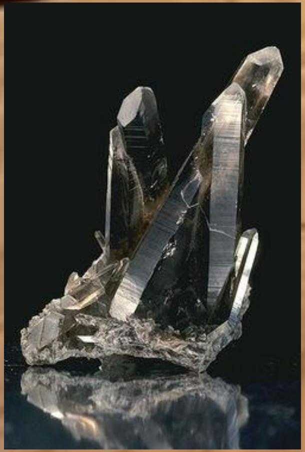
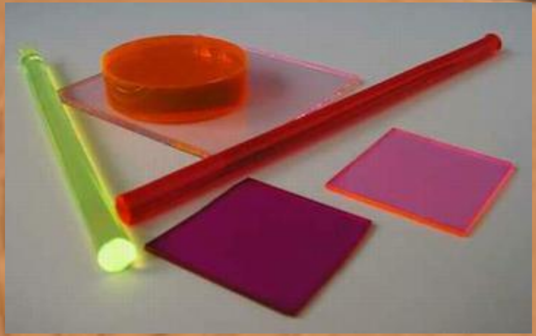
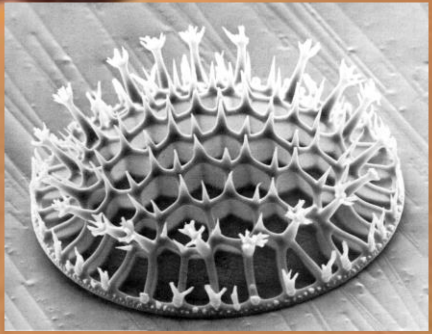
Silicon: from periodic table to biogenic silica

C. Bonhomme, Professor

Sorbonne University

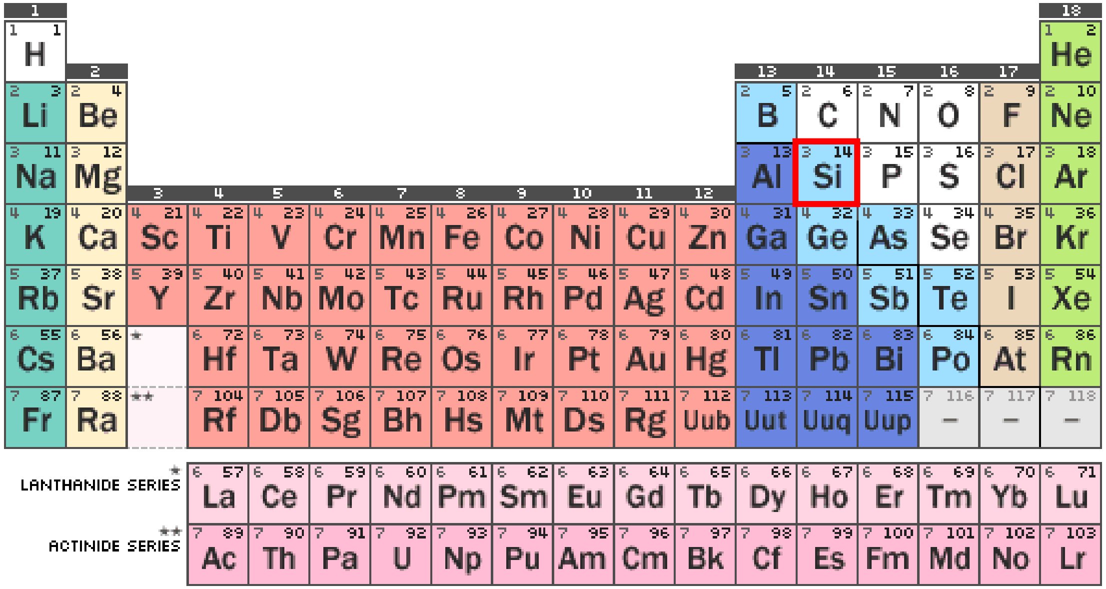






General properties

Silicon



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 1 H																	1 2 He
2 3 Li	2 4 Be											2 5 B	2 6 C	2 7 N	2 8 O	2 9 F	2 10 Ne
3 11 Na	3 12 Mg											3 13 Al	3 14 Si	3 15 P	3 16 S	3 17 Cl	3 18 Ar
4 19 K	4 20 Ca	4 21 Sc	4 22 Ti	4 23 V	4 24 Cr	4 25 Mn	4 26 Fe	4 27 Co	4 28 Ni	4 29 Cu	4 30 Zn	4 31 Ga	4 32 Ge	4 33 As	4 34 Se	4 35 Br	4 36 Kr
5 37 Rb	5 38 Sr	5 39 Y	5 40 Zr	5 41 Nb	5 42 Mo	5 43 Tc	5 44 Ru	5 45 Rh	5 46 Pd	5 47 Ag	5 48 Cd	5 49 In	5 50 Sn	5 51 Sb	5 52 Te	5 53 I	5 54 Xe
6 55 Cs	6 56 Ba	*	6 72 Hf	6 73 Ta	6 74 W	6 75 Re	6 76 Os	6 77 Ir	6 78 Pt	6 79 Au	6 80 Hg	6 81 Tl	6 82 Pb	6 83 Bi	6 84 Po	6 85 At	6 86 Rn
7 87 Fr	7 88 Ra	**	7 104 Rf	7 105 Db	7 106 Sg	7 107 Bh	7 108 Hs	7 109 Mt	7 110 Ds	7 111 Rg	7 112 Uub	7 113 Uut	7 114 Uuq	7 115 Uup	7 116 –	7 117 –	7 118 –
LANTHANIDE SERIES *			6 57 La	6 58 Ce	6 59 Pr	6 60 Nd	6 61 Pm	6 62 Sm	6 63 Eu	6 64 Gd	6 65 Tb	6 66 Dy	6 67 Ho	6 68 Er	6 69 Tm	6 70 Yb	6 71 Lu
ACTINIDE SERIES **			7 89 Ac	7 90 Th	7 91 Pa	7 92 U	7 93 Np	7 94 Pu	7 95 Am	7 96 Cm	7 97 Bk	7 98 Cf	7 99 Es	7 100 Fm	7 101 Md	7 102 No	7 103 Lr

$Z = 14$

Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

Si^{4+}: $1s^2\ 2s^2\ 2p^6$

$\chi(Si) = 1.8$

J. J. Berzelius (1823)

second natural abundance on earth (28%)

silica (SiO_2)

silicates (aluminosilicates...)

atomic mass: 28.085 g.mol^{-1}

^{28}Si (92.27 %)

^{29}Si (4.68 %)

^{30}Si (3.05 %)

From SiO_2 to Si

SiO_2

HCl

$SiCl_4, SiHCl_3$

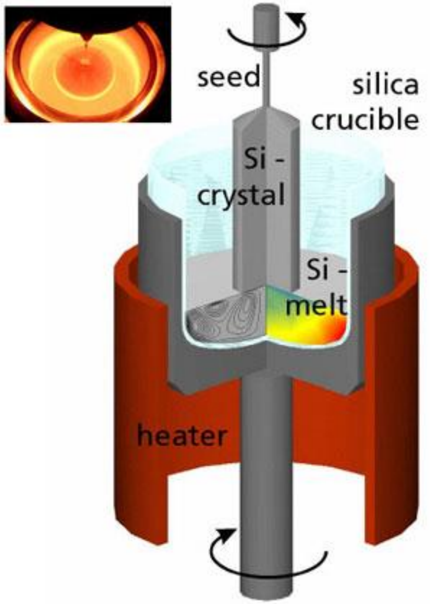
reduction 1000°C

Si (98-99 %)

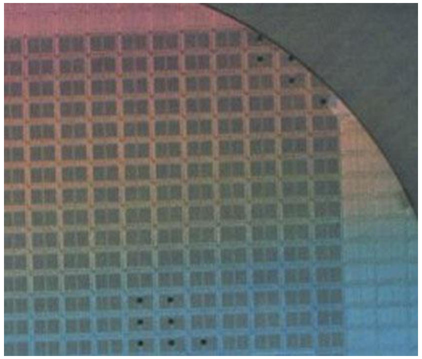
metallurgical Si

0.5 to 1 million tons per year!

electronic Si



Si > 99.9999 %

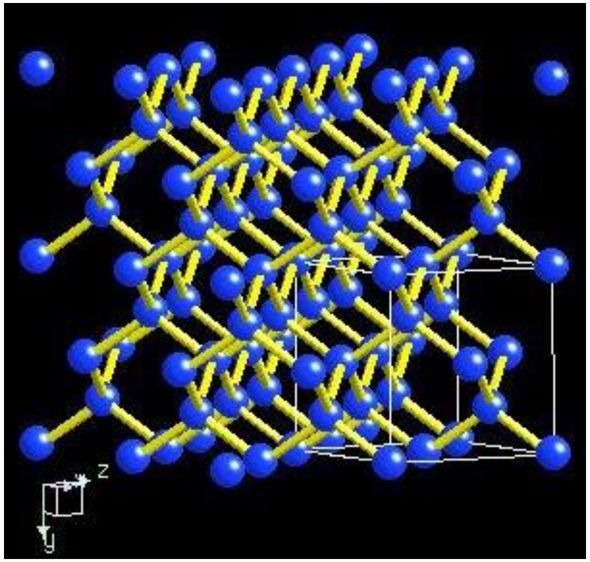


wafer (100-300 μm)

«diamond» like structure

cubic structure

a= 5.4307 Å



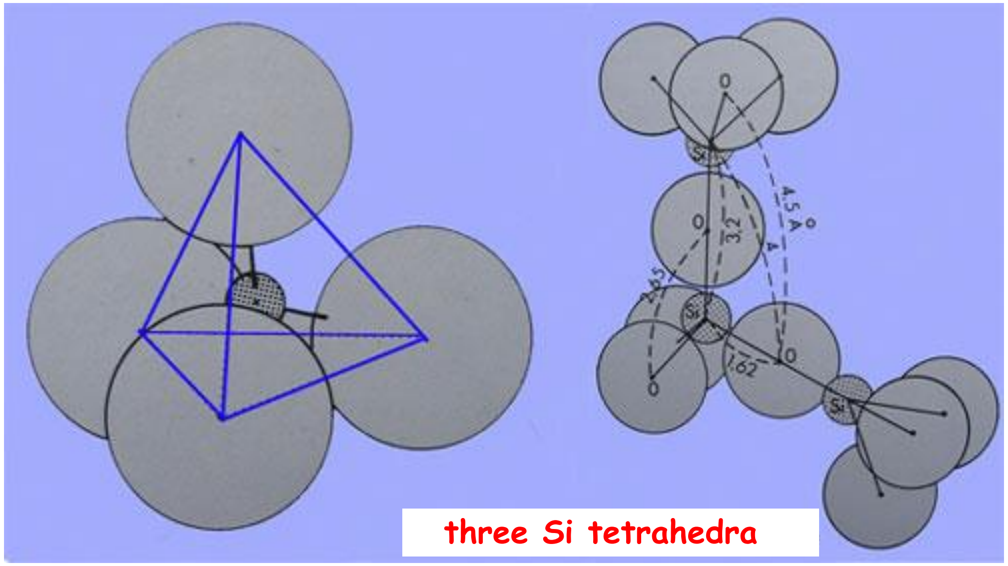
FP: 1410°C

BP: 2680°C

Si: chemical bonding

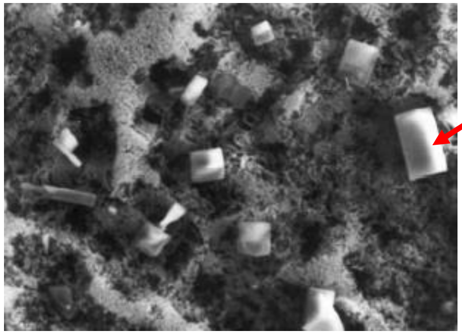
Si - H	1.48 Å
Si - Si	2.35 Å
Si - N	1.74 Å
Si - O	1.61 Å
Si - F	1.55 Å
Si -Cl	2.01 Å
Si -Br	2.15 Å
Si - C	1.80 Å

SiO_2



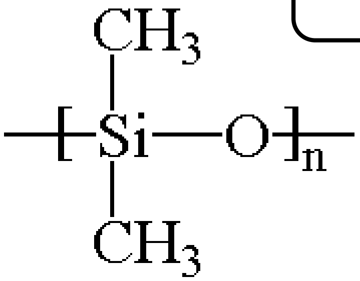
three Si tetrahedra

SiF_4

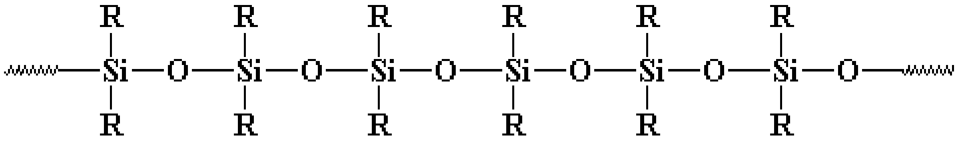


$(NH_4)_2SiF_6$

silicones



$$-\!\!\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n\!\!-$$



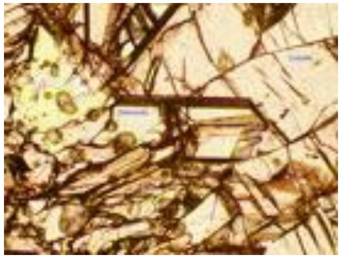
$$\sim\!\sim-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-O-\sim\!\sim$$

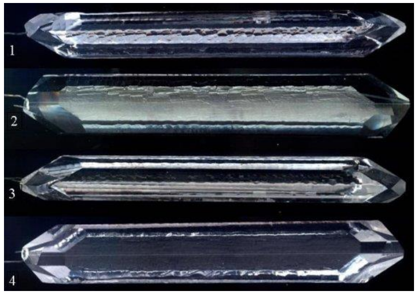
Crystalline and amorphous silica

SiO_2 polymorphs

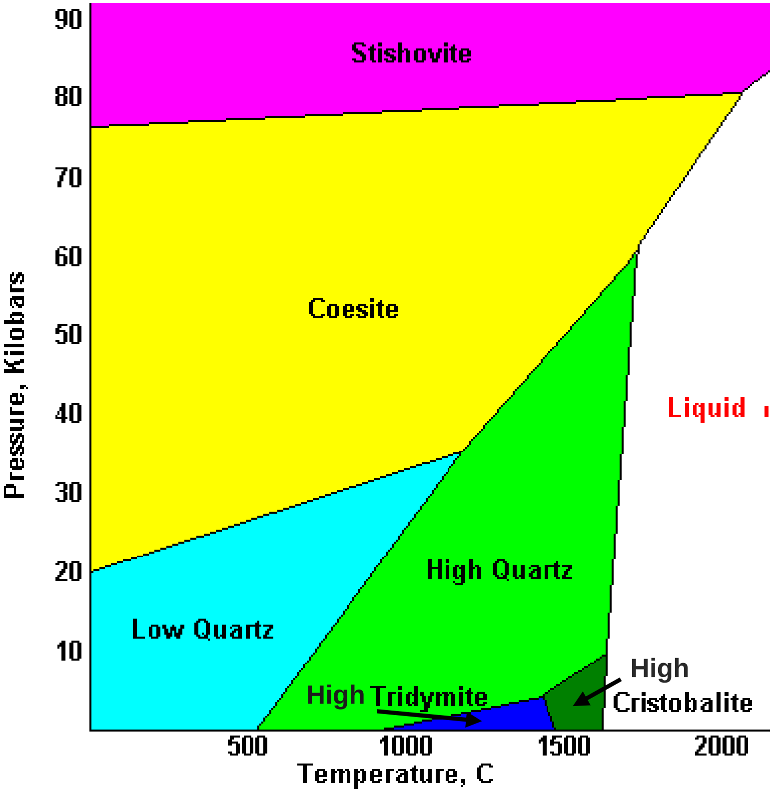
Coesite

Stishovite



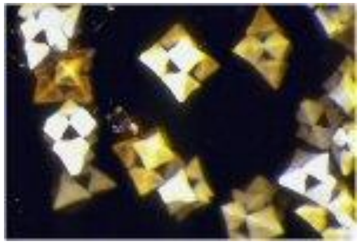


synthetic quartz



quartz

Tridymite



Cristobalite

X-Ray diffraction

$\lambda \approx 10^{-10}$ m = 1 Å

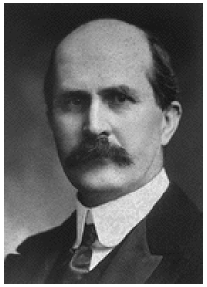
X-rays are waves: 1913

W. Röntgen

(1845-1923)

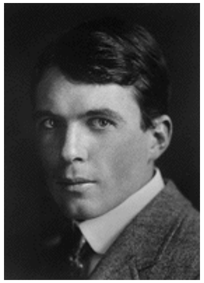
M. von Laue

(1879-1960)



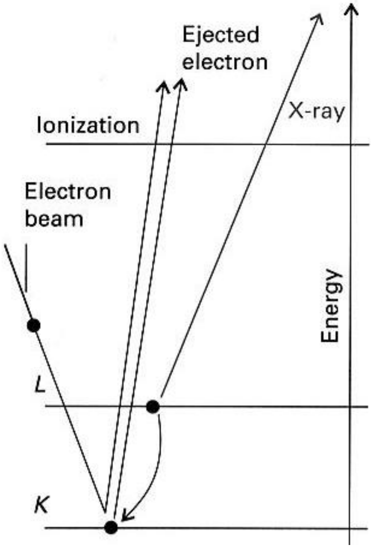
W. H. Bragg

(1862-1942)



W. L. Bragg

(1890-1971)



Polymorph (density)

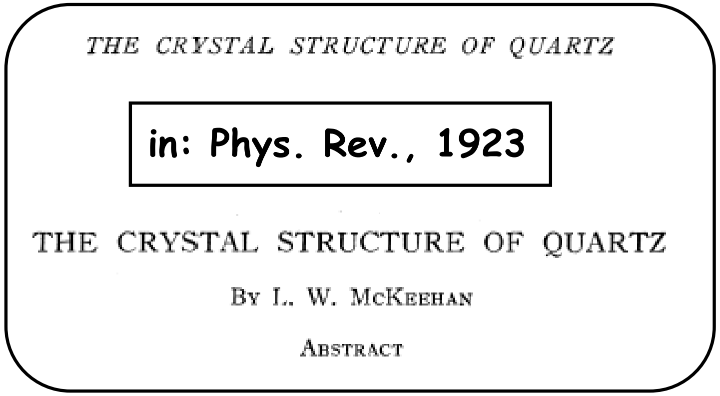
Low Quartz (2.65) trigonal

High Tridymite (2.28) hexagonal

High Cristobalite (2.21) cubic

Coesite (2.93) monoclinic

Stishovite (4.30) tetragonal



THE CRYSTAL STRUCTURE OF QUARTZ

in: Phys. Rev., 1923

THE CRYSTAL STRUCTURE OF QUARTZ

By L. W. McKeehan

Abstract

«Other» quartz

Amethyst

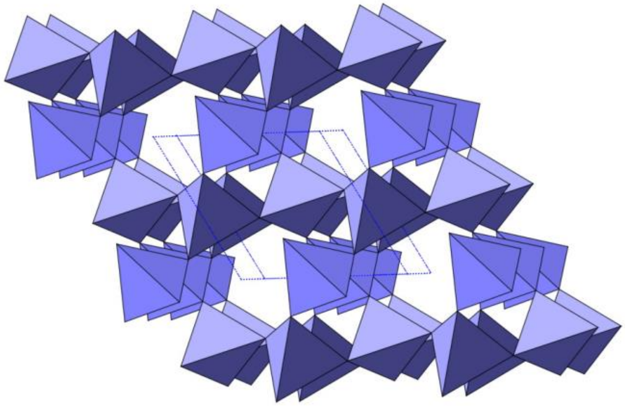
Citrine

Rose quartz

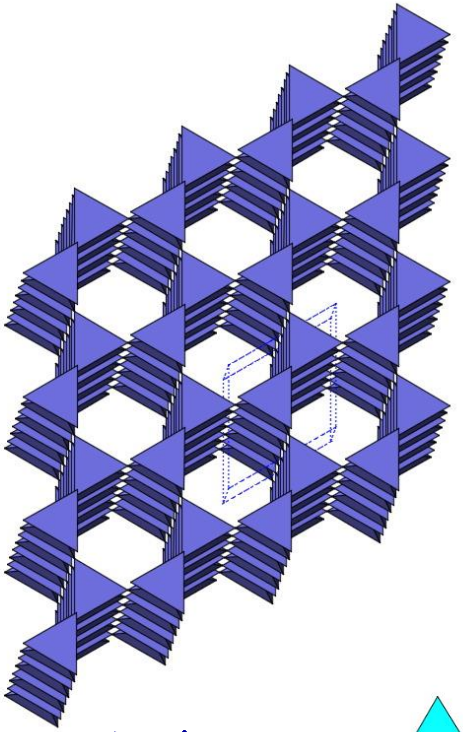
Smoky quartz

Agate

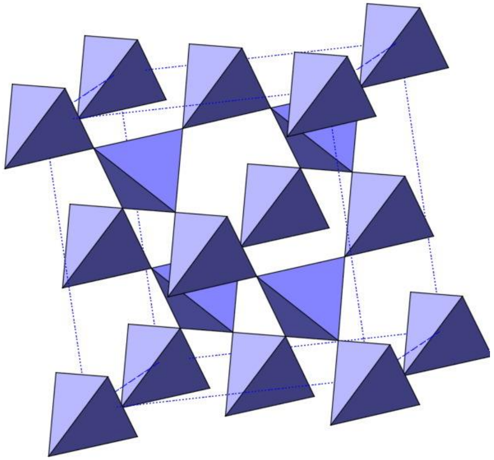
Various crystallographic structures



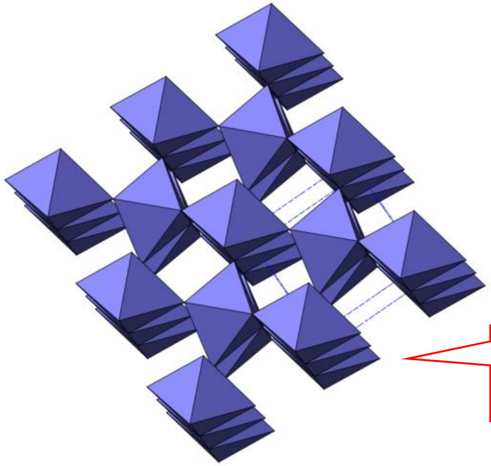
Quartz



Tridymite

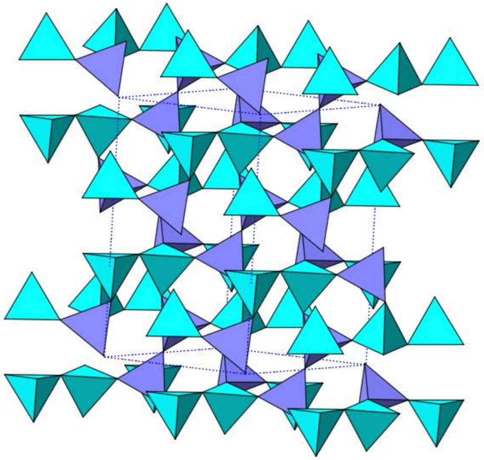


Cristobalite



SiO_6 octahedra!

Stishovite (6-fold coordination!)



Coesite

Amorphous silica

mineraloids

Lechatelierite

a pure silica glass (rare)

Obsidian

Newbury Crater, Oregon

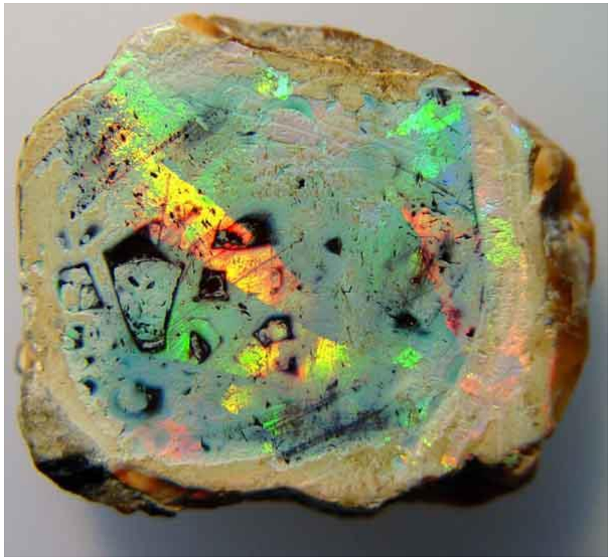
Fulgurite

lightning on sand!

Trinitite: start july 16, 1945!

