GJ
Coal	1	1	<0.1	85	6	9	28	120
Petrol	1	2	0	85	15	0	42	75
Methane	1	4	0	75	25	0	55	50
Wood	1	1.5	0.7	49	6	45	20	77



Lignin

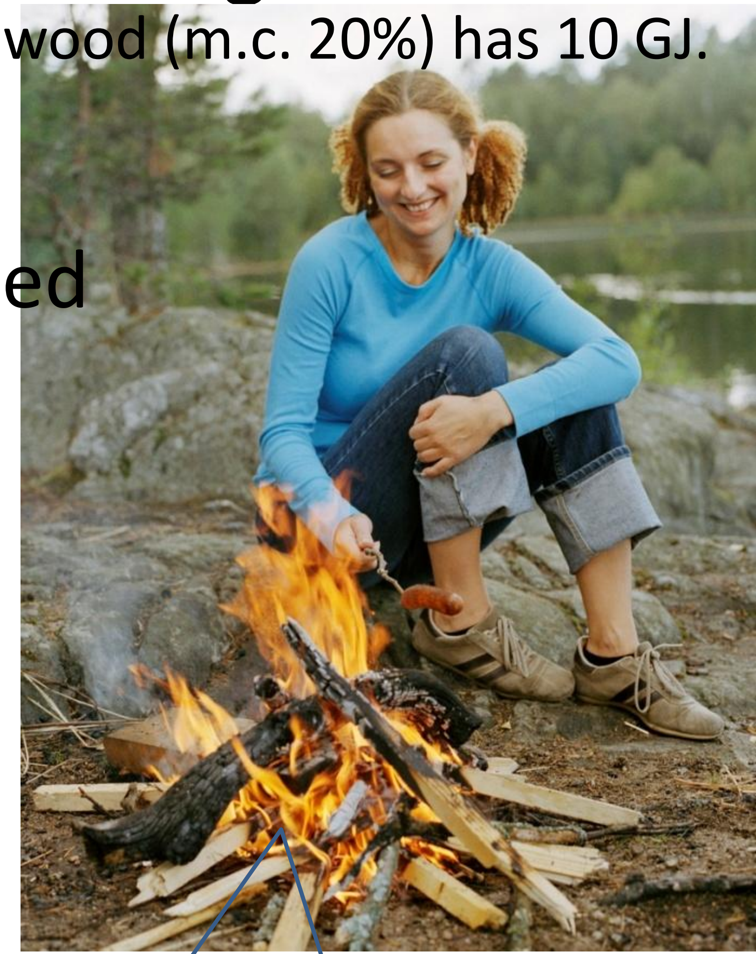


Schematic drawing of black pitch

Wikipedia

Wood is difficult energy for handling:

1m^3 of air-dried wood (m.c. 20%) has 10 GJ.



To boil 1ℓ of water, 0.4GJ is needed
＝40cm^{3}of wood enough?

Requisite for energy
- High energy efficiency
- Homogeneous
- Long storage
- Long distance transportable
- Accumulable

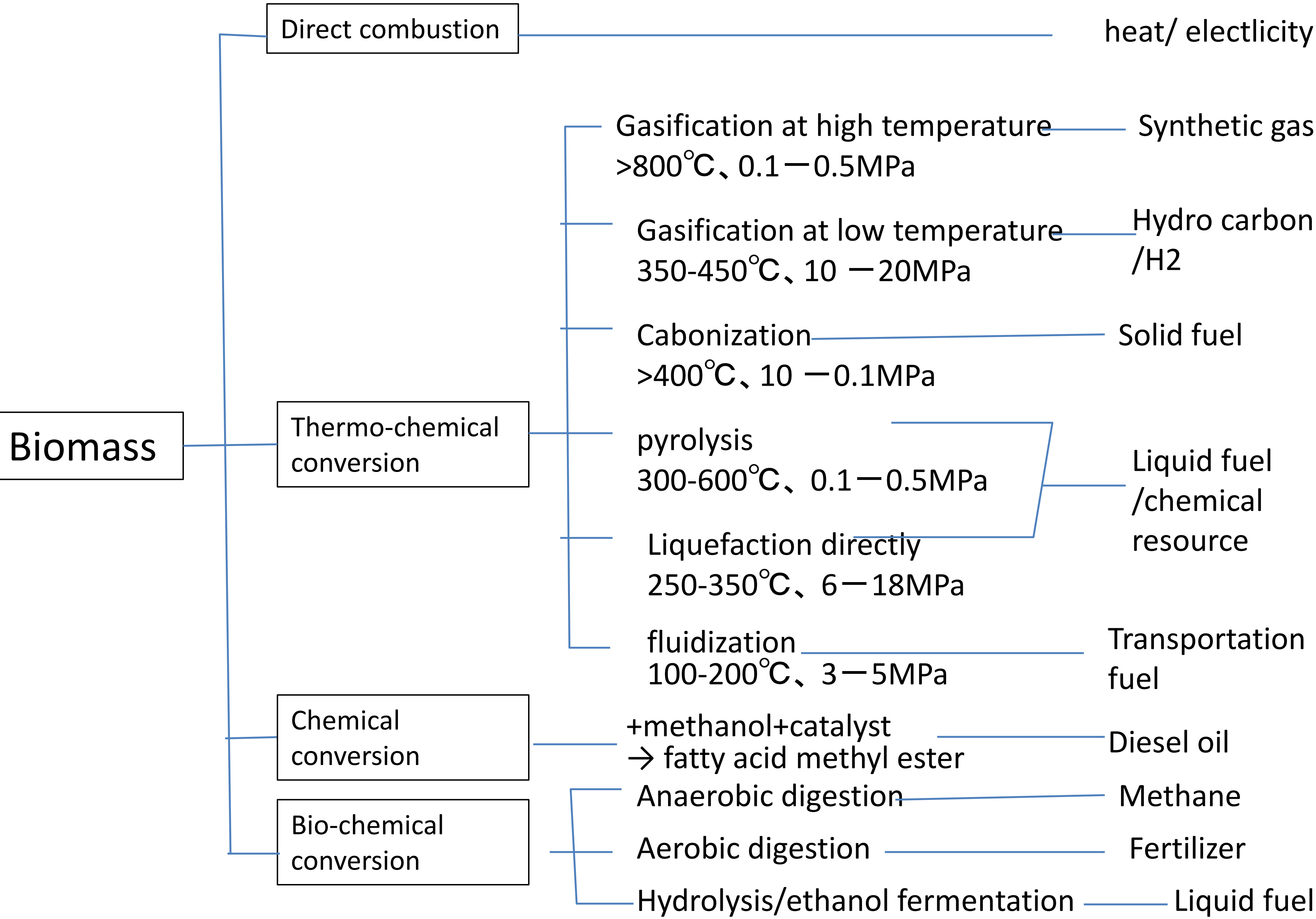
Fossil fuels

Practically, open fire needs the **50 times** of fulewood at least.

Trials of mankind for conversing biomass into energy corresponds to be **“artificial fossilization”** .

（熊崎実、2000）

4.3 Artificial modification of biomass into energy and materials



Biomass conversion technology （「バイオエネルギーの技術と応用」（柳下）改）