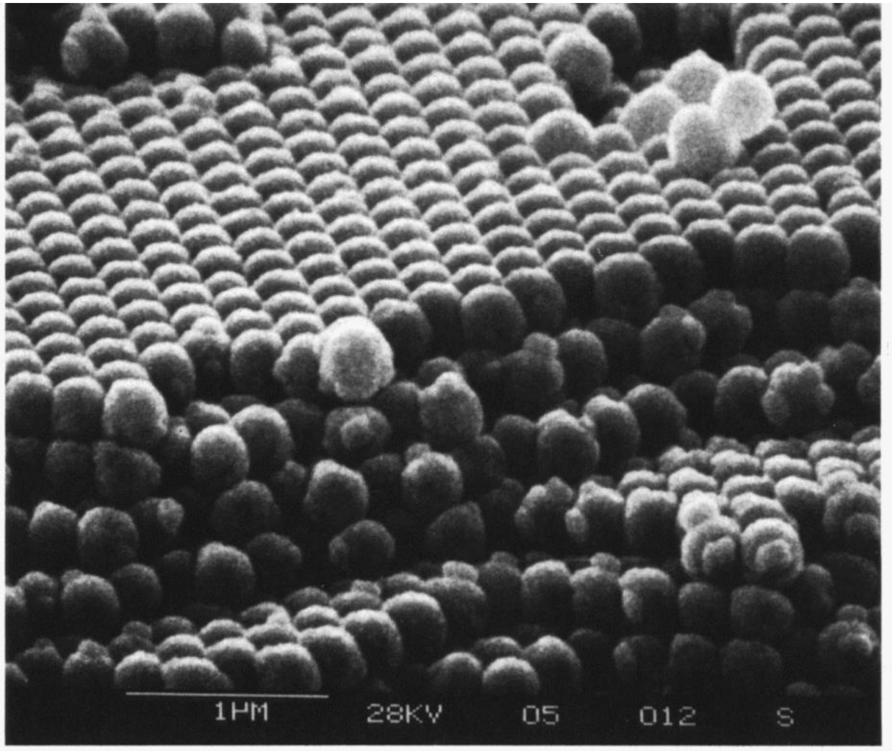
obsidian arrows
and scalpels

Hydrated silica: Opals



close-packed array of SiO_2 spheres

0.15 to 0.4 μm

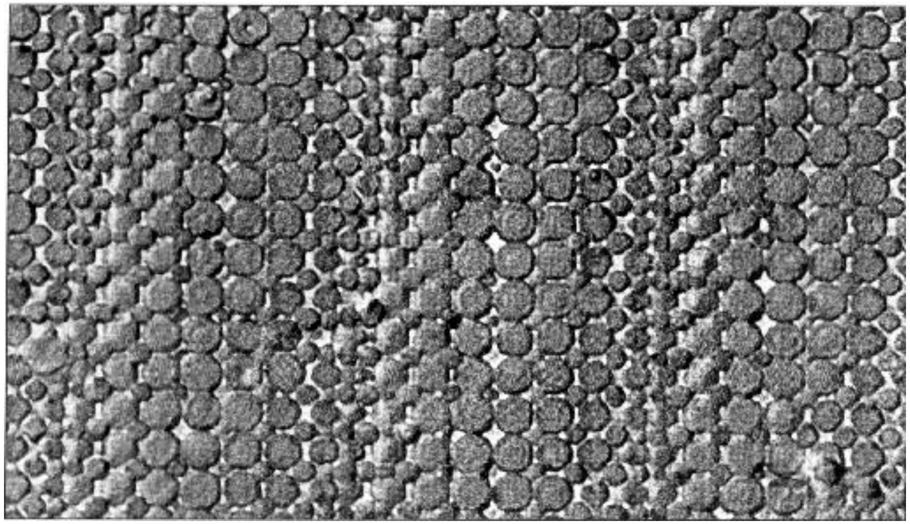


colloidal crystals

silica nanoparticles in an amorphous hydrated silica matrix

SiO_2,nH_2O

Other opals



J.V. Sanders, 1980

spheres of two different sizes!

concoidal fracture (like glass)

Nuclear Magnetic Resonance (NMR)

W. Pauli, Physique 1945

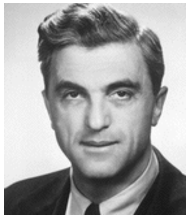
"for the discovery of the Exclusion Principle, also called the Pauli Principle"

G. Uhlenbeck, S. Goudsmit

"pères du spin"

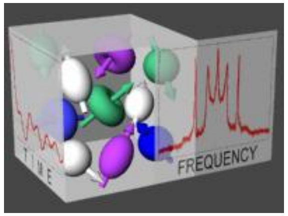
I. I. Rabi, Physique 1944

"for his resonance method for recording the magnetic properties of atomic nuclei"



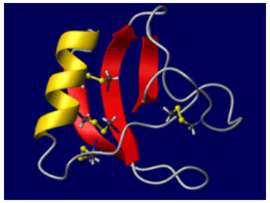
F. Bloch, E. M. Purcell, Physique 1952

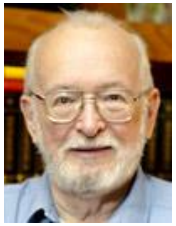
"for the development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith"

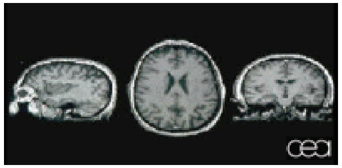


K. Wüthrich, Chimie 2002

"for his development of NMR spectroscopy for determining the three dimensional structure of biological macromolecules in solution"





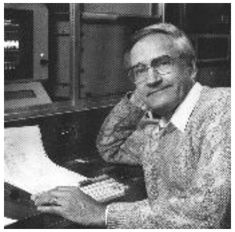


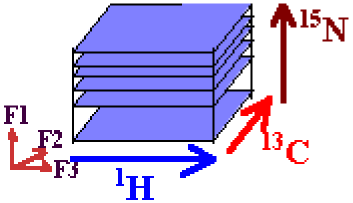
P. C. Lauterbur, P. Mansfield, Médecine 2003

"for their discoveries concerning magnetic resonance imaging"

R. R. Ernst, Chimie 1991

"for his contribution to the development of the methodology of high resolution NMR spectroscopy"





NMR basics

$\hat{\mu} = \gamma \hbar \hat{I}$

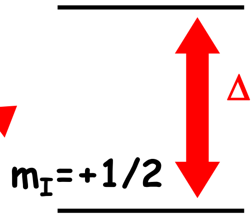
magnetic moment

spin angular momentum

gyromagnetic ratio

$E = - \mu . B$

B_0 (~15T)



$\boxed{\Delta m_I = \pm 1}$

$\Delta E = \gamma h B_0 / 2\pi$

$\boxed{\nu_0 = \gamma B_0 / 2\pi}$

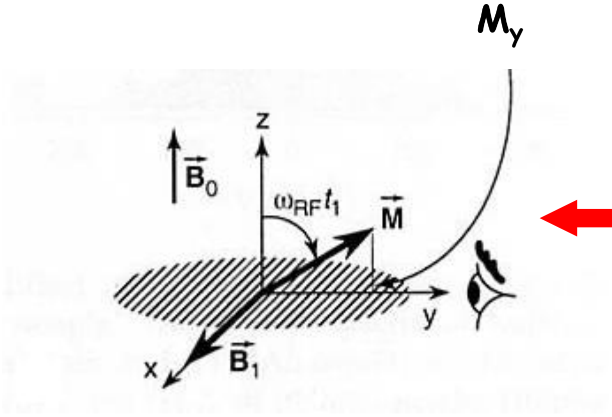
Larmor frequency!

Boltzmann equation

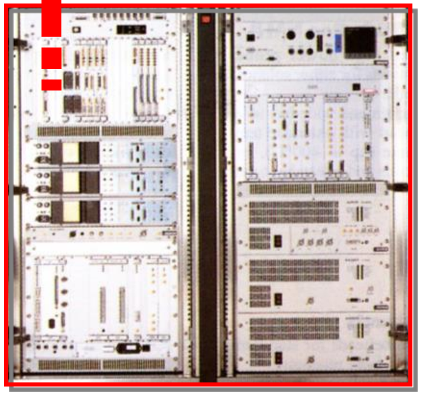
Curie law

$$M = \frac{N \gamma^2 h^2 B_0 I(I+1)}{12 \pi^2 kT}$$

M

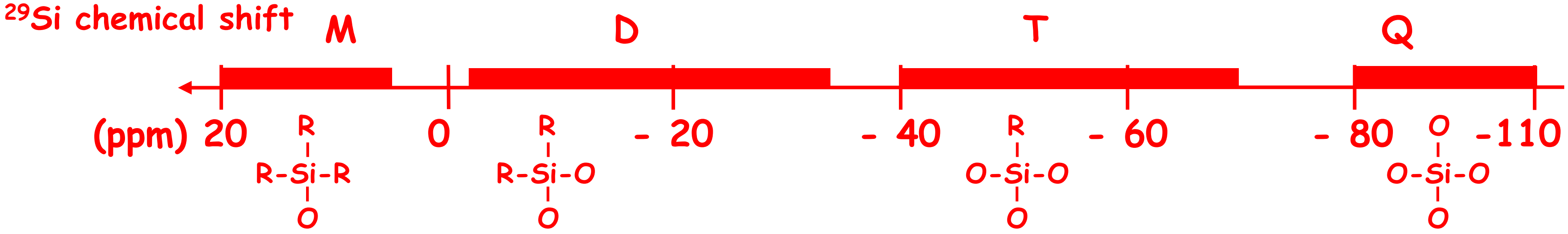


Man, Encyclopedia of analytical chemistry, 2000, 12228.



B_1(RF): on resonance!

^{29}Si chemical shifts



^{29}Si chemical shift

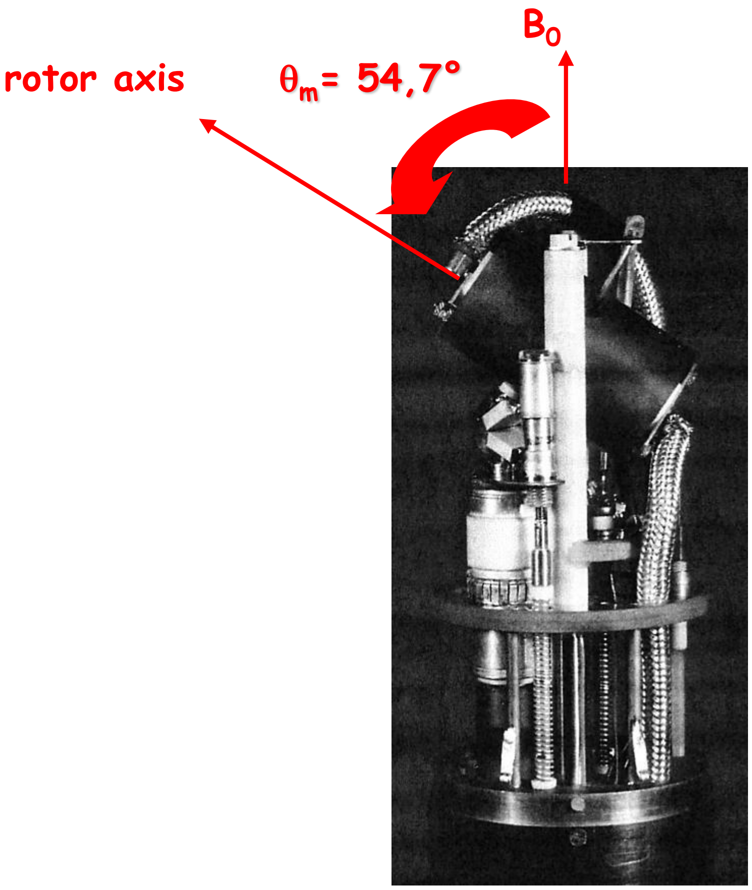
M

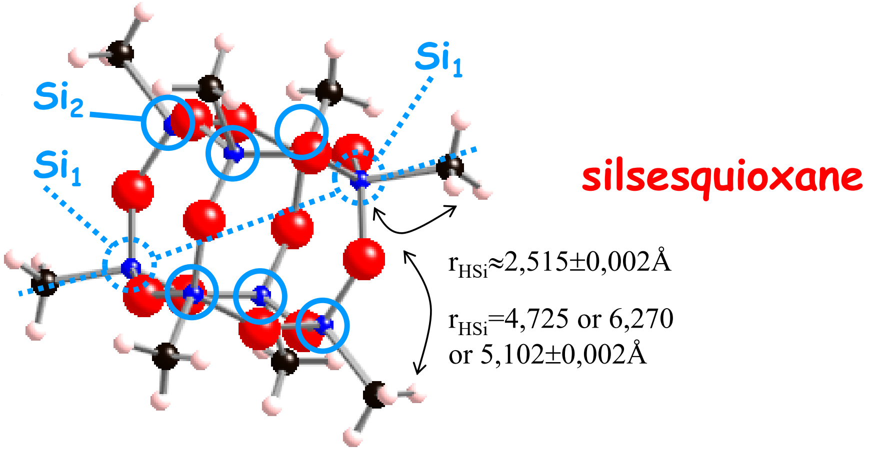
D

T

Q

(ppm) 20 0 - 20 - 40 - 60 - 80 -110

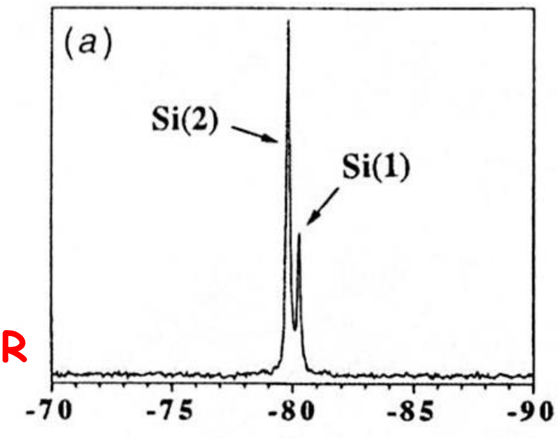




silsesquioxane

$r_{HSi} \approx 2,515 \pm 0,002$Å

r_{HSi}=4,725 or 6,270 or 5,102±0,002Å

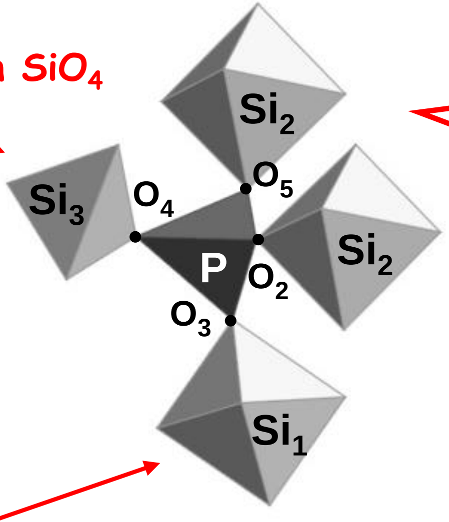


MAS ^{29}Si NMR

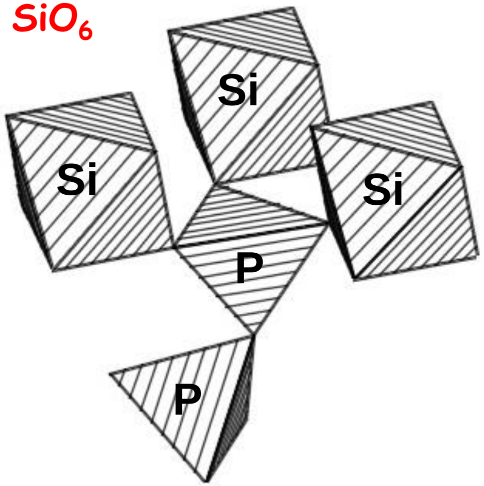
4- and 6-fold coordinated Si atoms

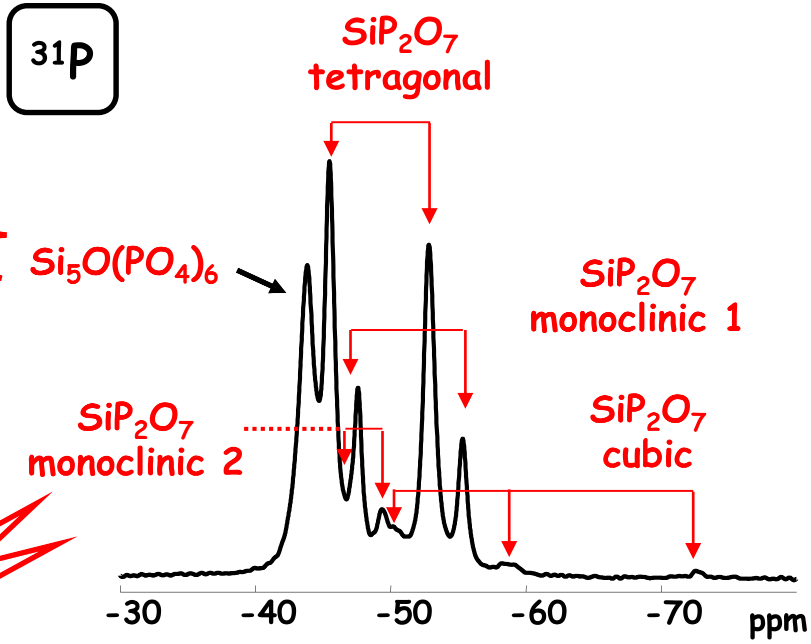
an example: Si-O-P bonds

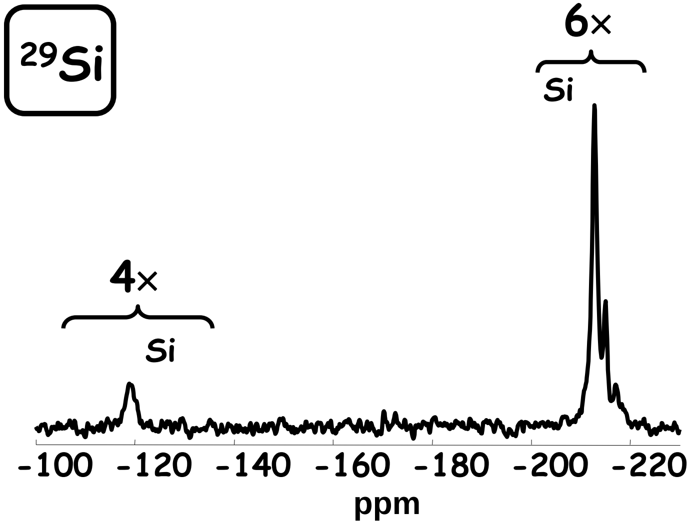
tetrahedron SiO_4



octahedron SiO_6

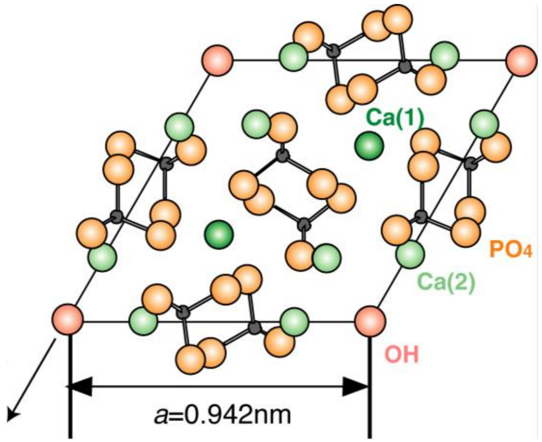






C. Coelho, Paris 6

Silica and biocompatibility



$Ca_{10}\,(PO_4)_6\,(OH)_2$

Mg^{2+}, Zn^{2+}, Na^{+}, K^{+} ...

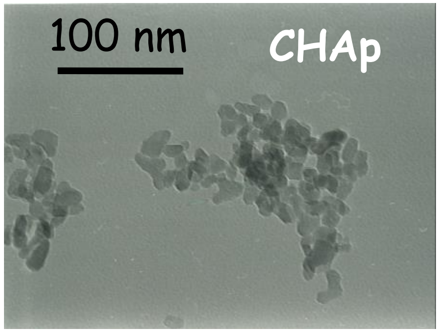
SO_4^{2-}, CO_3^{2-} ...

CO_3^{2-}, F^{-}, Cl^{-} ...

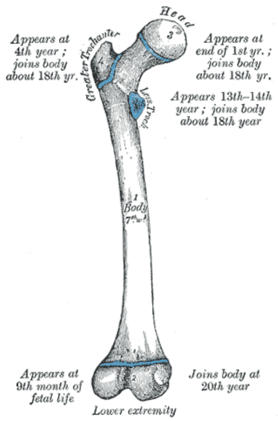
$Ca_{10}\,\underbrace{(PO_4)_6}_{B}\,\underbrace{(OH)_2}_{A}$

SiO_4^{4-}

CO_3^{2-}



nano-crystalline CHAp

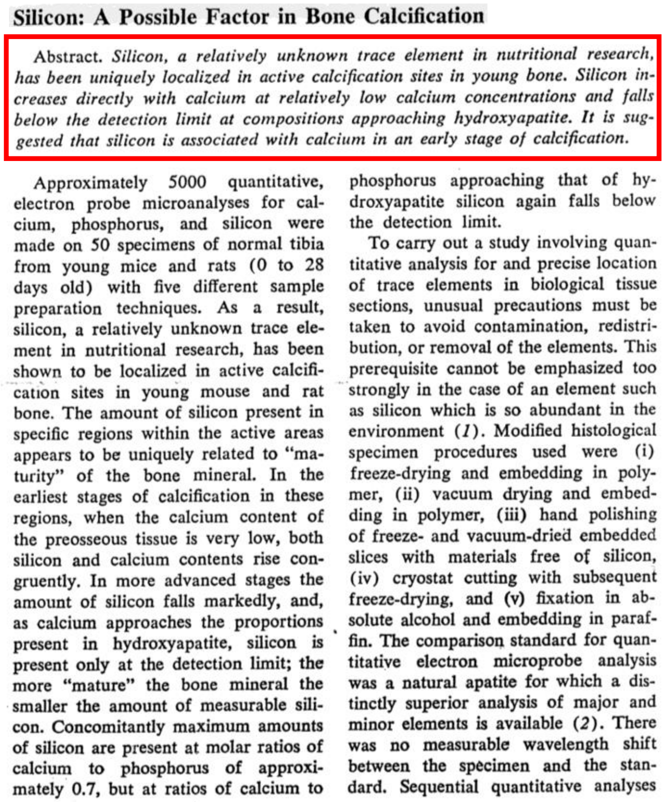


bone

$Ca_{10-x/2}[(PO_4)_{6-x}(CO_3)_x]\ [(OH)_{2-2y}(CO_3)_y]$

carbonated hydroxyapatite $x \neq 0$

The role of silica towards biocompatibility



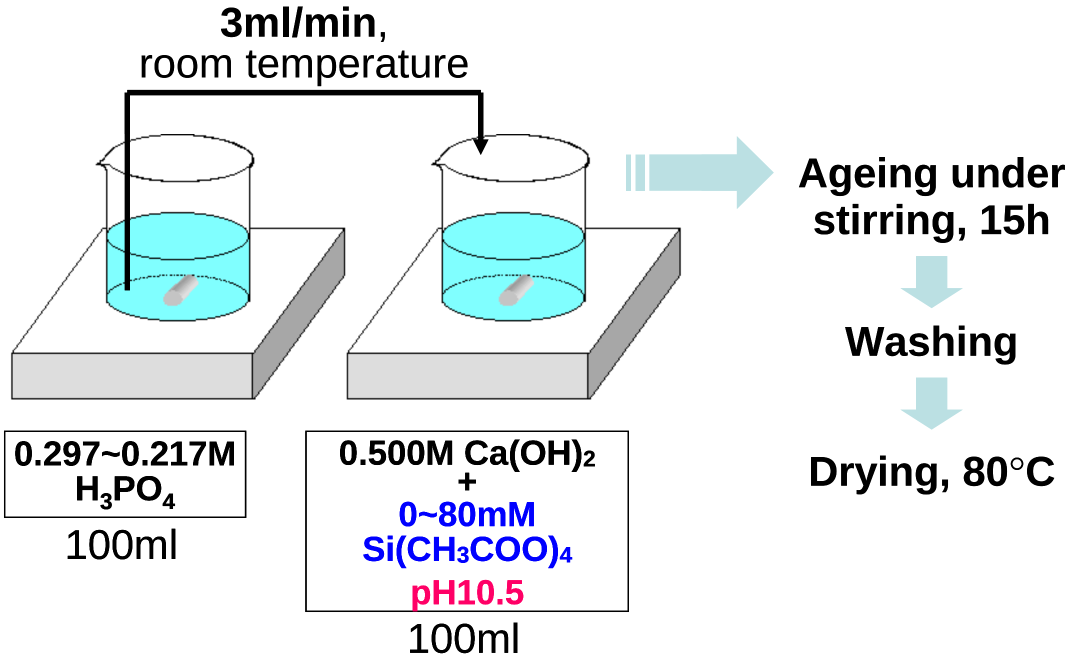
Silicon: A Possible Factor in Bone Calcification

Abstract. *Silicon, a relatively unknown trace element in nutritional research, has been uniquely localized in active calcification sites in young bone. Silicon increases directly with calcium at relatively low calcium concentrations and falls below the detection limit at compositions approaching hydroxyapatite. It is suggested that silicon is associated with calcium in an early stage of calcification.*

Approximately 5000 quantitative, electron probe microanalyses for calcium, phosphorus, and silicon were made on 50 specimens of normal tibia from young mice and rats (0 to 28 days old) with five different sample preparation techniques. As a result, silicon, a relatively unknown trace element in nutritional research, has been shown to be localized in active calcification sites in young mouse and rat bone. The amount of silicon present in specific regions within the active areas appears to be uniquely related to "maturity" of the bone mineral. In the earliest stages of calcification in these regions, when the calcium content of the preosseous tissue is very low, both silicon and calcium contents rise congruently. In more advanced stages the amount of silicon falls markedly, and, as calcium approaches the proportions present in hydroxyapatite, silicon is present only at the detection limit; the more "mature" the bone mineral the smaller the amount of measurable silicon. Concomitantly maximum amounts of silicon are present at molar ratios of calcium to phosphorus of approximately 0.7, but at ratios of calcium to phosphorus approaching that of hydroxyapatite silicon again falls below the detection limit.

To carry out a study involving quantitative analysis for and precise location of trace elements in biological tissue sections, unusual precautions must be taken to avoid contamination, redistribution, or removal of the elements. This prerequisite cannot be emphasized too strongly in the case of an element such as silicon which is so abundant in the environment (*1*). Modified histological specimen procedures used were (i) freeze-drying and embedding in polymer, (ii) vacuum drying and embedding in polymer, (iii) hand polishing of freeze- and vacuum-dried embedded slices with materials free of silicon, (iv) cryostat cutting with subsequent freeze-drying, and (v) fixation in absolute alcohol and embedding in paraffin. The comparison standard for quantitative electron microprobe analysis was a natural apatite for which a distinctly superior analysis of major and minor elements is available (*2*). There was no measurable wavelength shift between the specimen and the standard. Sequential quantitative analyses

E. Carlisle, Science 1970



3ml/min,
room temperature

0.297~0.217M
H_3PO_4
100ml

0.500M $Ca(OH)_2$
+
0~80mM
$Si(CH_3COO)_4$
pH10.5
100ml

Ageing under stirring, 15h

Washing

Drying, 80°C

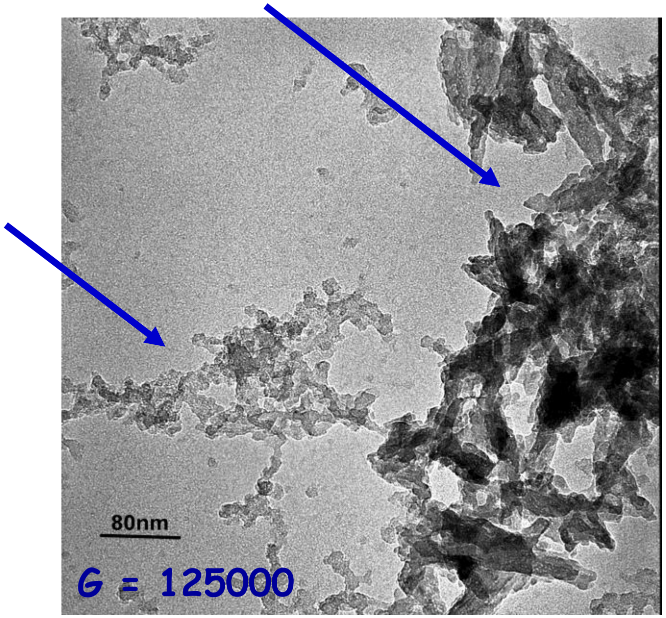
silicate substituted HAp:

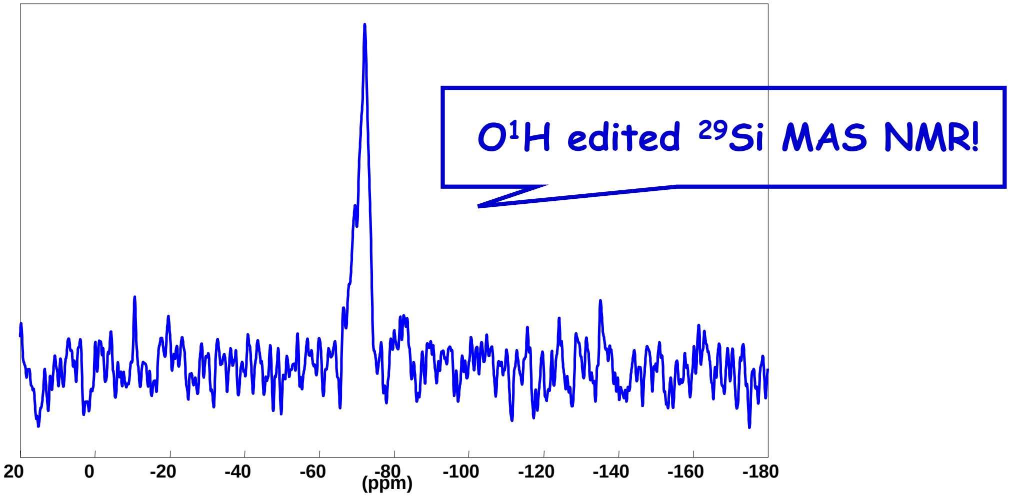
a synthetic approach (4.8 wt. %)

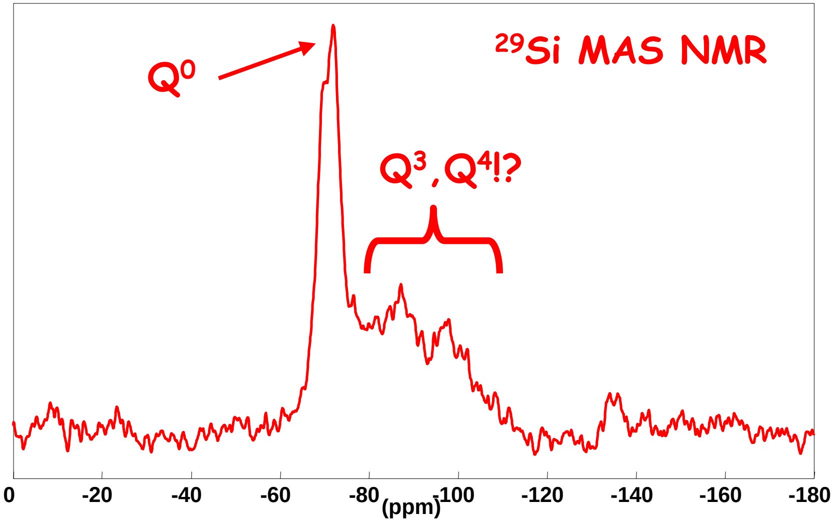
G. Gasquères

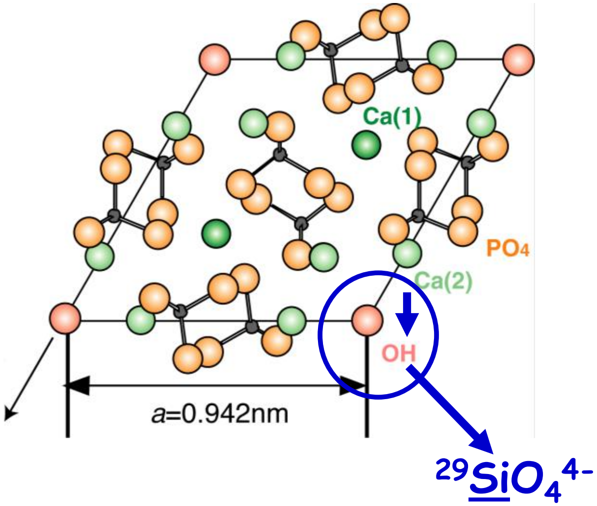
S. Hayakawa

Structural characterization



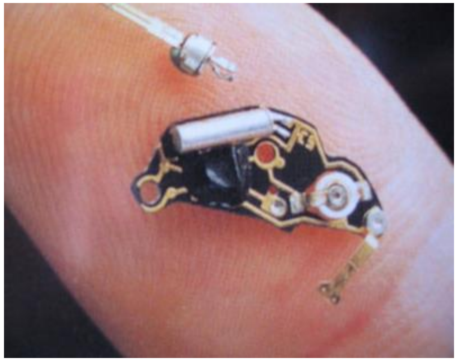




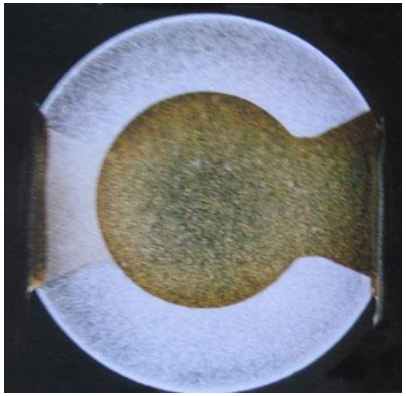


SiO_2 applications

«quartz clock»: piezoelectricity



W. Morrison 1929!



birefringency

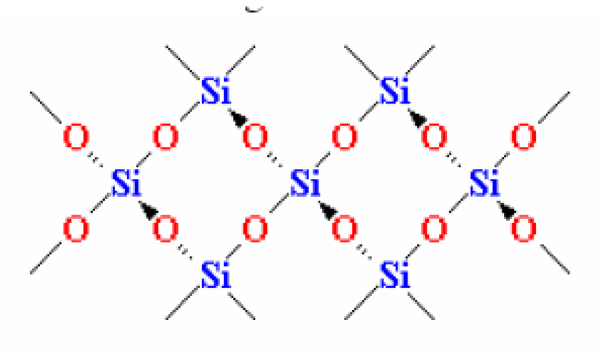
tensorial properties

silica wire

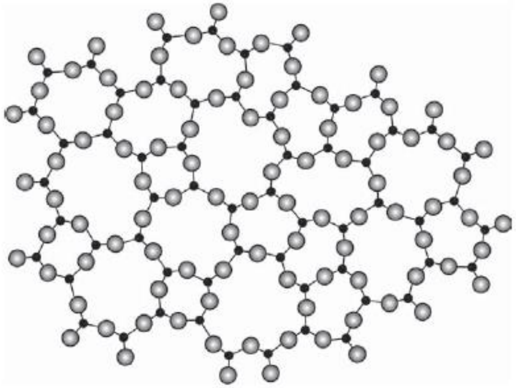
T ~ 1000°C

Glass

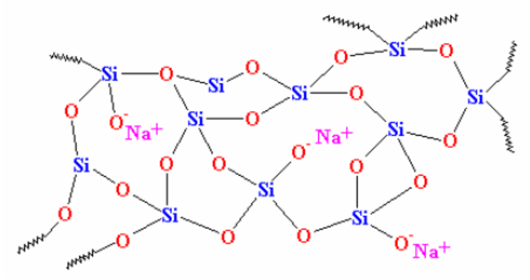
Glass structure



crystalline phase



glass



PILKINGTON

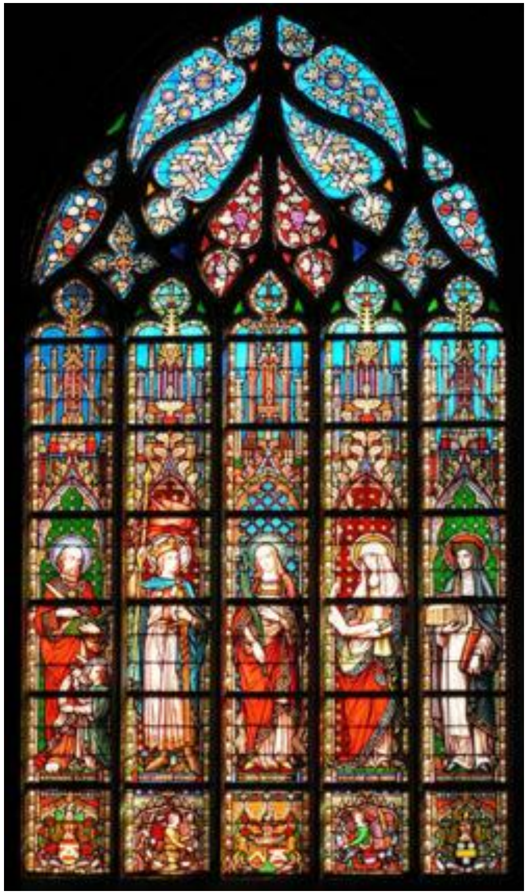
SAINT-GOBAIN

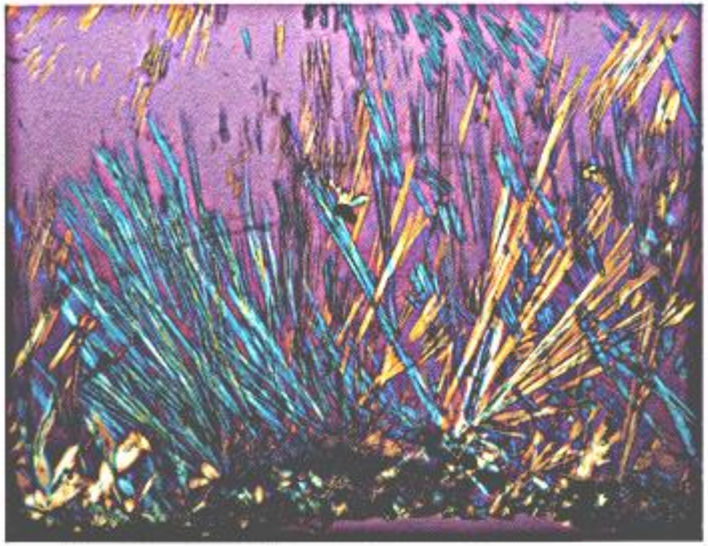
The **future** of individual architecture
starts with SCHOTT **today**
▶ **more**

colored glass

Cyclotella meneghiniana

Devitrification of glasses



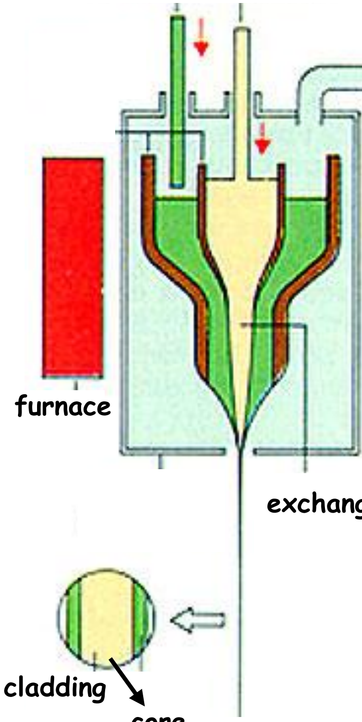


microcrystals in glass

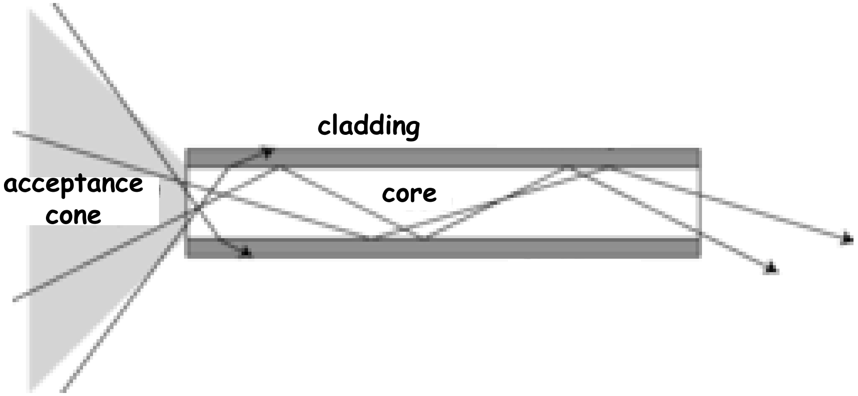
devitrified glass (by heating)

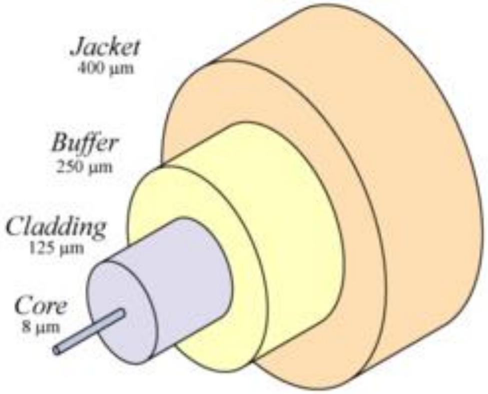
Fibers

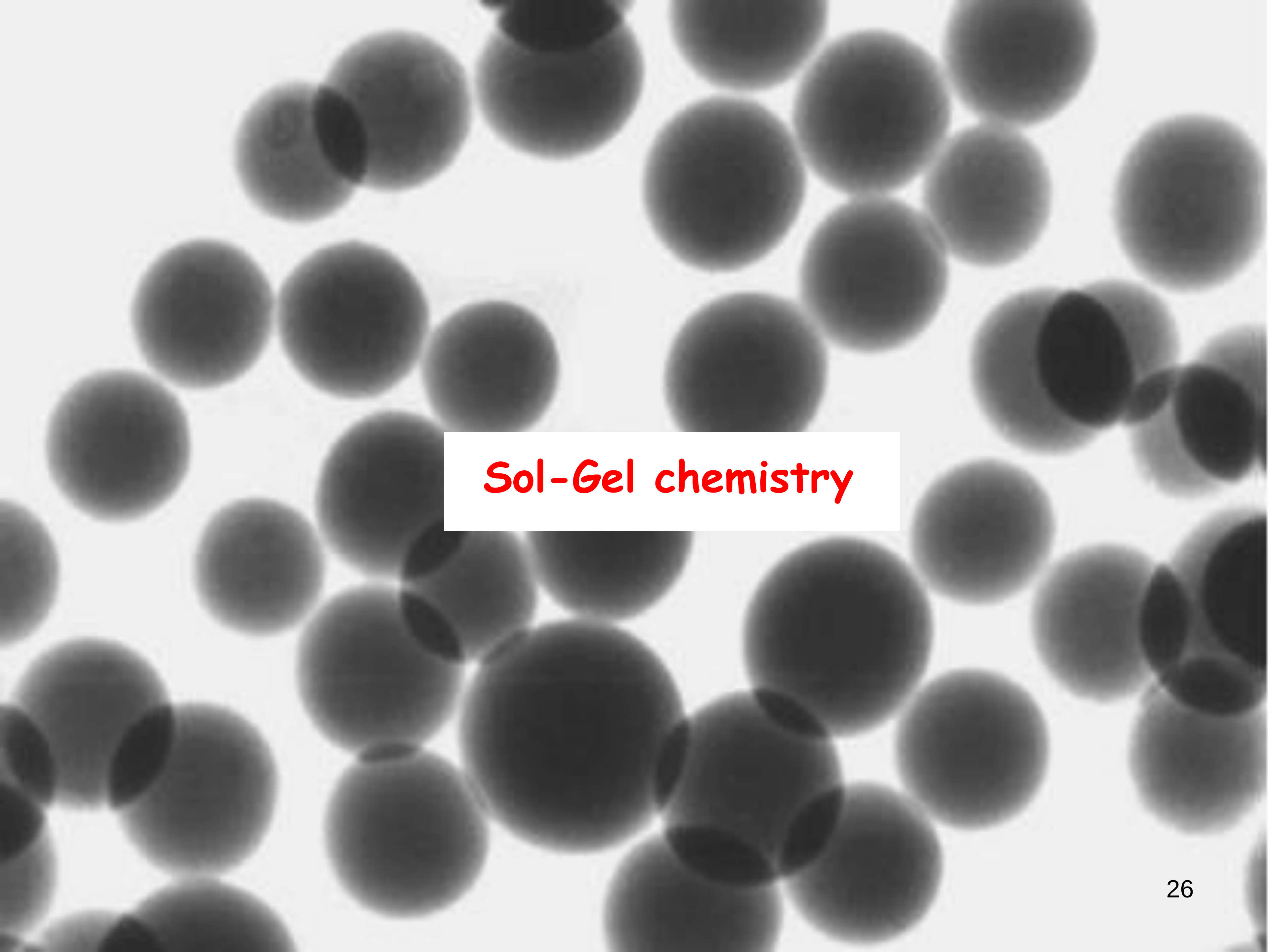
optical fibers



bundle of fiberglass

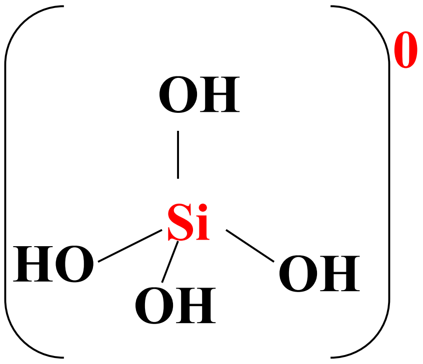






Sol-Gel chemistry

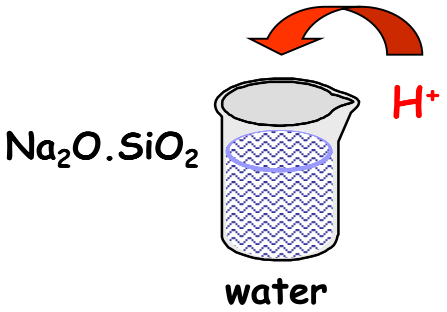
Silicic acid

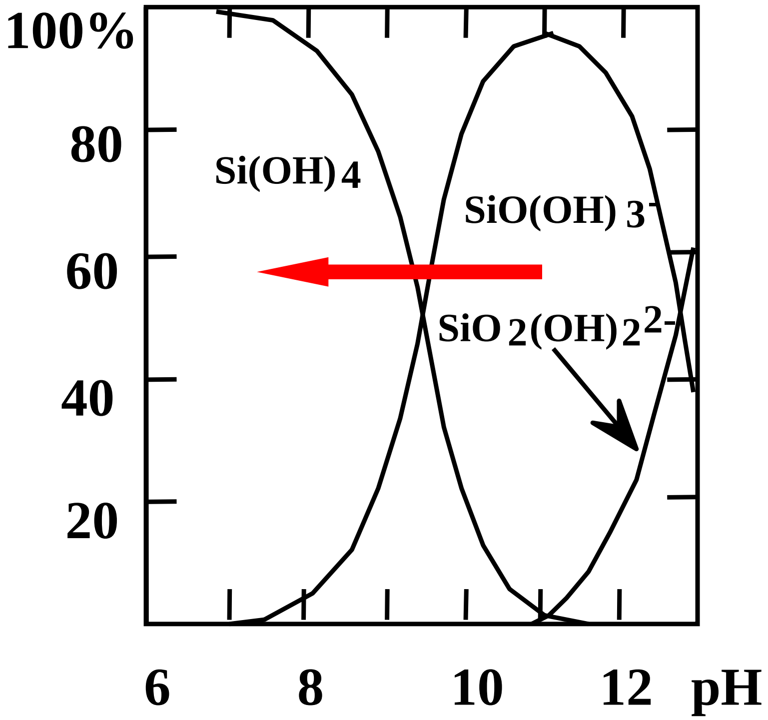


a weak acid

precipitation of silica

silica is soluble at high pH: *silicates*





speciation

Inorganic polymerization

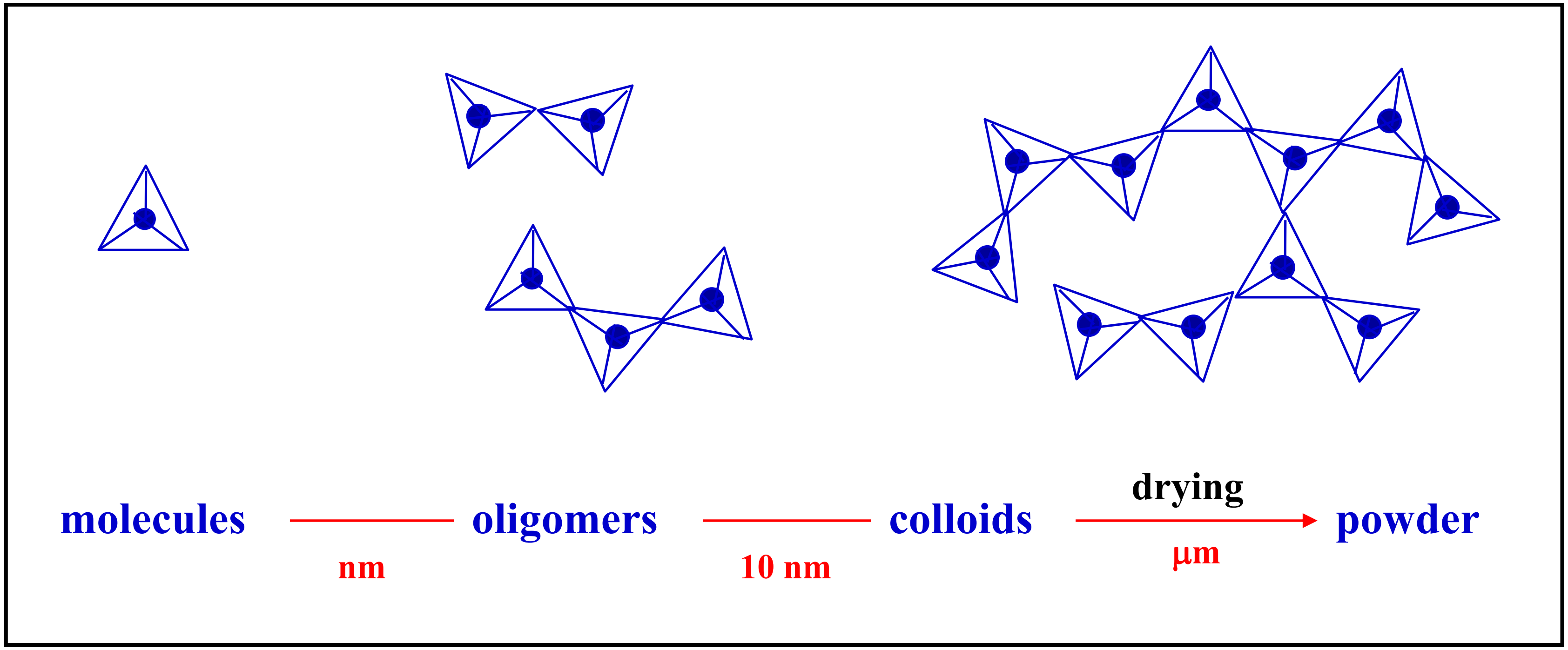
$SiO_3(OH)^{3-}$

$SiO_2(OH)_2^{2-}$

$SiO(OH)_3^-$

$Si(OH)_4$

silica



molecules

nm

oligomers

10 nm

colloids

drying

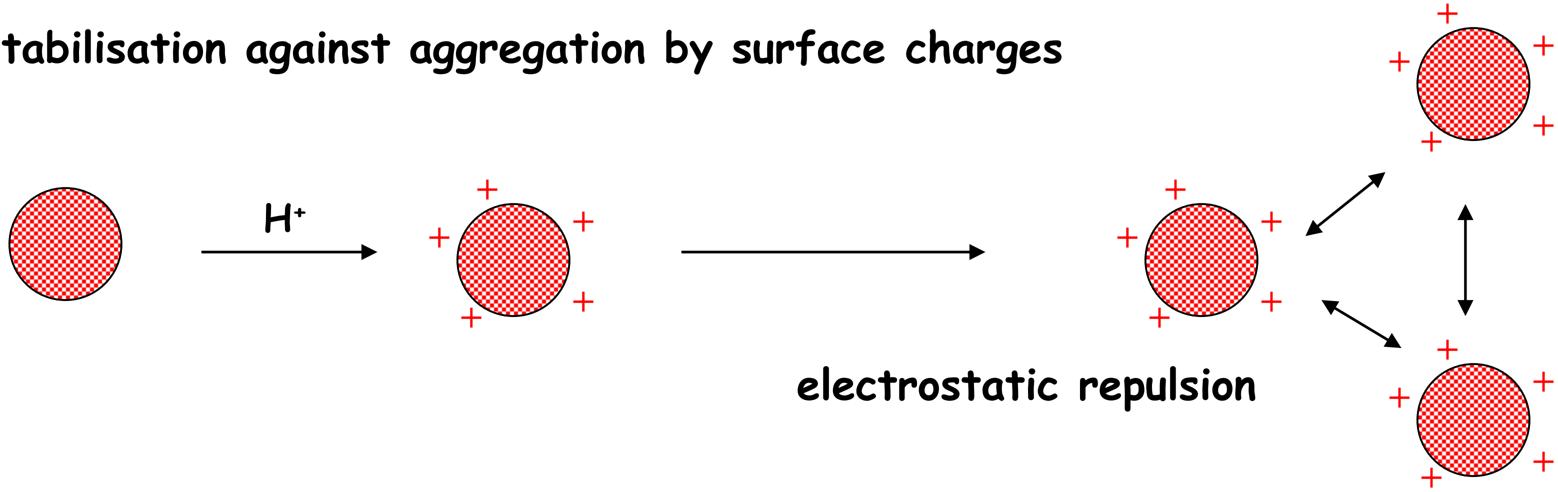
μm

powder

colloidal silica particles

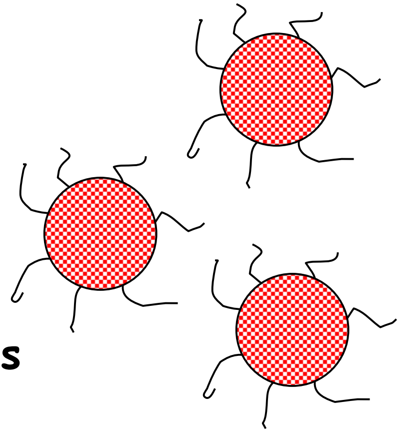
Stabilization of colloids

stabilisation against aggregation by surface charges



electrostatic repulsion

stabilisation by steric hindrance



grafted polymers

Precipited silica

- industrial product: charge, chromatography,...
- amazing chemistry!

Rhodia

degussa.

ÉTUDES DE BIOPHYSIQUE

LA BIOLOGIE
SYNTHÉTIQUE

PAR

STÉPHANE LEDUC

PROFESSEUR A L'ÉCOLE DE MÉDECINE DE NANTES

AVEC 118 FIGURES DANS LE TEXTE

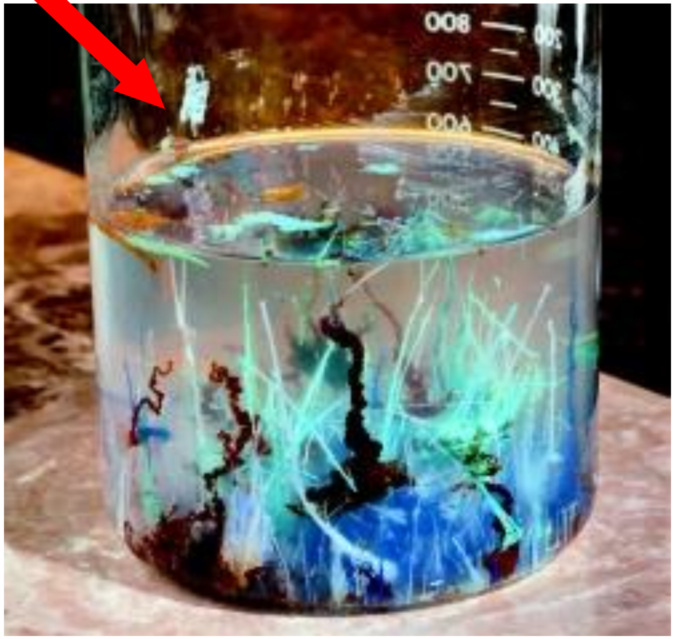
A. POINAT, ÉDITEUR
121, BOULEVARD SAINT-MICHEL PARIS
1912

silicates

$CuSO_4$

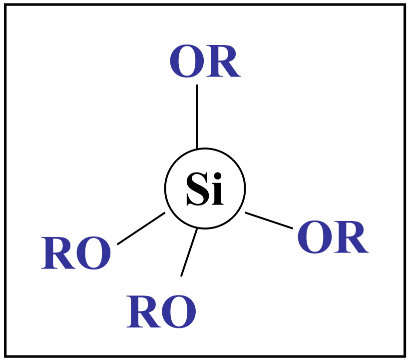
$FeCl_3$ $Ni(NO_3)_2$

metal salts

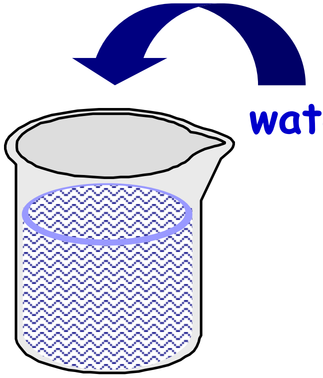


Silicon alcoxides

molecular precursor



R = CH_3, C_2H_5, ...

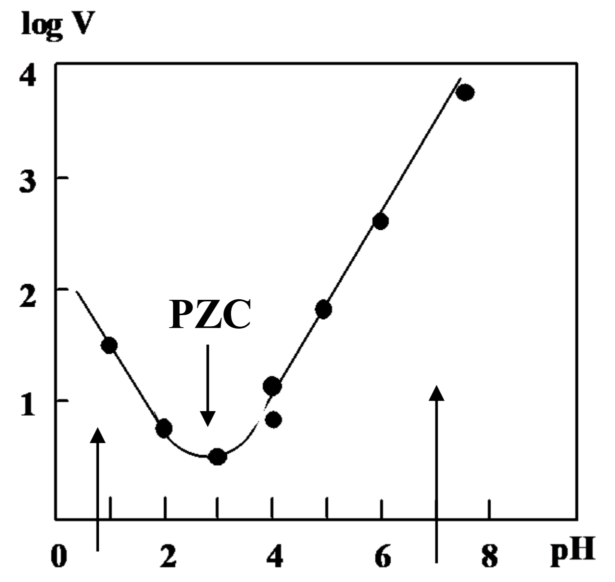


water

alcoxide

hydrolysis
Si-OH bonds

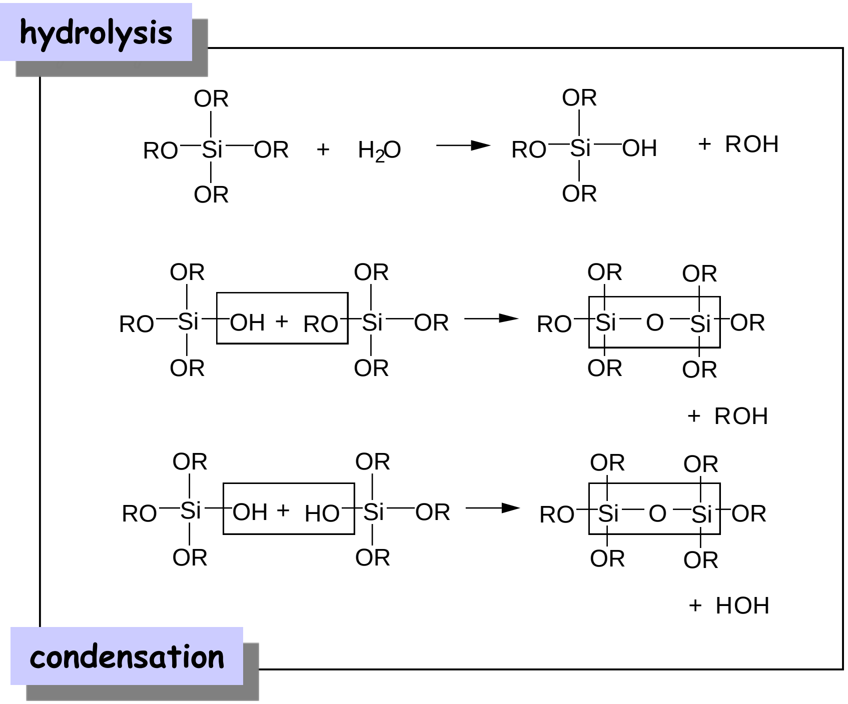
condensation
Si-O-Si bonds



acid catalysis base catalysis

Sol-Gel chemistry

inorganic polymerization



hydrolysis

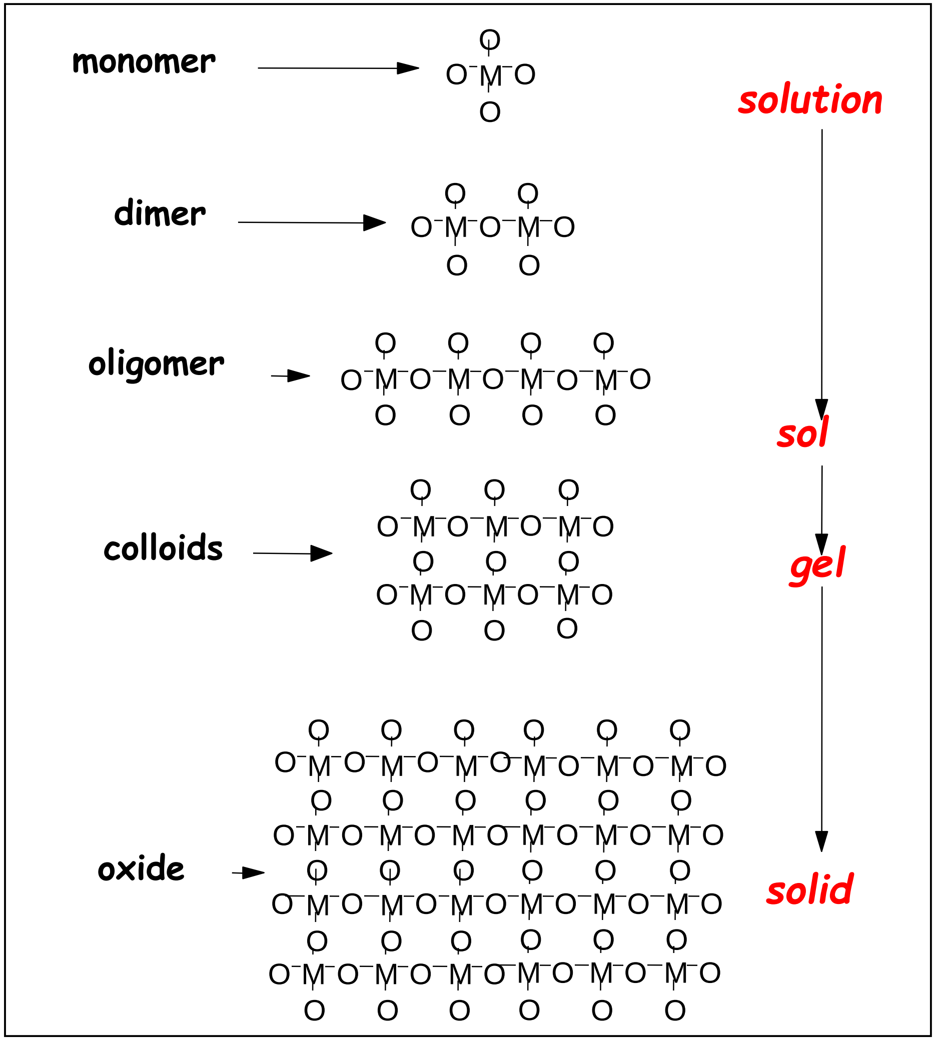
$$\mathrm{RO{-}\overset{OR}{\underset{OR}{Si}}{-}OR} + H_2O \rightarrow \mathrm{RO{-}\overset{OR}{\underset{OR}{Si}}{-}OH} + ROH$$

$$\mathrm{RO{-}\overset{OR}{\underset{OR}{Si}}{-}\boxed{OH + RO}{-}\overset{OR}{\underset{OR}{Si}}{-}OR} \rightarrow \mathrm{RO{-}\boxed{\overset{OR}{\underset{OR}{Si}}{-}O{-}\overset{OR}{\underset{OR}{Si}}}{-}OR} + ROH$$

$$\mathrm{RO{-}\overset{OR}{\underset{OR}{Si}}{-}\boxed{OH + HO}{-}\overset{OR}{\underset{OR}{Si}}{-}OR} \rightarrow \mathrm{RO{-}\boxed{\overset{OR}{\underset{OR}{Si}}{-}O{-}\overset{OR}{\underset{OR}{Si}}}{-}OR} + HOH$$

condensation

chemistry of materials oxides

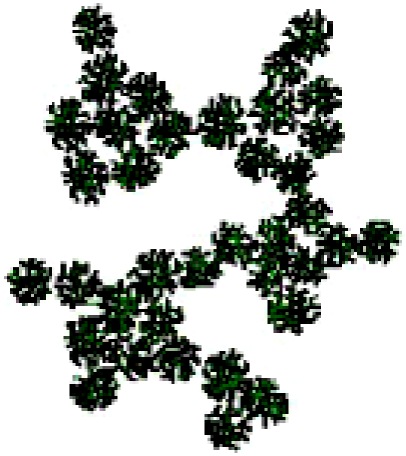


The role of catalysis

- Acid-catalyzed
  - yield primarily linear or randomly branched polymer

fibers

nanoparticles



- Base-catalyzed
  - yield highly branched clusters

Control of the shape

acid catalysis (pH < 3) – route A

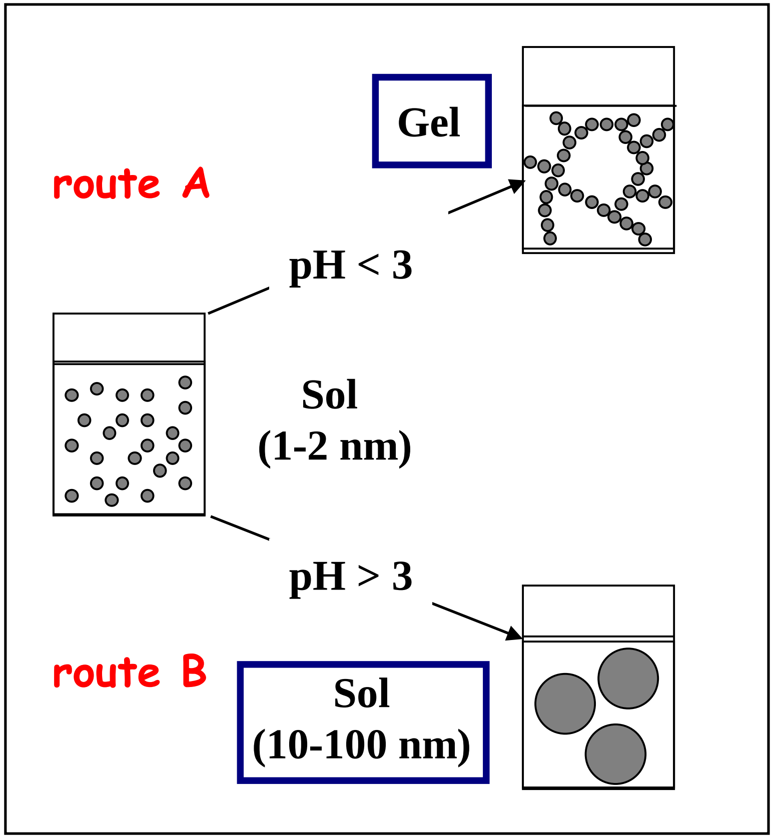
chain polymers

microporous gels (pores < 20Å)

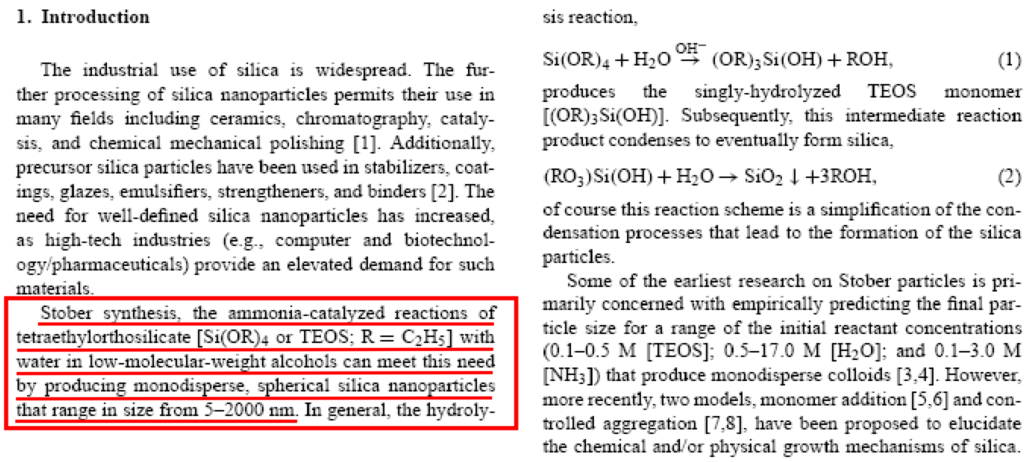
base catalysis (pH >3) – route B

spherical particles (Stöber silica)

mesoporous gels (pores > 20Å)



Stöber silica



1. Introduction

The industrial use of silica is widespread. The further processing of silica nanoparticles permits their use in many fields including ceramics, chromatography, catalysis, and chemical mechanical polishing [1]. Additionally, precursor silica particles have been used in stabilizers, coatings, glazes, emulsifiers, strengtheners, and binders [2]. The need for well-defined silica nanoparticles has increased, as high-tech industries (e.g., computer and biotechnology/pharmaceuticals) provide an elevated demand for such materials.

Stober synthesis, the ammonia-catalyzed reactions of tetraethylorthosilicate [Si(OR)$_4$ or TEOS; R = C_2H_5] with water in low-molecular-weight alcohols can meet this need by producing monodisperse, spherical silica nanoparticles that range in size from 5–2000 nm. In general, the hydrolysis reaction,

$$Si(OR)_4 + H_2O \xrightarrow{OH^-} (OR)_3Si(OH) + ROH, \quad (1)$$

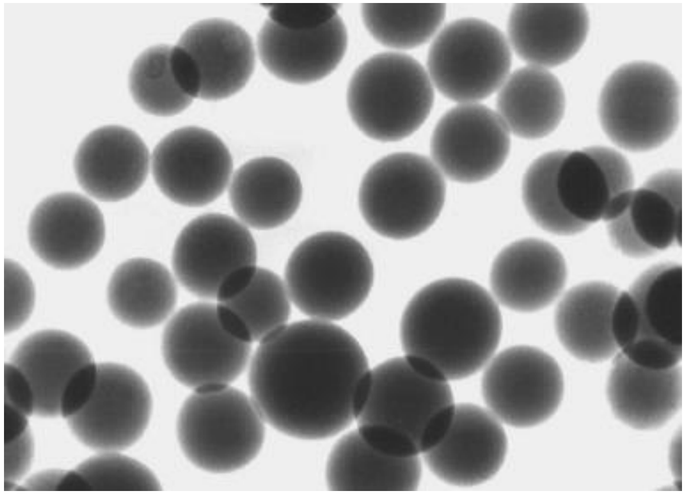
produces the singly-hydrolyzed TEOS monomer [(OR)$_3$Si(OH)]. Subsequently, this intermediate reaction product condenses to eventually form silica,

$$(RO_3)Si(OH) + H_2O \rightarrow SiO_2 \downarrow + 3ROH, \quad (2)$$

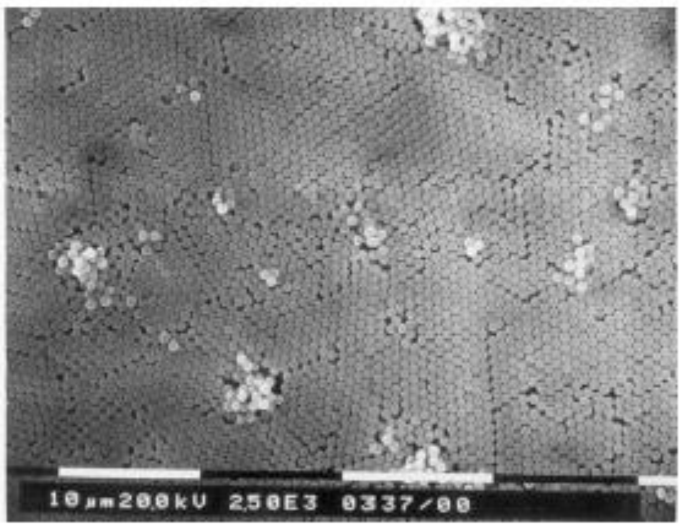
of course this reaction scheme is a simplification of the condensation processes that lead to the formation of the silica particles.

Some of the earliest research on Stober particles is primarily concerned with empirically predicting the final particle size for a range of the initial reactant concentrations (0.1–0.5 M [TEOS]; 0.5–17.0 M [H_2O]; and 0.1–3.0 M [NH_3]) that produce monodisperse colloids [3,4]. However, more recently, two models, monomer addition [5,6] and controlled aggregation [7,8], have been proposed to elucidate the chemical and/or physical growth mechanisms of silica.

Stöber, 1968

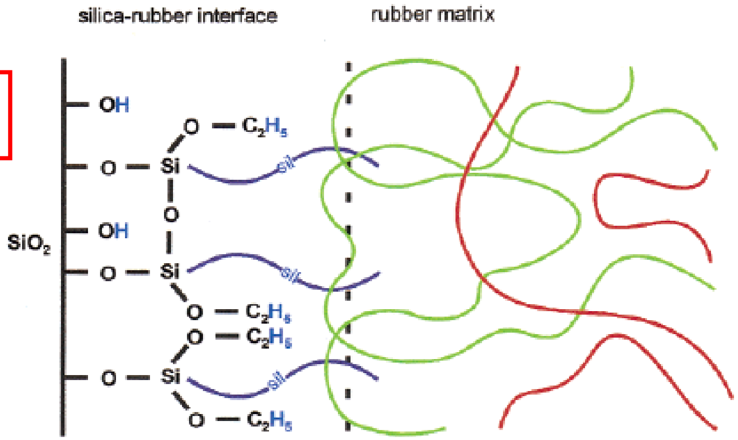


monodispersed silica colloids



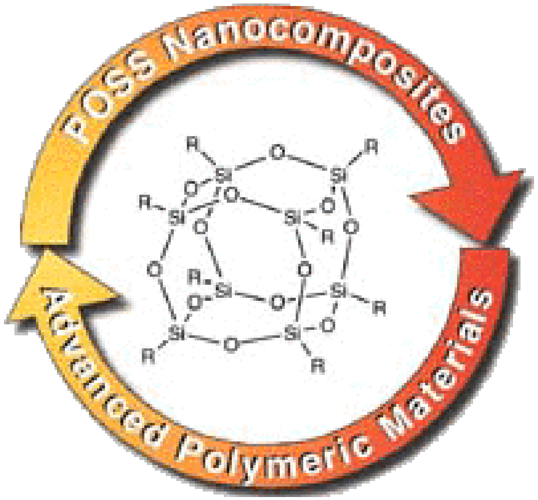
Stöber silica monolayer

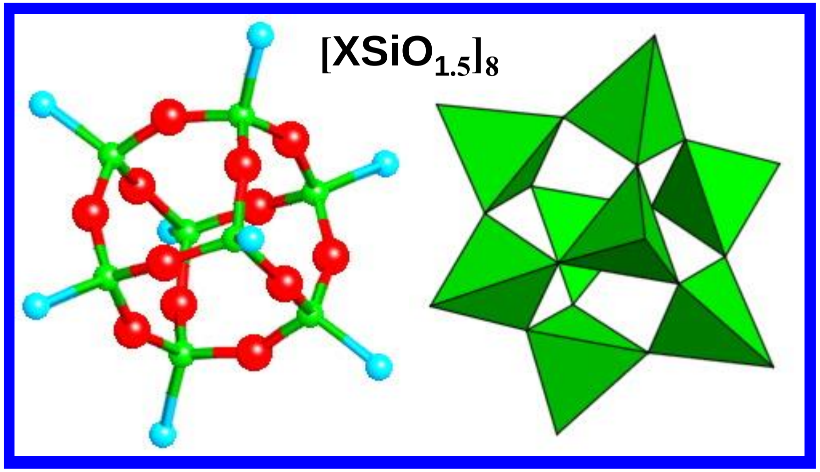
5-2000 nm



interaction between Stöber silica and rubber

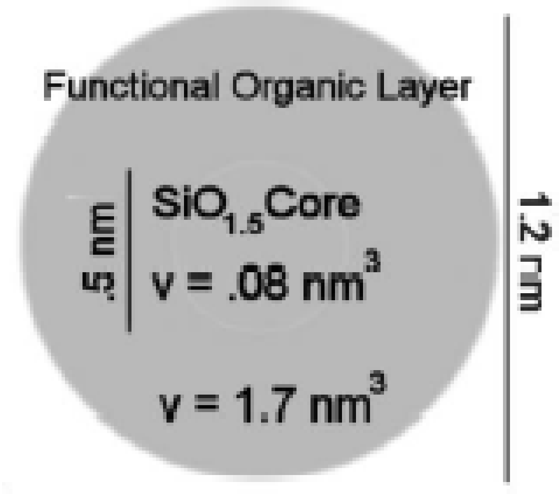
Silsesquioxanes



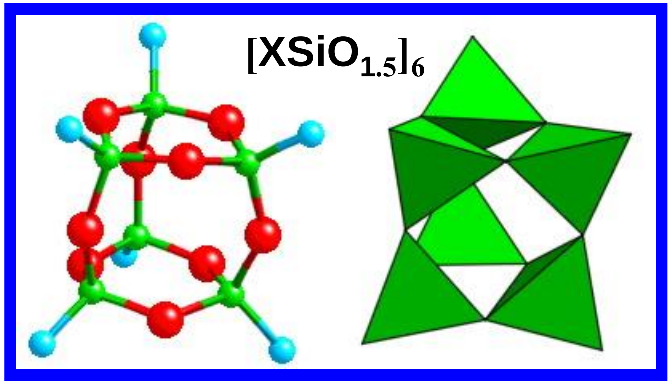


$[\ RSiO_{1.5}\ ]_n$

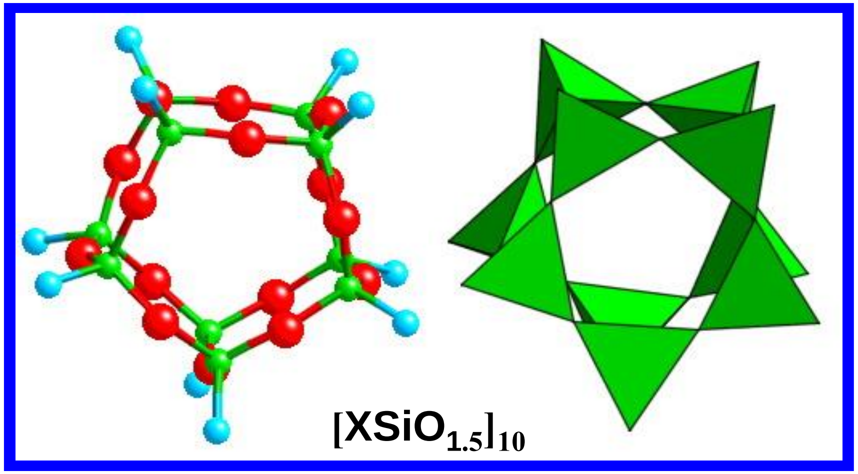
Polyhedral Oligomeric SilSesquioxanes



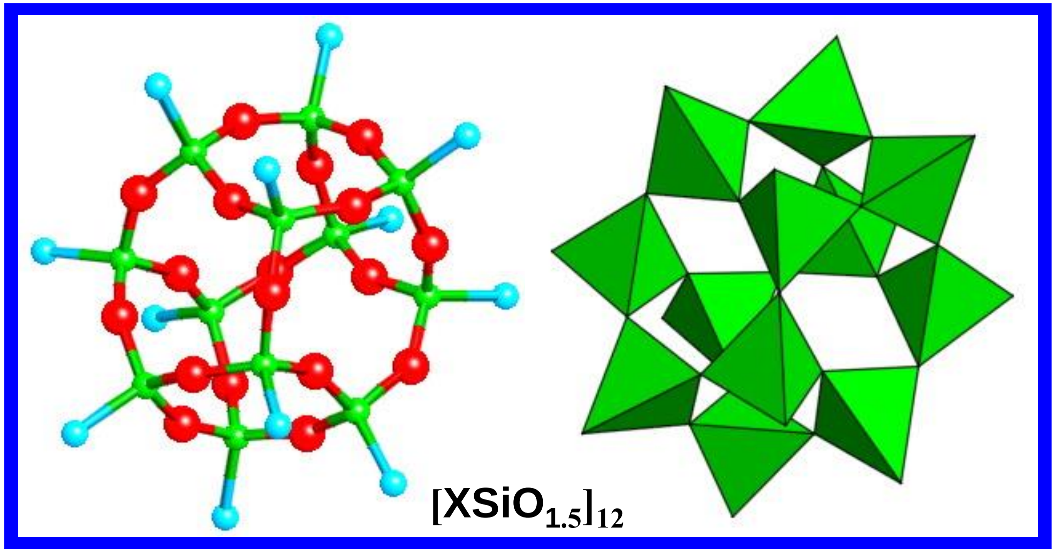
Other silsesquioxanes



$[XSiO_{1.5}]_6$



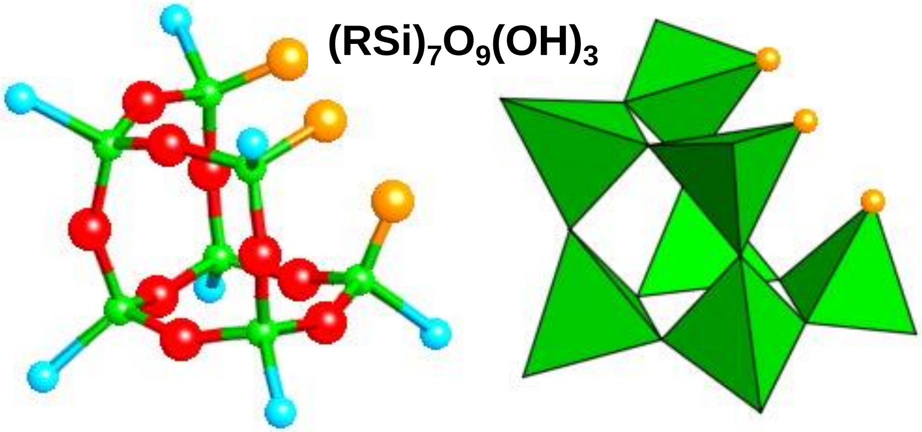
$[XSiO_{1.5}]_{10}$



$[XSiO_{1.5}]_{12}$

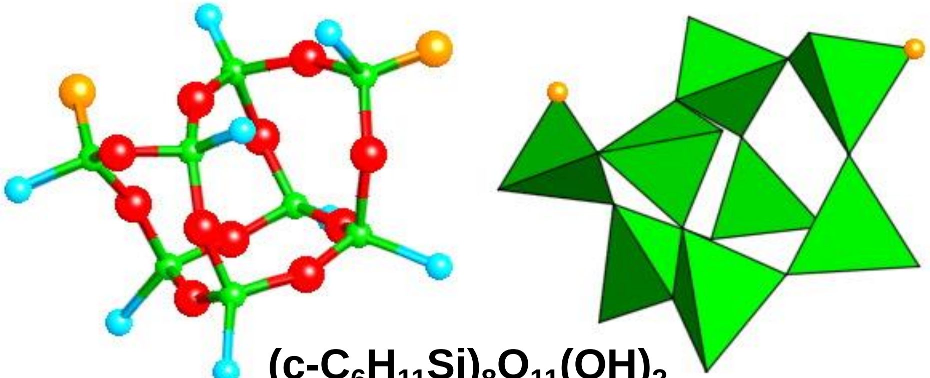
Courtesy of F. Ribot

Incomplete POSS



$(RSi)_7O_9(OH)_3$

R = c-C_5H_9, c-C_6H_{11}, c-C_7H_{13}, Bu^i



$(c\text{-}C_6H_{11}Si)_8O_{11}(OH)_2$

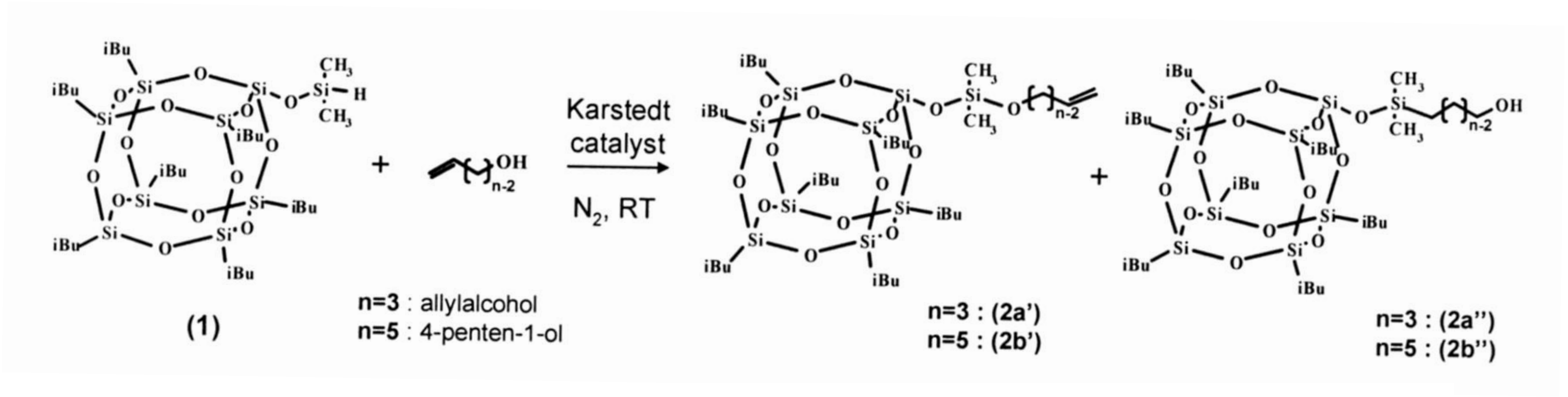
Courtesy of F. Ribot

Chemistry and silsesquioxanes

Modification and Characterization of Si-Based Nanobuilding Blocks Precursors for Hybrid Materials

F. Mammeri, 2005

Fayna Mammeri [1], Najiba Douja [1], Christian Bonhomme [2], François Ribot [2],
Florence Babonneau [2] and Sandra Dirè [1]
[1] Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali,
Università di Trento, Via Mesiano 77, 38050 Trento, Italy
[2] Laboratoire de Chimie de la Matière Condensée, UMR-CNRS 7574,
Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France

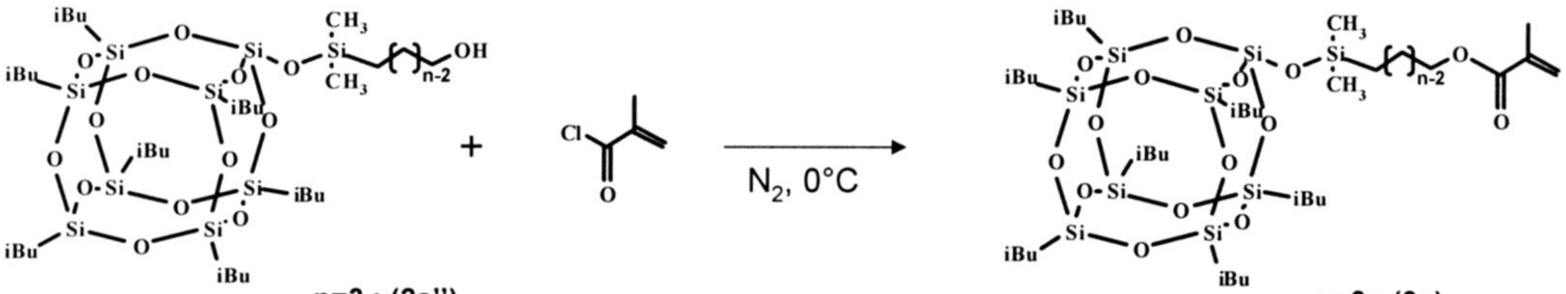


(1)

n=3 : allylalcohol
n=5 : 4-penten-1-ol

n=3 : (2a')
n=5 : (2b')

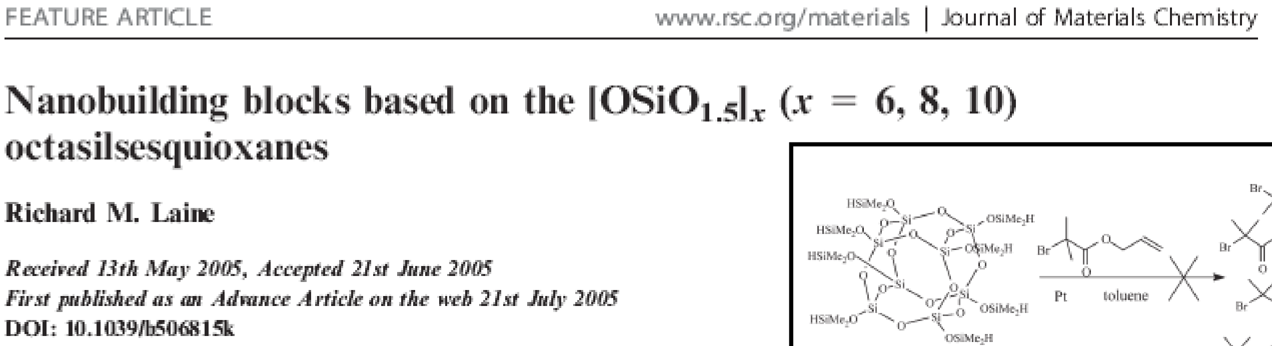
n=3 : (2a'')
n=5 : (2b'')



n=3 : (2a'')
n=5 : (2b'')

n=3 : (3a)
n=5 : (3b)

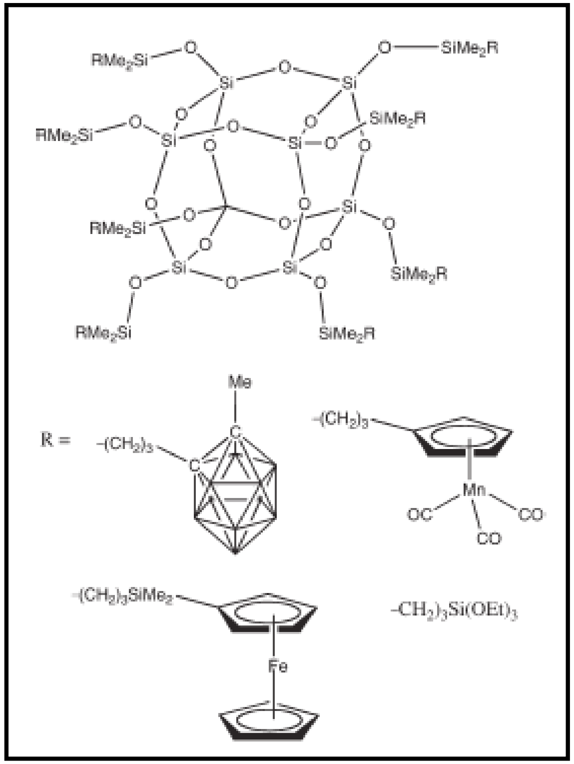
Modified silsesquioxanes



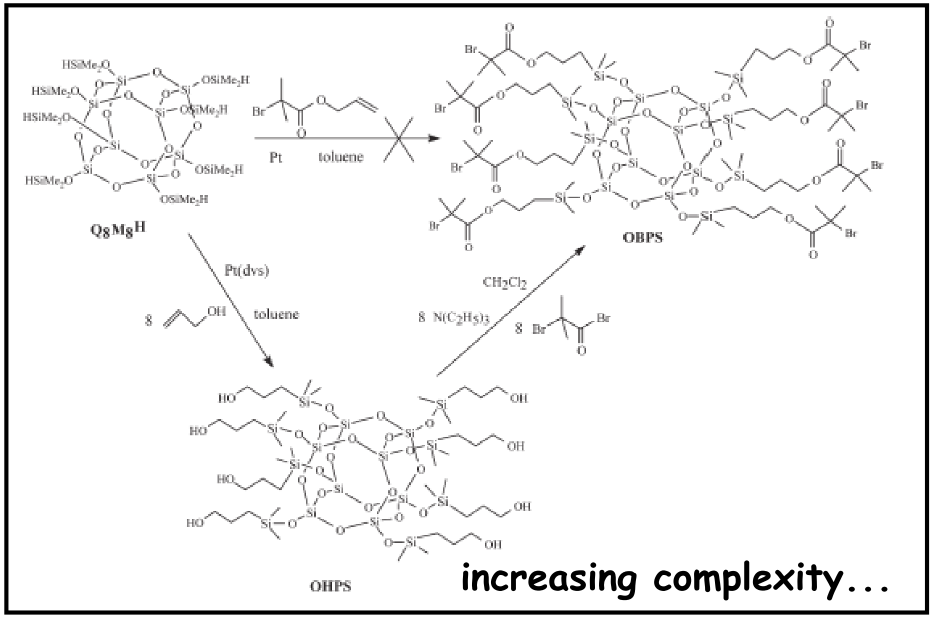
Nanobuilding blocks based on the $[OSiO_{1.5}]_x$ (x = 6, 8, 10) octasilsesquioxanes

Richard M. Laine

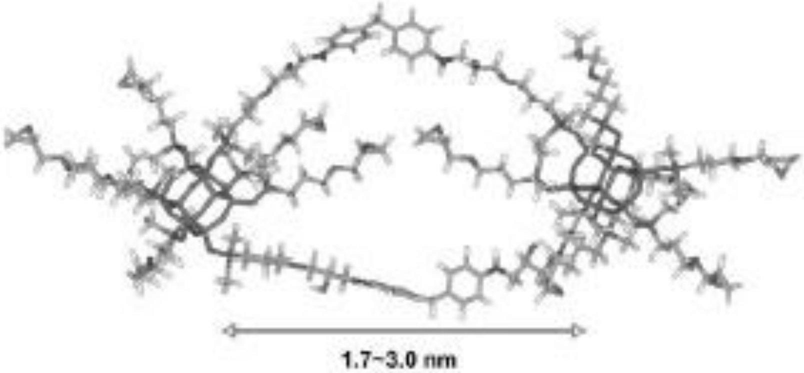
Received 13th May 2005, Accepted 21st June 2005
First published as an Advance Article on the web 21st July 2005
DOI: 10.1039/b506815k



...obtained by hydrosilylation

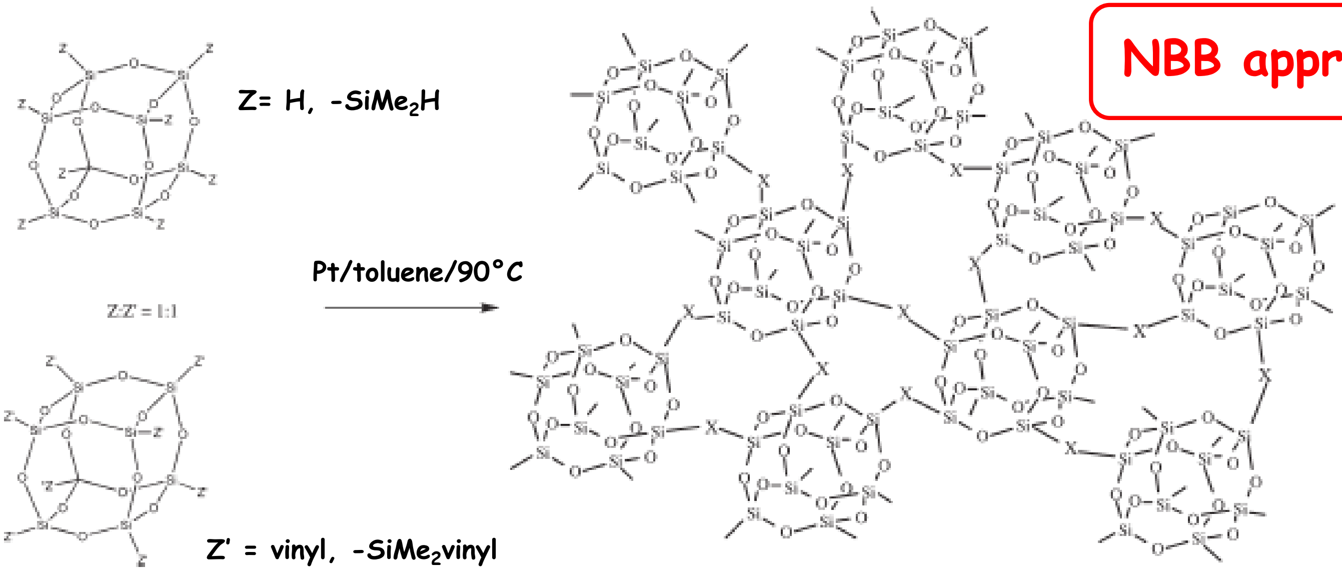


increasing complexity...



molecular modeling

Silsesquioxanes as NanoBuildingBlocks (NBB)



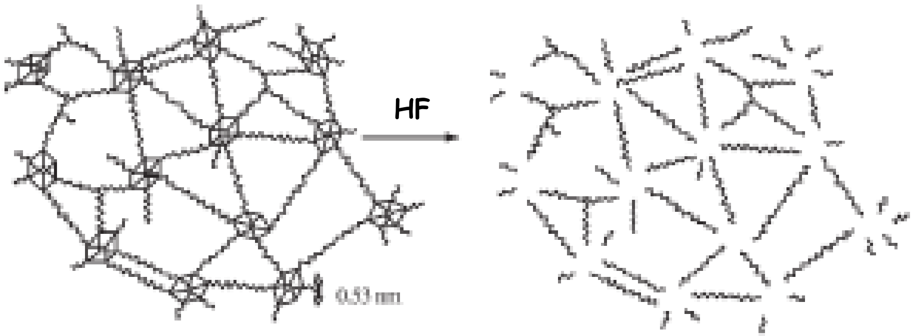
Z= H, $-SiMe_2H$

Pt/toluene/90°C

Z' = vinyl, $-SiMe_2vinyl$

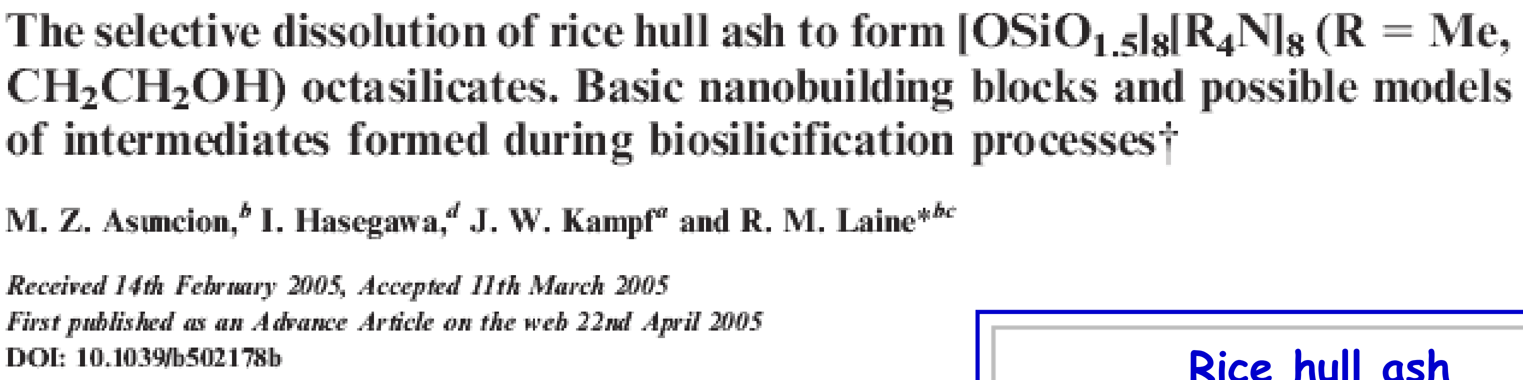
NBB approach

R. Laine, 1998



HF dissolution

Starting from natural materials



The selective dissolution of rice hull ash to form $[OSiO_{1.5}]_8[R_4N]_8$ (R = Me, CH_2CH_2OH) octasilicates. Basic nanobuilding blocks and possible models of intermediates formed during biosilicification processes†

M. Z. Asuncion,[b] I. Hasegawa,[d] J. W. Kampf[a] and R. M. Laine*[bc]

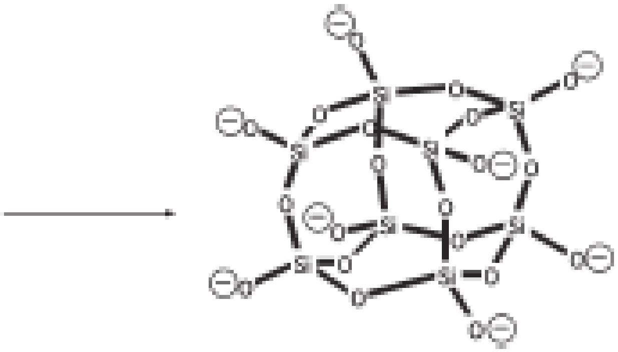
Received 14th February 2005, Accepted 11th March 2005
First published as an Advance Article on the web 22nd April 2005
DOI: 10.1039/b502178b

Rice hull ash

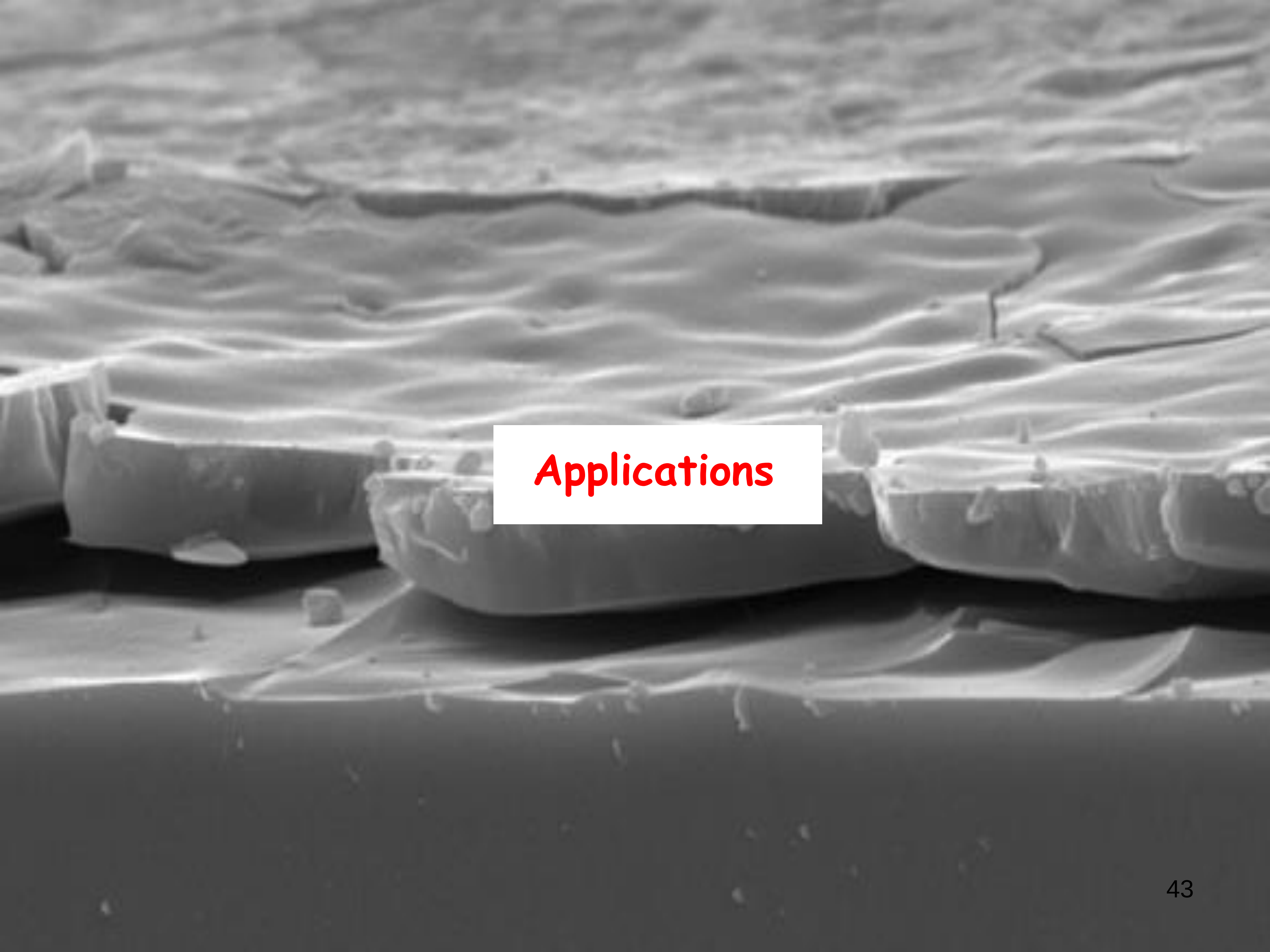
80-98 wt % amorphous silica!

Rice hull ash

8 $R_4N^+OH^-$



$[R_4N^+]_8$



Applications

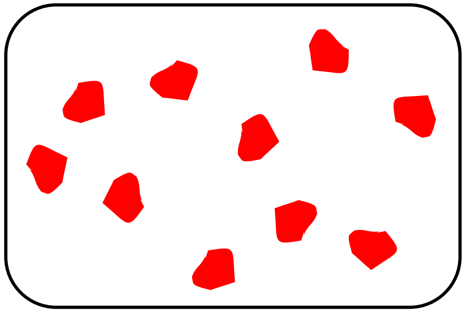
Hybrid organic-inorganic materials

organic component (molecules, polymers, …)

inorganic component (M-O-M, …)

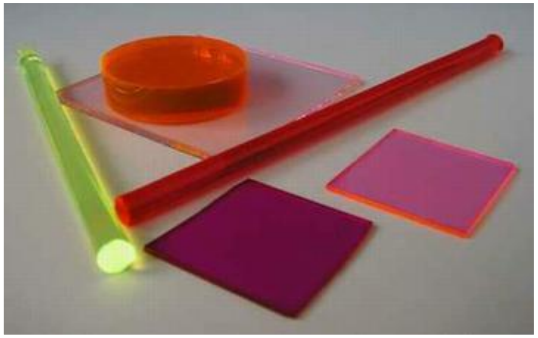
intimate "mixture"
(domain sizes from 1 to 100 nm)

hybrid organic-inorganic materials
(nano-composites)



infinite range

chemist's imagination and hability



nanometric oxide particles in a polymer

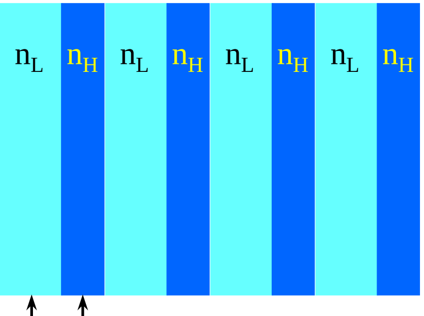
organic dyes in a glass

Organic dyes and laser materials

- any organic dye can be embedded
- more resistant than in solution
- large pieces
- materials can be polished (optical quality)

© F. Chaput, PMC - Ecole polytechnique

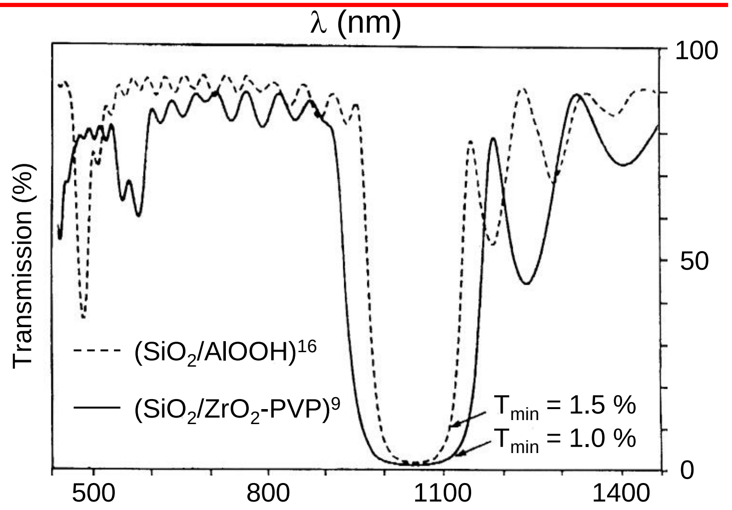
Dip-coating: reflective coatings

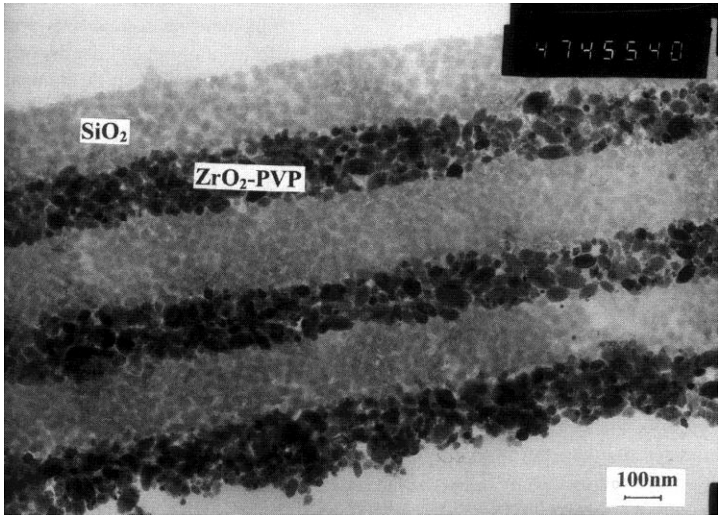


ZrO_2 + PVP (20%) ⇒ $n_H = 1.72$

$SiO_2 \Rightarrow n_L = 1.22$

$$R = \left[\frac{\left(\frac{n_H}{n_L}\right)^{2N} - 1}{\left(\frac{n_H}{n_L}\right)^{2N} + 1} \right]^2$$



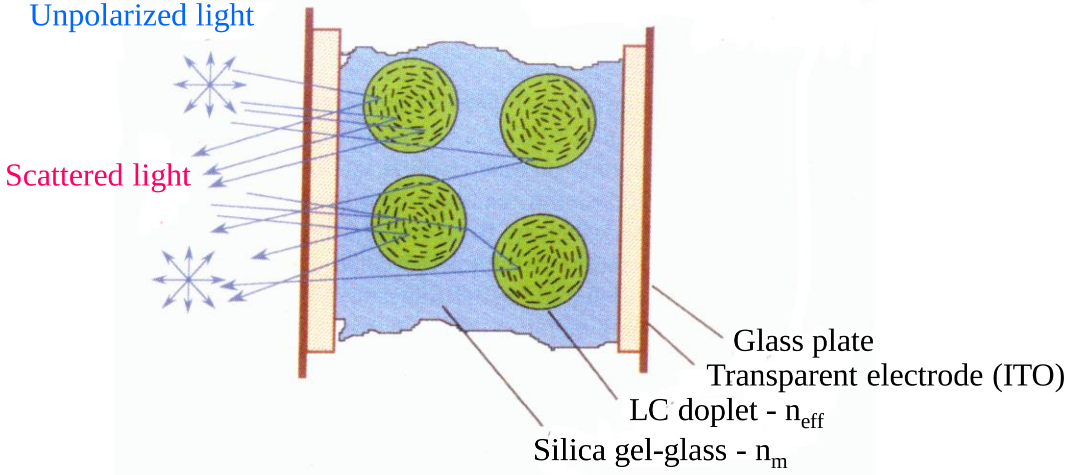


©CEA - France

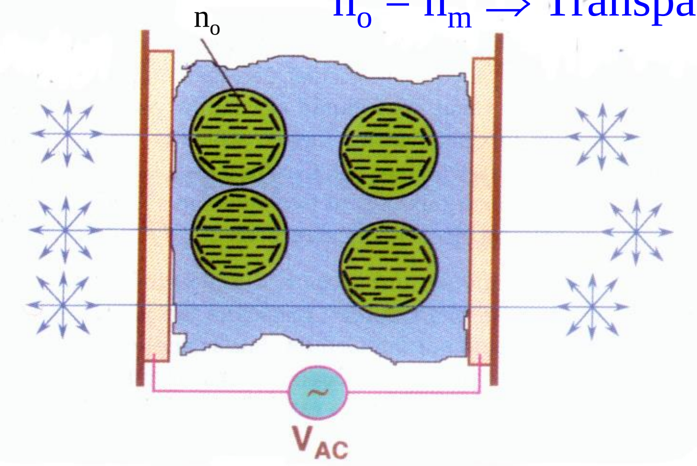
Electrooptical switching

encapsulation of liquid crystal microdroplets in a thin film

$n_{eff} \neq n_m \Rightarrow$ Opaque (OFF state)



$n_o = n_m \Rightarrow$ Transparent (ON state)



© Saint-Gobain - France

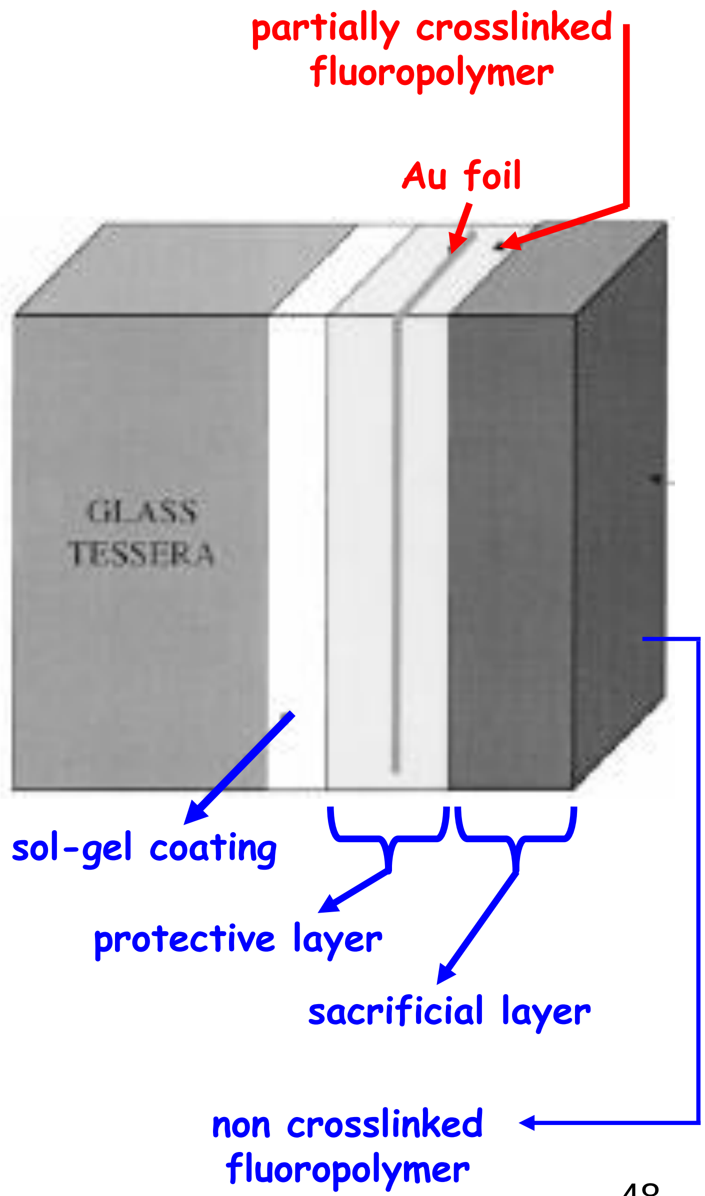
Sol-Gel coatings and long-term protection

art conservation: organic polymers vs inorganic coatings...

desirable properties

- thermal expansion match with the glass
- low diffusion coefficients for SO_2 and H_2O gases
- transparency
- chemical bonding to the glass surface
- longevity/UV resistance
- possibility of inserting a gold foil within the coating
- option to remove and re-apply the coating if necessary

→ multilayer coatings



Last Judgment Mosaic in Prague

before cleaning

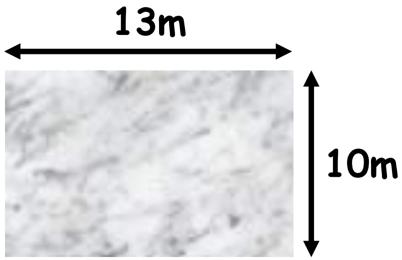
after cleaning

after regilding

Bescher *et al.* 2000

Getty Conservation Institute

St. Vitus cathedral
(14th century)



1 million pieces of tesserae in mortar

www.getty.edu/conservation

Water, hydrophobicity and hydrophilicity

hydrophobic / hydrophilic

descriptors of surfaces

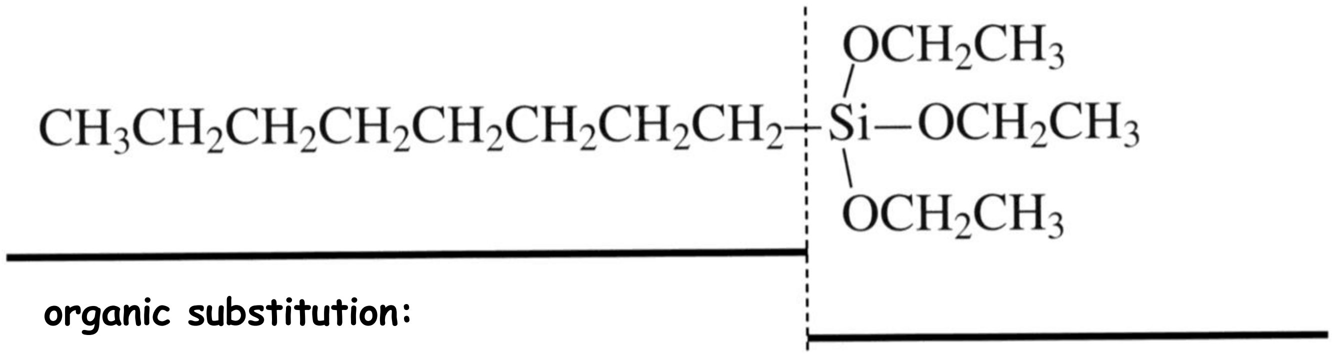
a hydrophobic surface tends *not to adsorb water* or be wetted by water

a hydrophilic surface tends *to adsorb water* or be wetted by water

silanes and surface modification

$\underbrace{R–Si}–(OR')_3$

C–Si bond!



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2–Si(OCH_2CH_3)_3$$

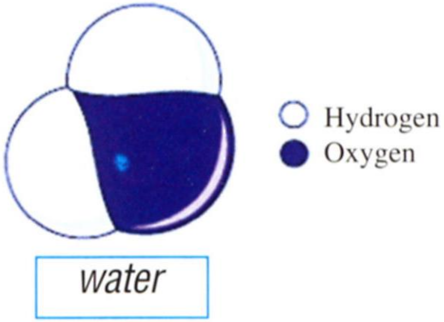
organic substitution:

- properties
- reactivity

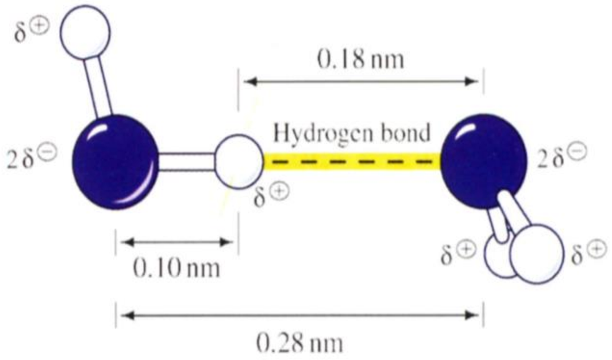
alkoxy groups:

- hydrolysis / condensation
- surface modification

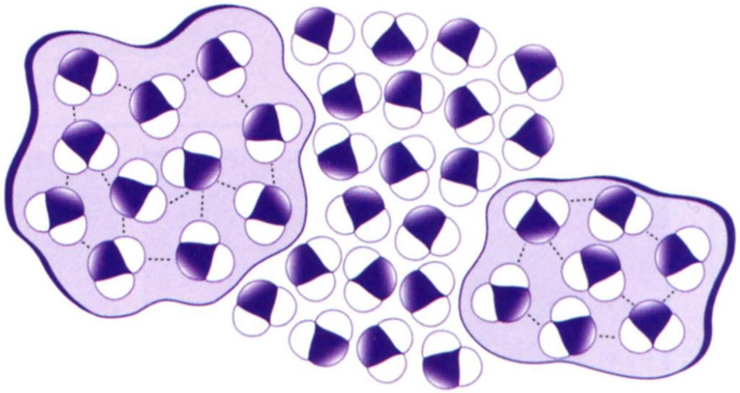
Water: an «universal» solvant



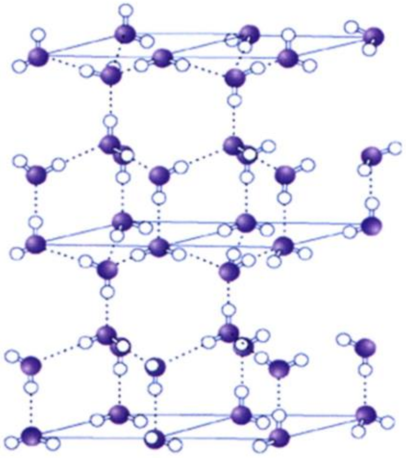
a dipolar molecule



hydrogen bond ~ 20 $kJ.mol^{-1}$



liquid water: the strong influence of *hydrogen bond* interactions



molecules of water in ice

Wettability and contact angle

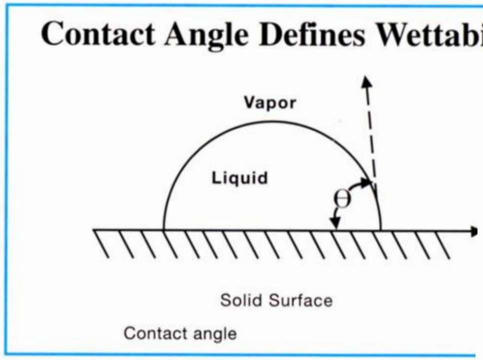
a simple quantitative method

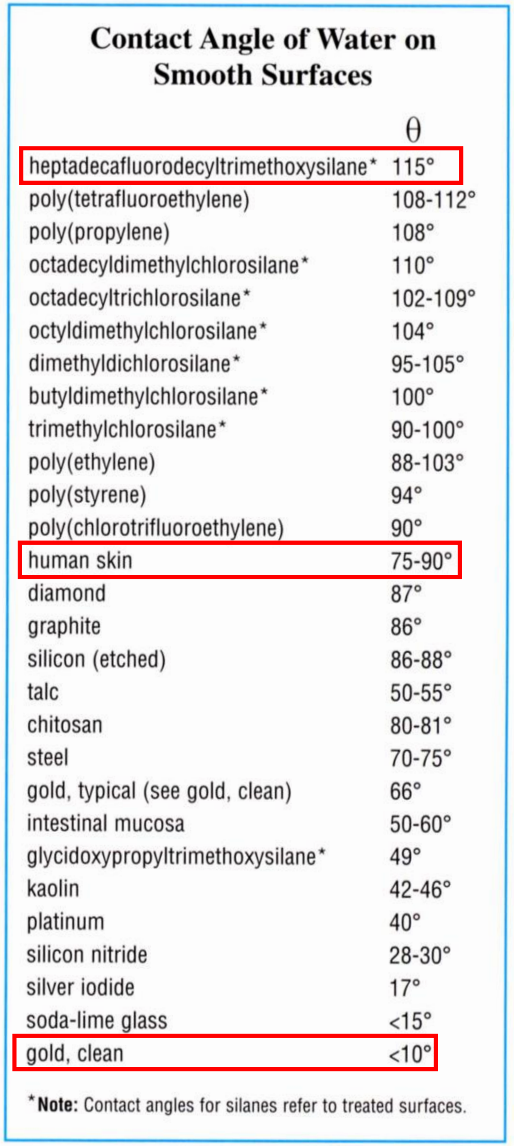
$\theta < 30°$: hydrophilic surface

$\theta < 10°$: superhydrophilic

$\theta > 90°$: hydrophobic

$\theta > 150°$: superhydrophobic

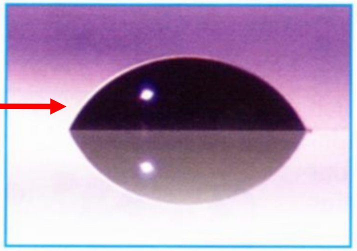

Contact Angle Defines Wettability

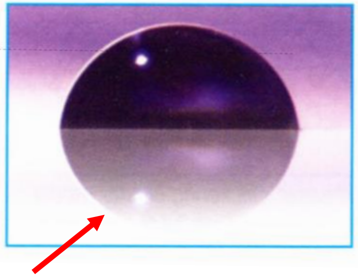

Contact Angle of Water on Smooth Surfaces

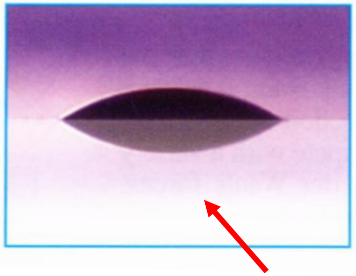
	θ
heptadecafluorodecyltrimethoxysilane*	115°
poly(tetrafluoroethylene)	108-112°
poly(propylene)	108°
octadecyldimethylchlorosilane*	110°
octadecyltrichlorosilane*	102-109°
octyldimethylchlorosilane*	104°
dimethyldichlorosilane*	95-105°
butyldimethylchlorosilane*	100°
trimethylchlorosilane*	90-100°
poly(ethylene)	88-103°
poly(styrene)	94°
poly(chlorotrifluoroethylene)	90°
human skin	75-90°
diamond	87°
graphite	86°
silicon (etched)	86-88°
talc	50-55°
chitosan	80-81°
steel	70-75°
gold, typical (see gold, clean)	66°
intestinal mucosa	50-60°
glycidoxypropyltrimethoxysilane*	49°
kaolin	42-46°
platinum	40°
silicon nitride	28-30°
silver iodide	17°
soda-lime glass	<15°
gold, clean	<10°

*Note: Contact angles for silanes refer to treated surfaces.

ordinary: «typical wetting»







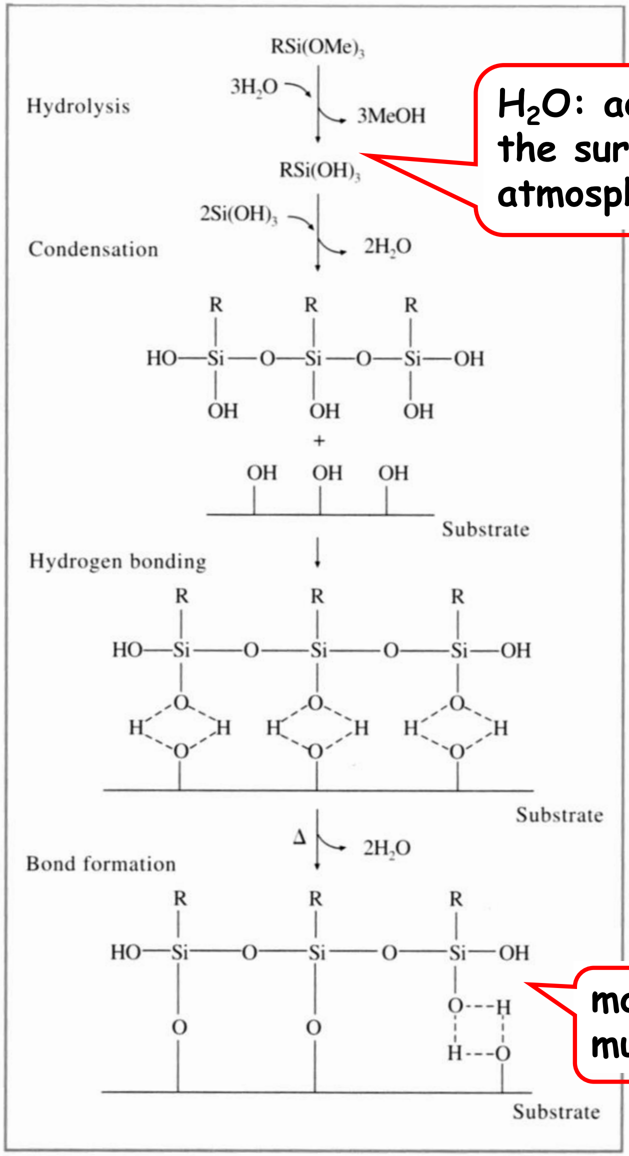
hydrophobic: «poor wetting»

hydrophilic: «good wetting»

Surface modification: possible schematic views

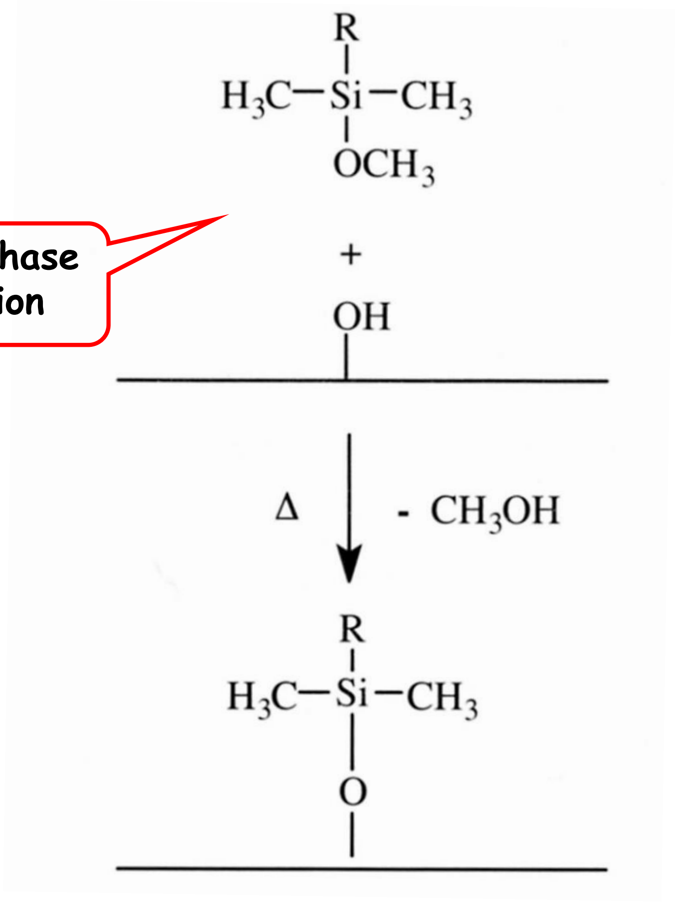
hydrolytic deposition

anhydrous deposition



H_2O: added, on the surface, atmosphere...

monolayers or multilayers



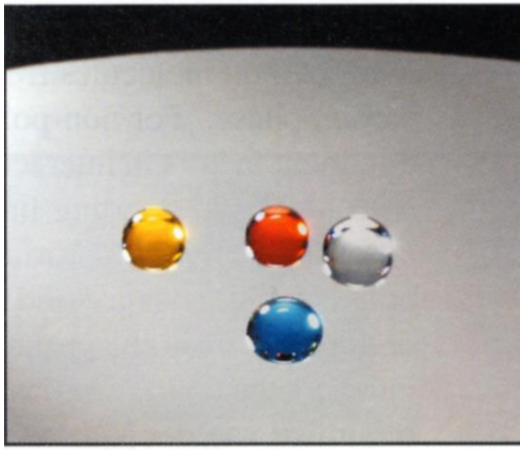
vapor phase deposition

50°-120°C

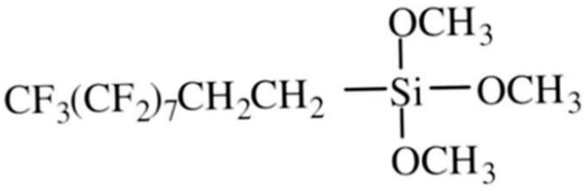
4-12 hours

Surface modification: selection of silanes

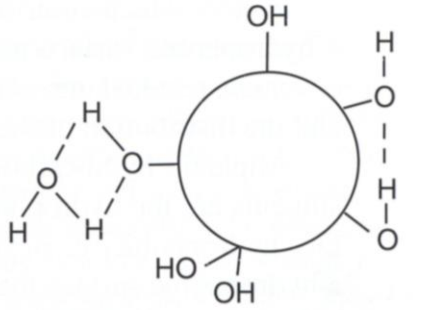
- ♦ concentration of surface hydroxyl groups
- ♦ type of surface hydroxyl groups
- ♦ hydrolytic stability of the bond formed
- ♦ dimensions of the substrate



Water droplets on a (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trimethoxysilane-treated silicon wafer exhibit high contact angles, indicative of the low surface energy. Surfaces are both hydrophobic and resist wetting by hydrocarbon oils. *(water droplets contain dye for photographic purposes).*



$$CF_3(CF_2)_7CH_2CH_2-Si(OCH_3)_3$$



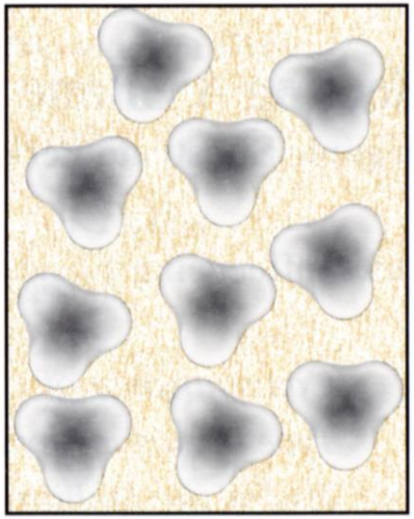
Silane Effectiveness on Inorganics

SUBSTRATES

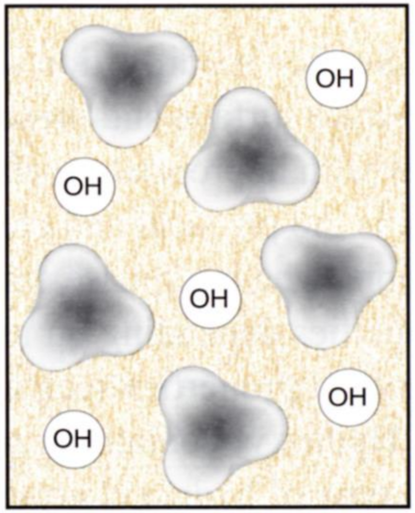
Silica
Quartz
Glass
Aluminum (AlO(OH))
Alumino-silicates (e.g. clays)
Silicon
Copper
Tin (SnO)
Talc
Inorganic Oxides (e.g. Fe_2O_3, TiO_2, C
Steel, Iron
Asbestos
Nickel
Zinc
Lead
Marble, Chalk ($CaCO_3$)
Gypsum ($CaSO_4$)
Barytes ($BaSO_4$)
Graphite
Carbon Black

some solutions: monoalkoxysilanes, dipodal silanes...

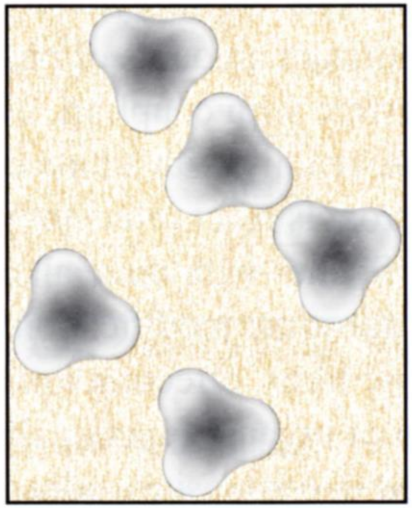
Hypothetical trimethylsilylated surfaces



complete coverage



incomplete hydroxyl reaction



few bonding opportunities

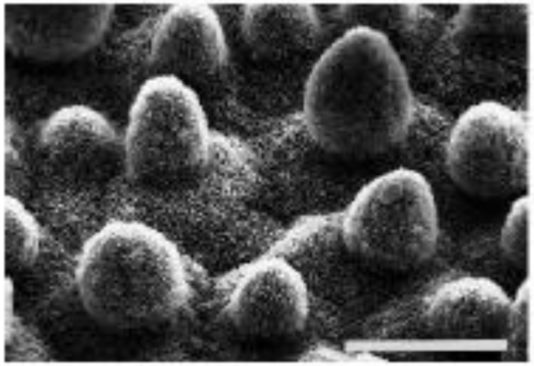
$= (CH_3)_3Si$ = trimethylsilyl

pyrogenic silica: 5-7 OH/nm^2 (less than 50% are reacted)

Lotus effect

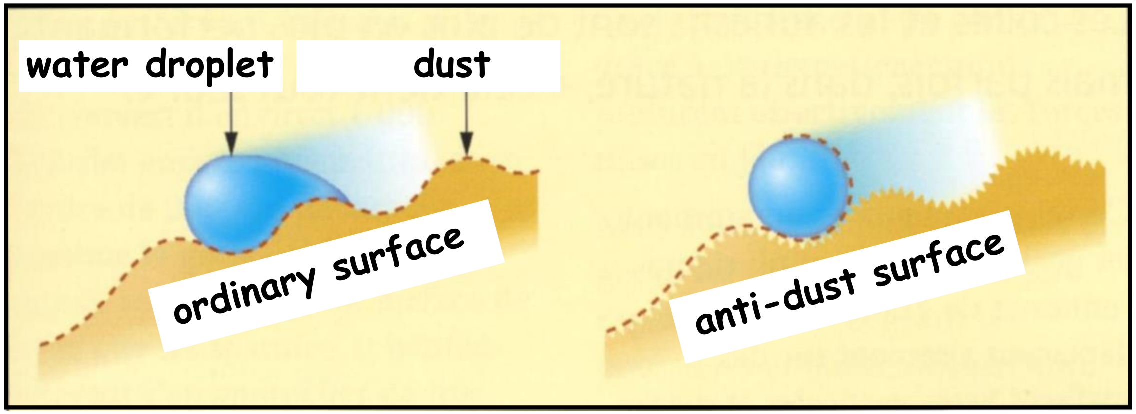
SEM picture of Lotus leaf

Nelumbo nucifera



wax crystals

Self-cleaning surface

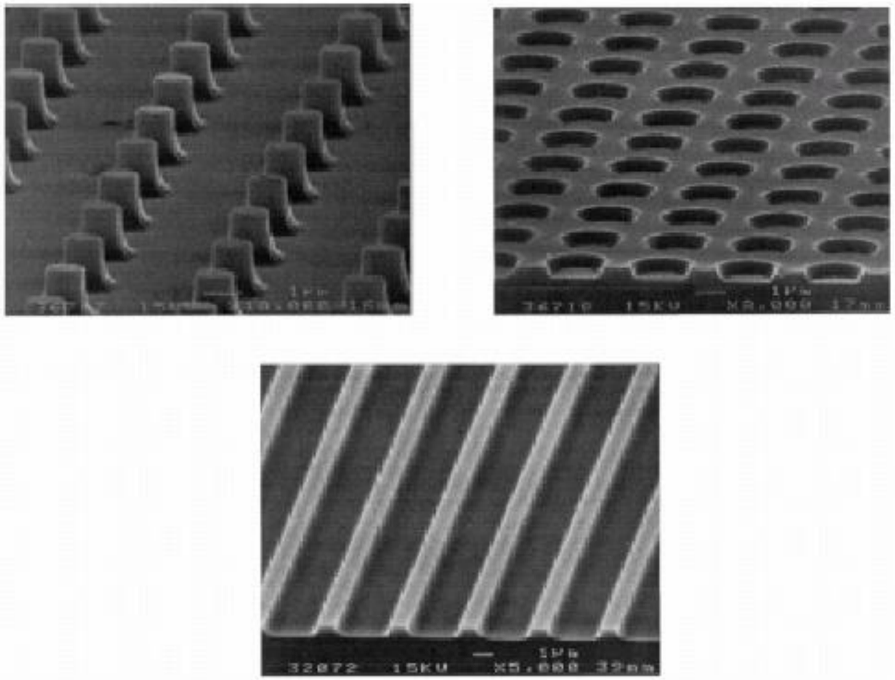


R. Moret (*in* Nanomonde, CNRS ed)

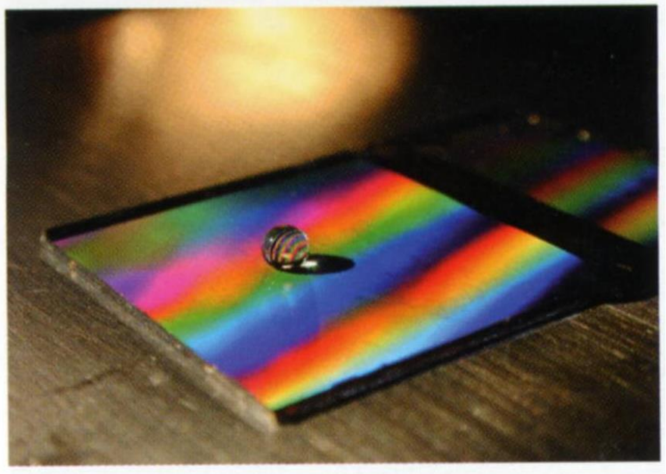
Lotus leaf surface

Tropaelum majus (capucine)

Mimicking nature



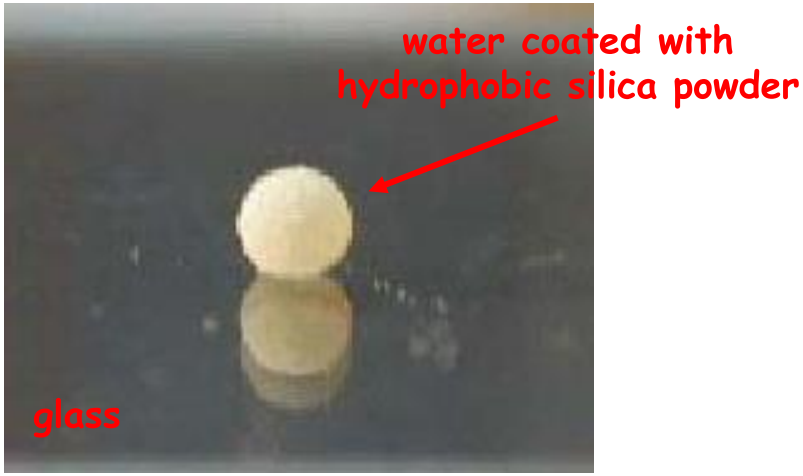
structured surfaces (Bico *et al.* 1999)



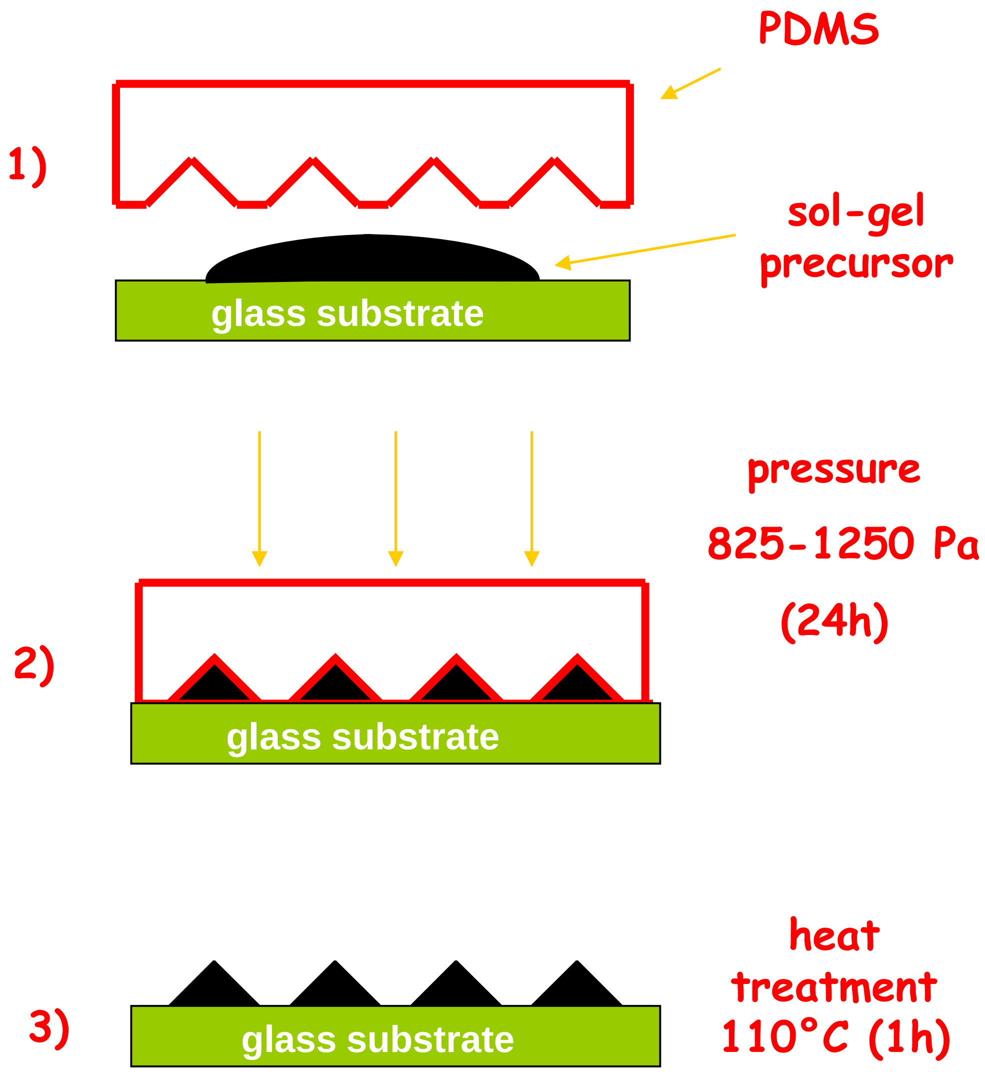
superhydrophobic coating

inverting the idea!

Aussillous *et al.* 2001



Patterning



1)

PDMS

sol-gel precursor

glass substrate

pressure

825-1250 Pa

(24h)

2)

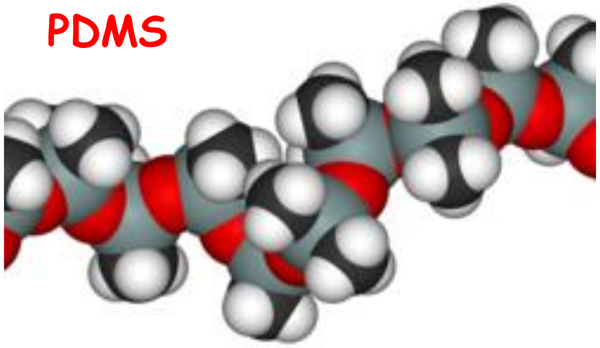
glass substrate

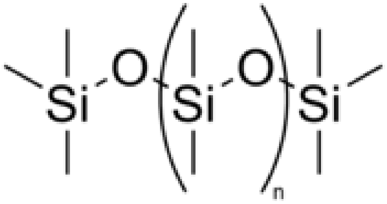
3)

glass substrate

heat treatment 110°C (1h)

PDMS





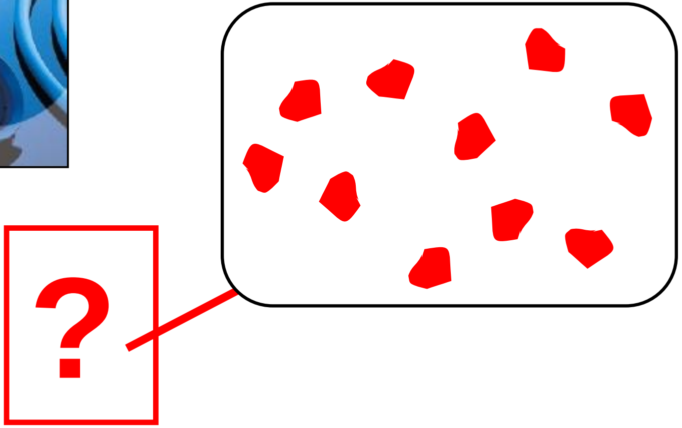
polydimethylsiloxane

Courtesy of A. Pauletti

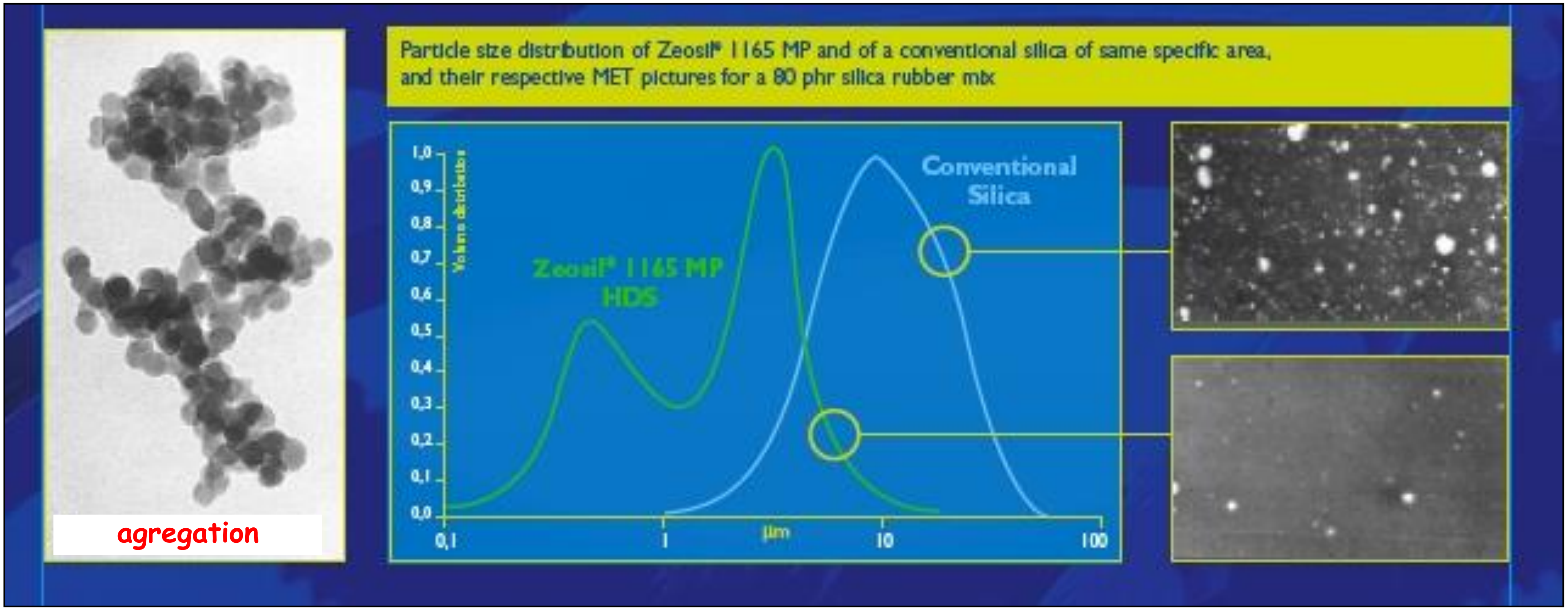
Characterization of modified silica nanoparticles: a spectroscopic challenge

Rhodia

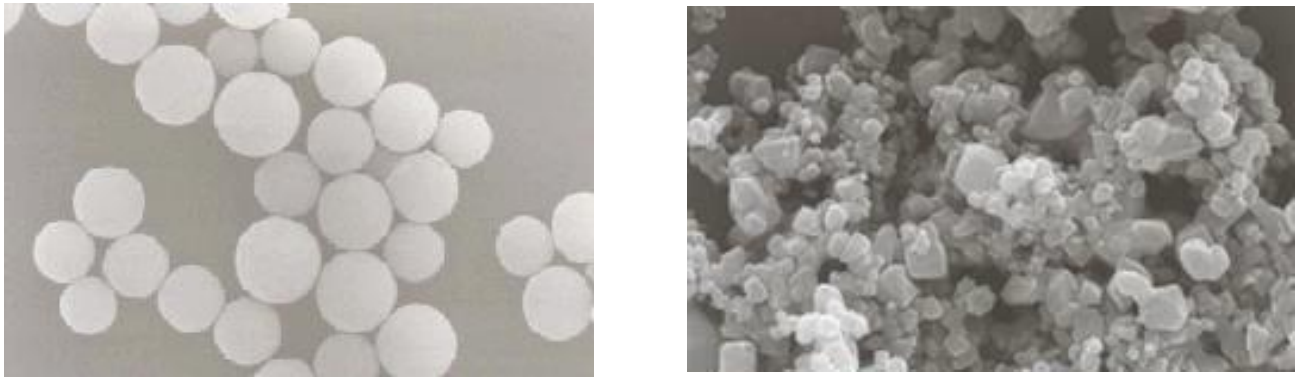
Zeosil®
High Performance Silicas



Morphology

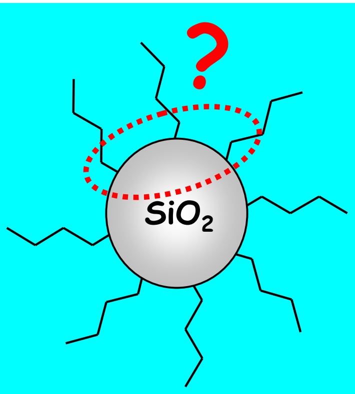


Particle size distribution of Zeosil® 1165 MP and of a conventional silica of same specific area, and their respective MET pictures for a 80 phr silica rubber mix

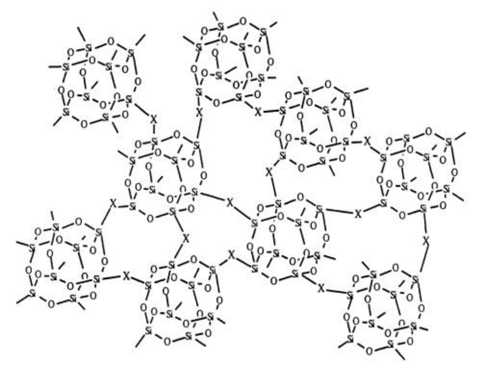


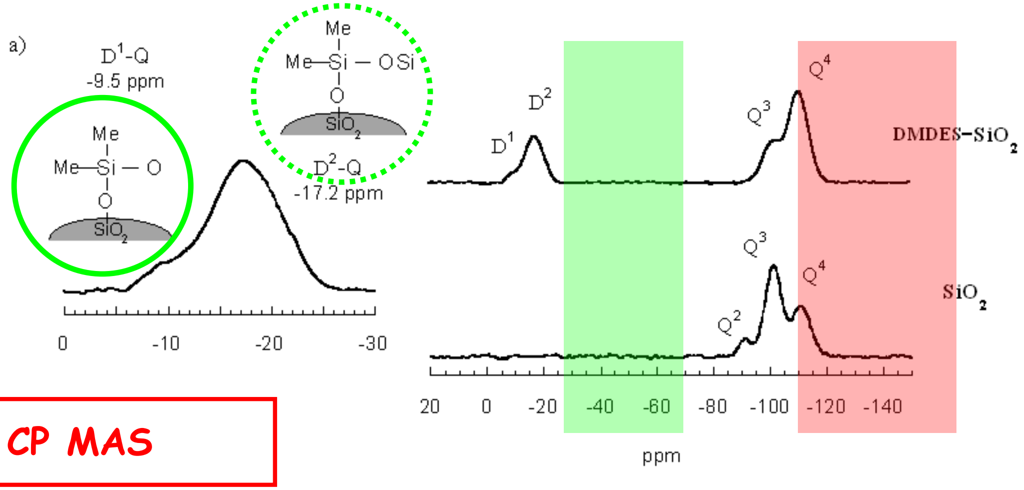
silica nanoparticles (Φ ~ 15 - 500 nm)

Grafting on silica nanoparticles: ^{29}Si

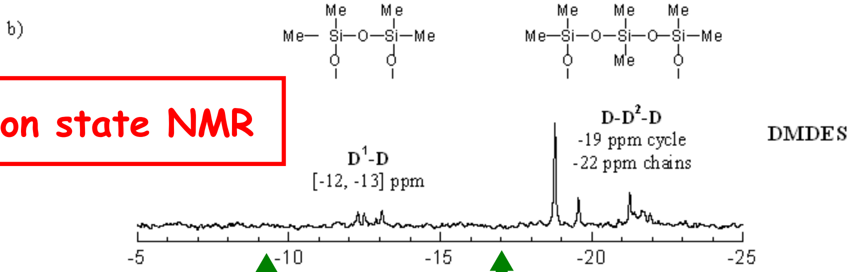


F. Mammeri, *MRS Proc.* 847 (2005)

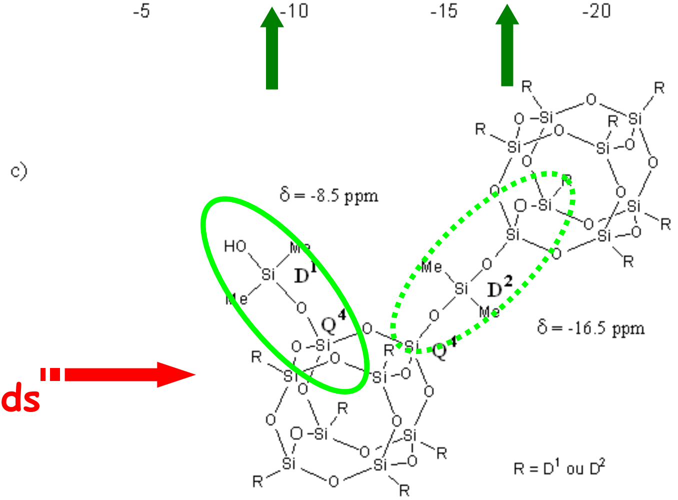




^{29}Si CP MAS



solution state NMR



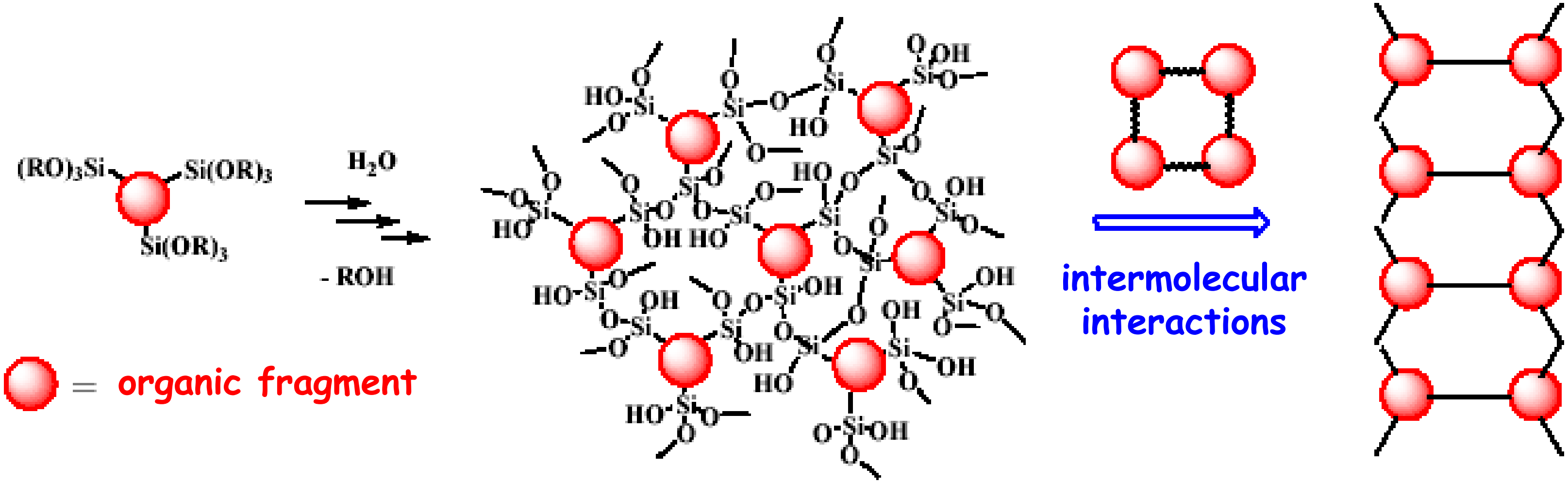
chemical shifts: ^{29}Si

S. de Monredon, Paris 6

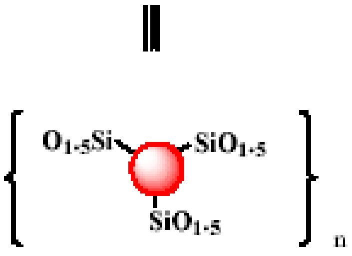
Coll.: Rhodia company

model compounds

Hybrid organic/silica materials



non linear optic
photochromism
catalysis
...



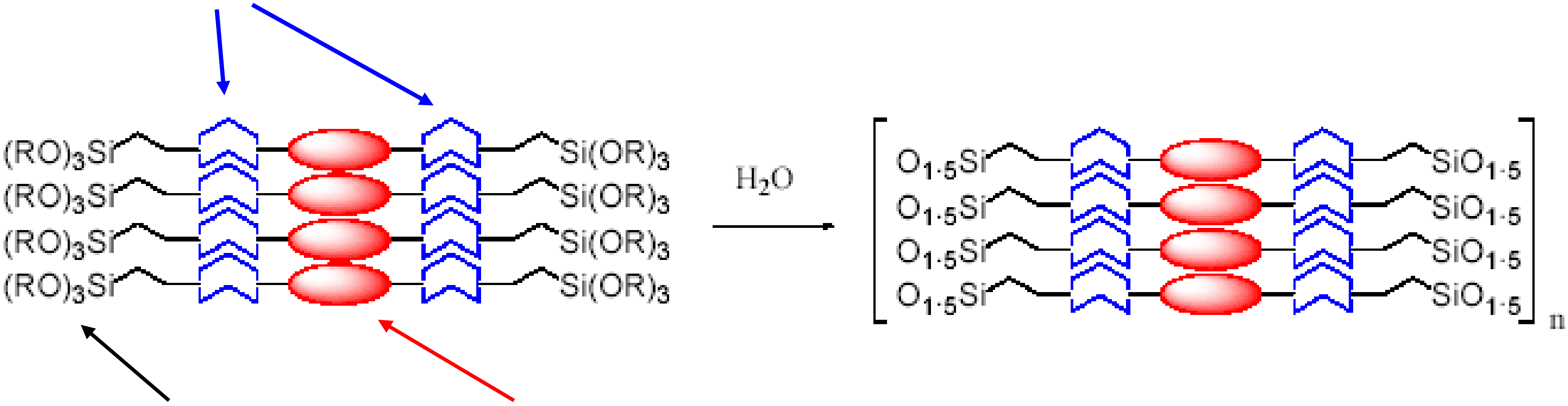
silsesquioxane

organization
structuration
periodicity

Dr. M. Wong Chi Man, CNRS, Montpellier

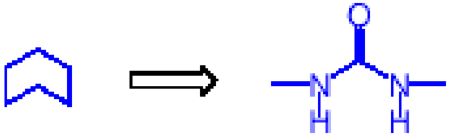
Self-organized hybrid silica

self-association



hydrolysis/condensation

principal organic fragment



urea function

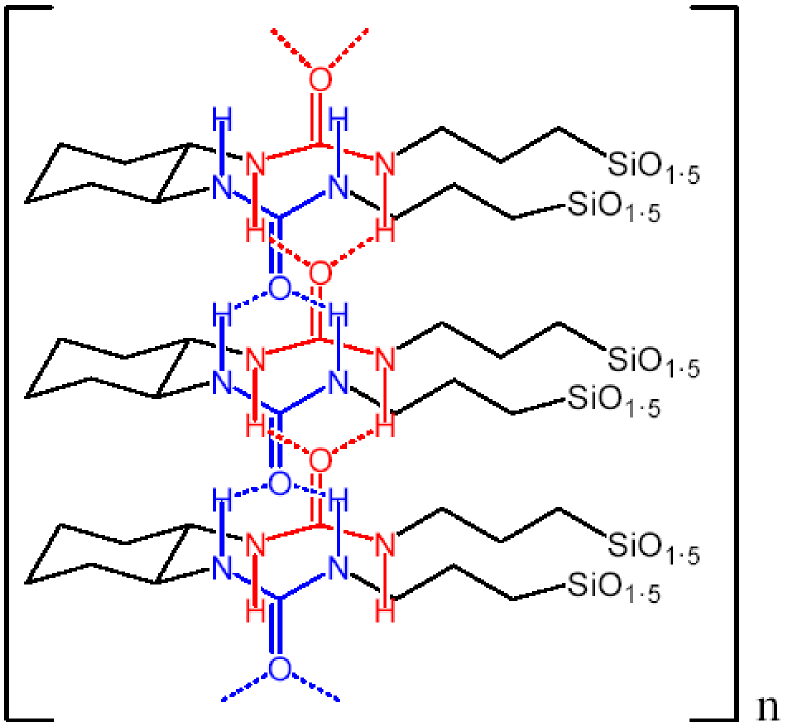
chiral fragment

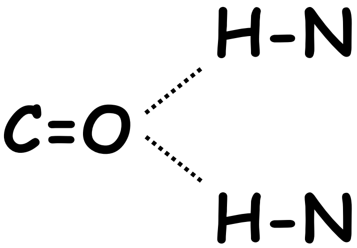
flexible chain

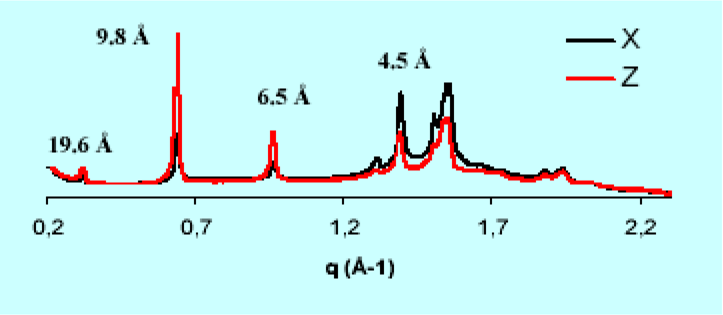
rigid

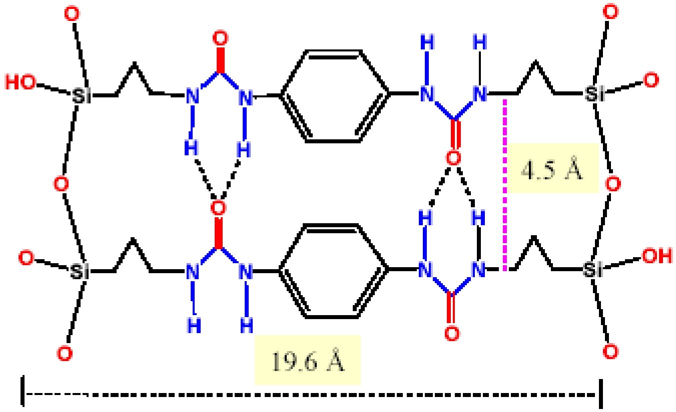
Dr. M. Wong Chi Man, CNRS, Montpellier

H-bond networks









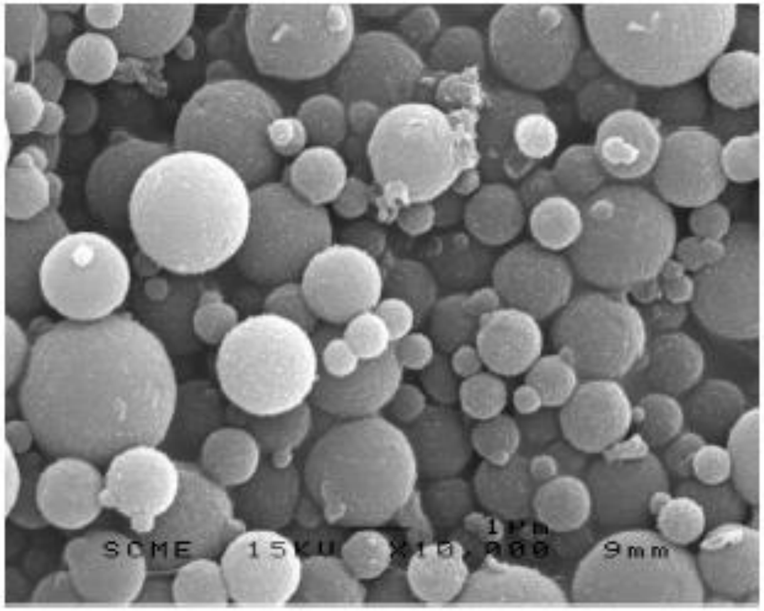
Dr. M. Wong Chi Man, CNRS, Montpellier

Influence of the precursor on morphology

- basic conditions

pure enantiomer (chiral fragment)

hollow tubes

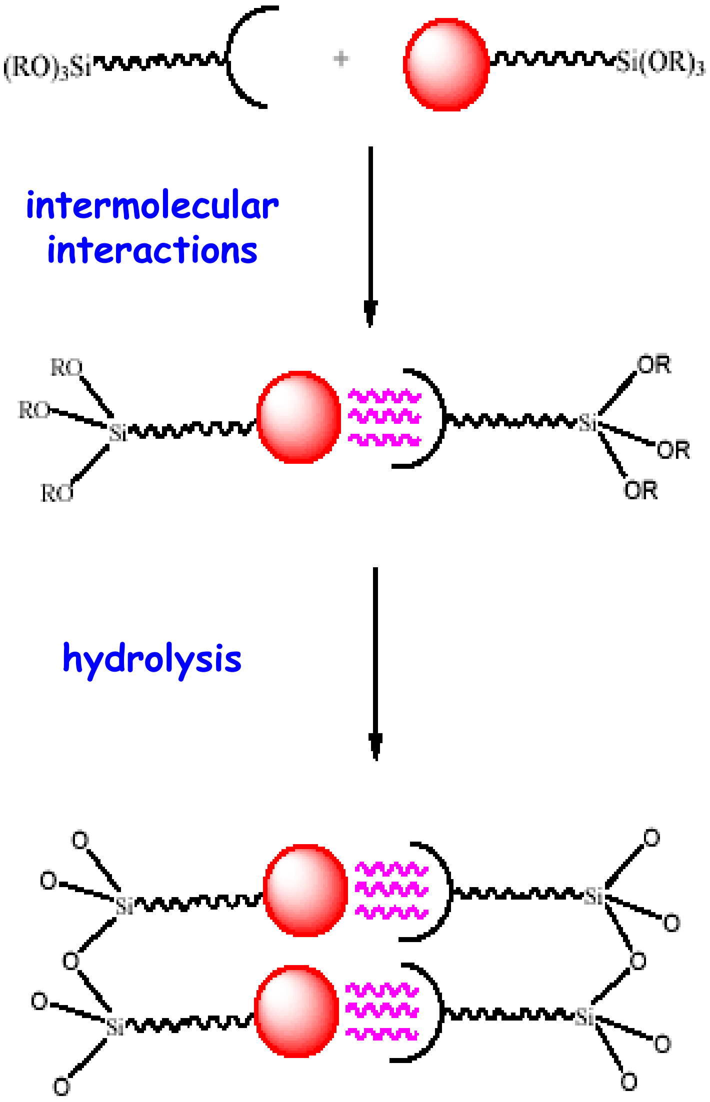


racemic mixture

Chem. Eur. J., 2003, **9**, 1594

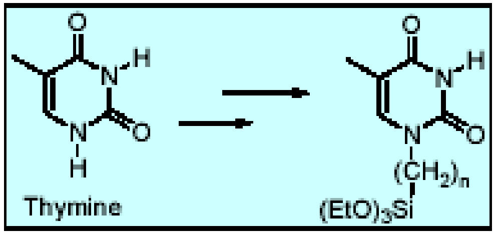
spheres

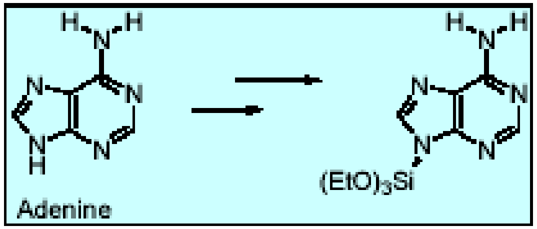
Towards bio-inspired materials...

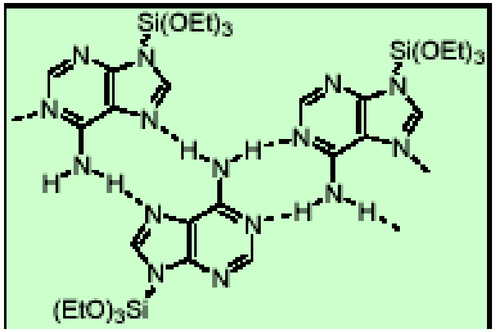


intermolecular interactions

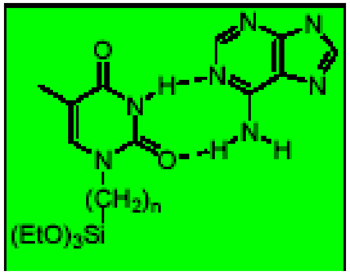
hydrolysis





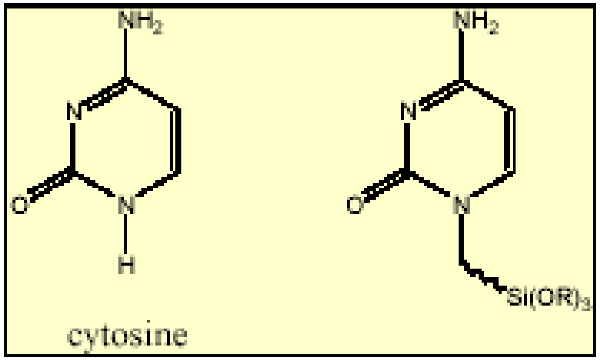


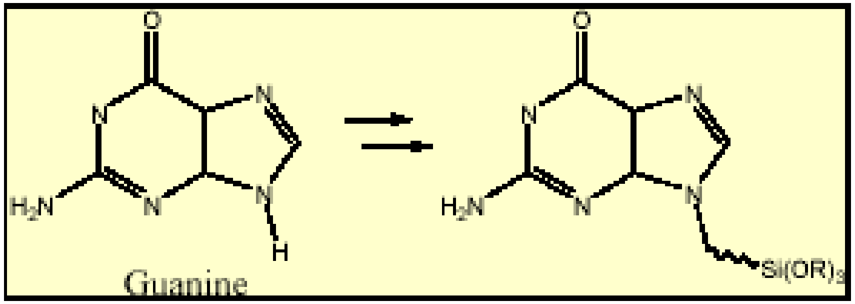
homo self-association

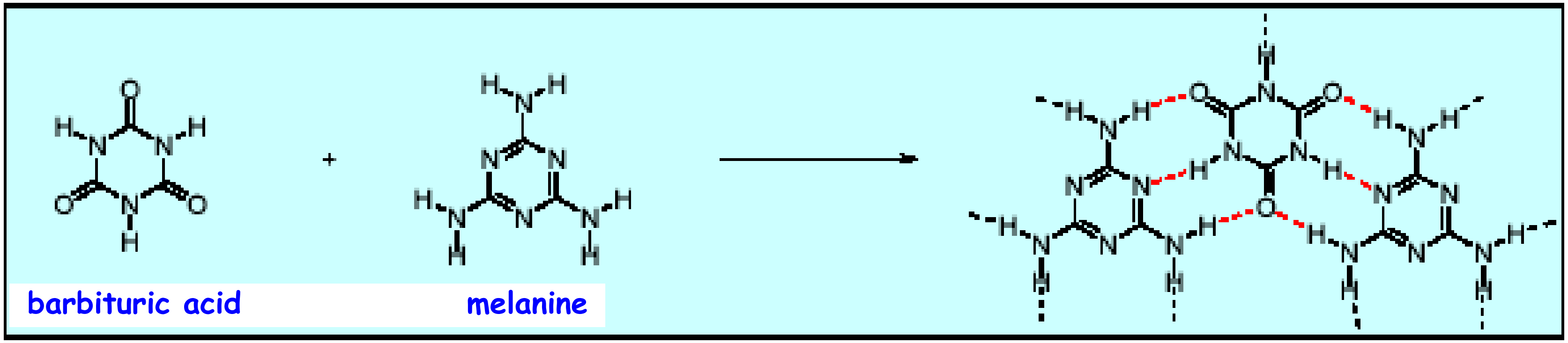


hetero self-association

Other associations



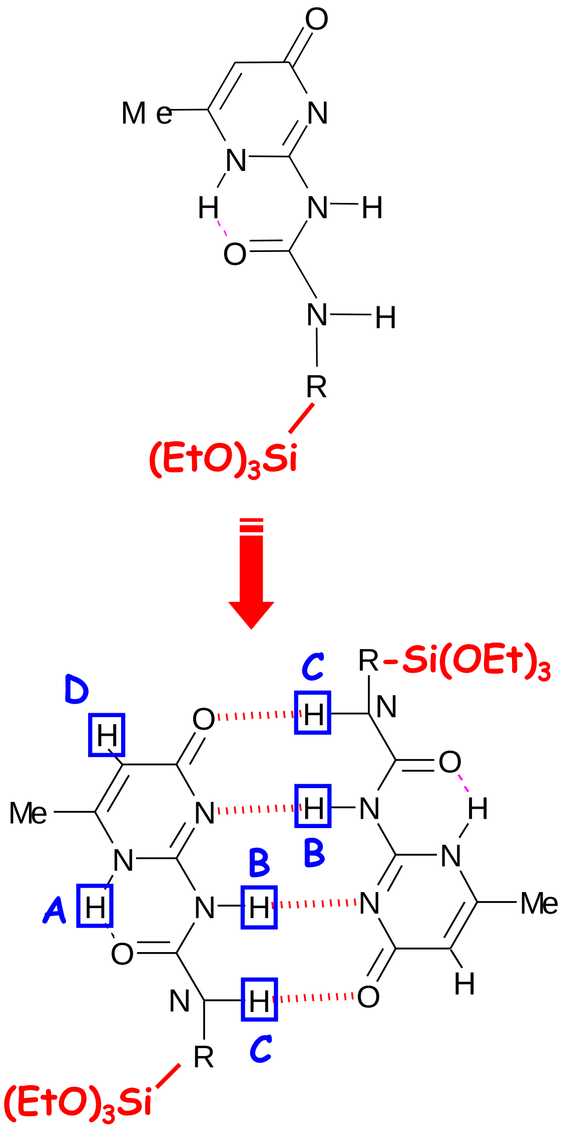


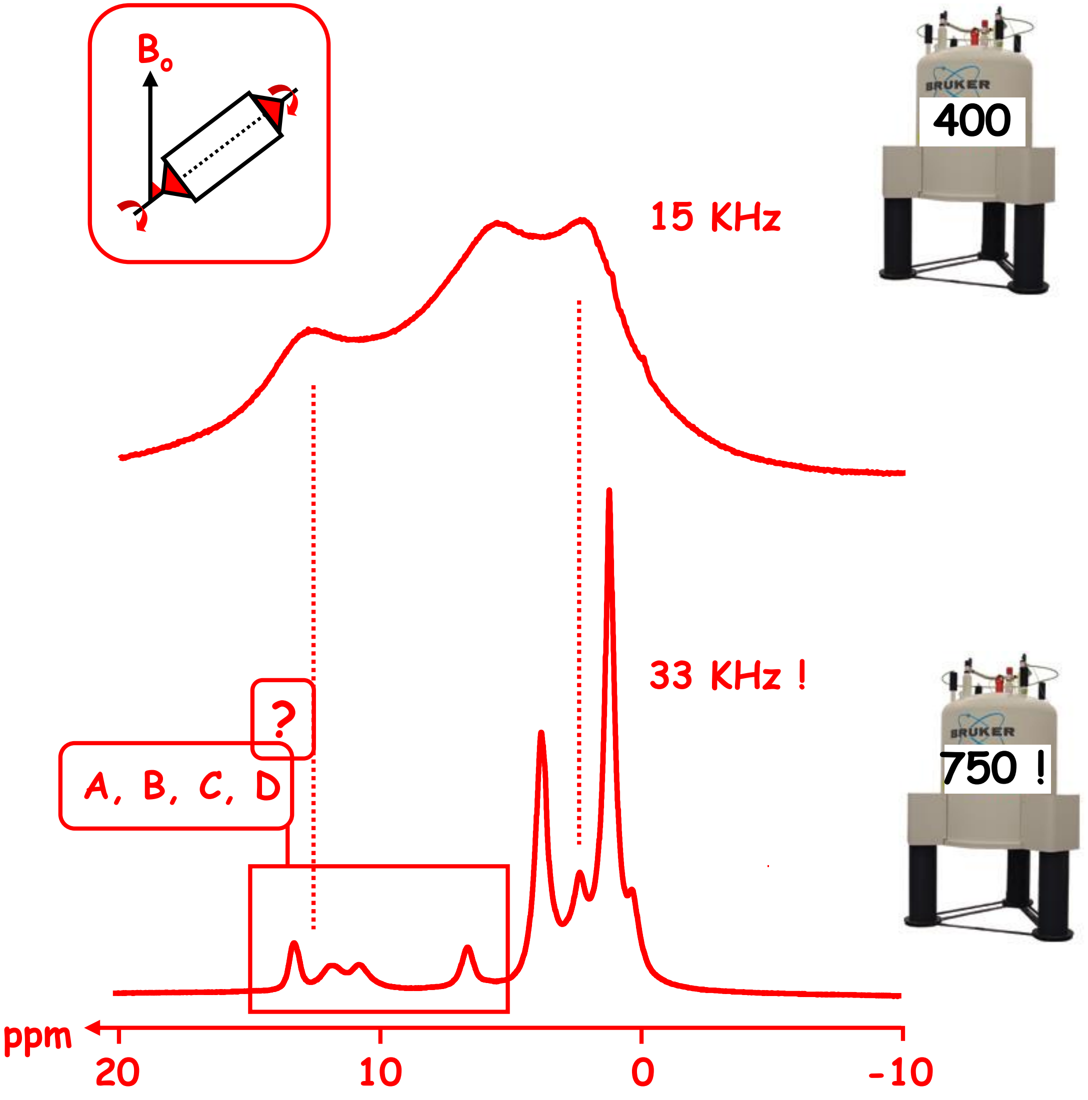


barbituric acid

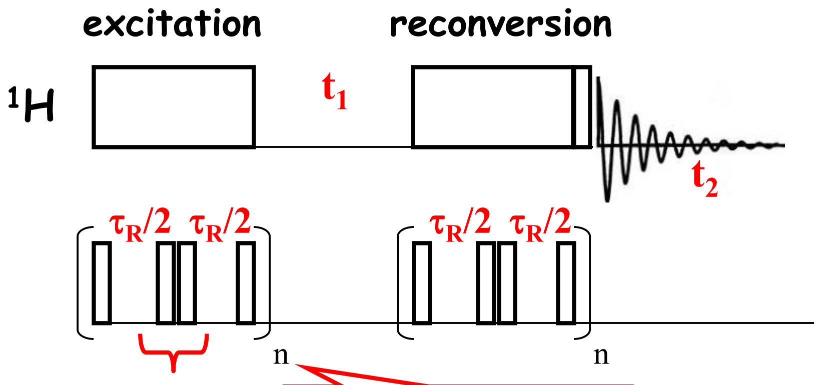
melanine

Ureidopyrimidinone derivatives: ^1H spectroscopy





^1H DQ spectroscopy (Double Quantum)



BAck to BAck

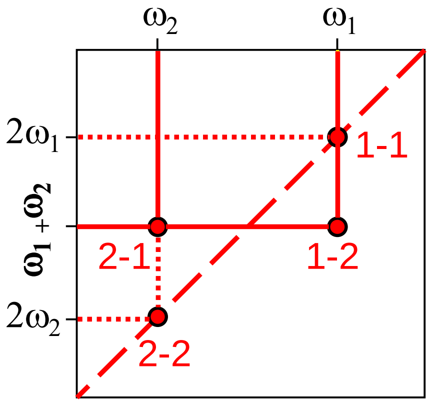
2Q hamiltonian!

$D_{HH} \propto 1/r^3$

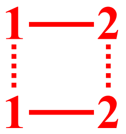
^1H .... ^1H
r

I=1/2 I=1/2

2Q
<++| ⇔ |-->



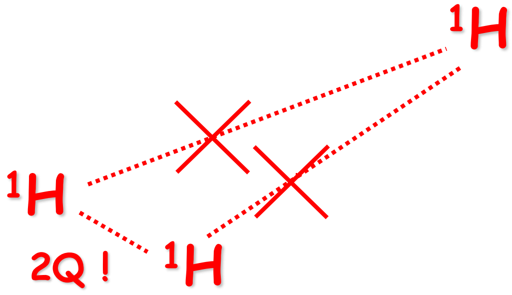
1Q dim.



dipolar links

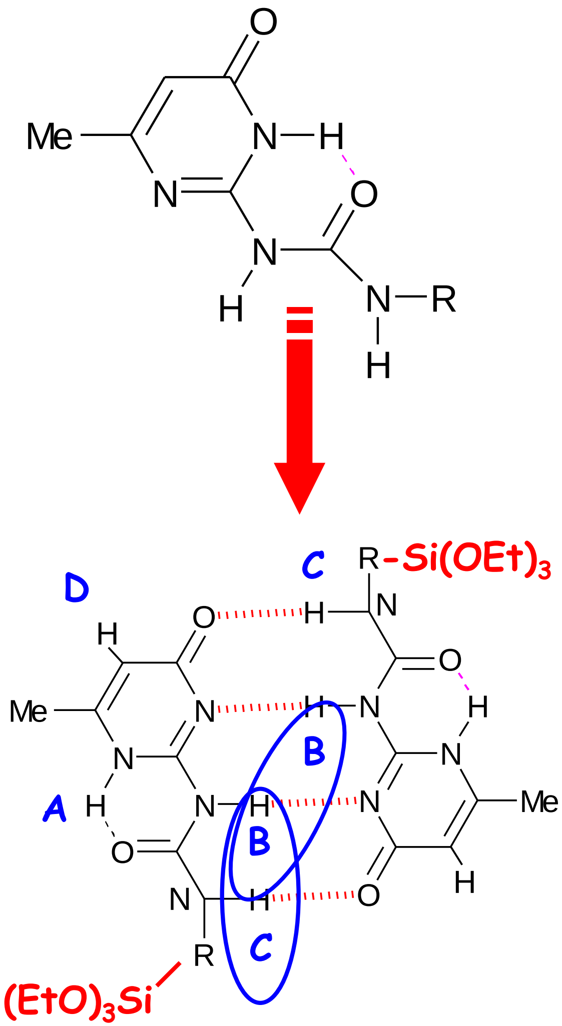
2Q dim.

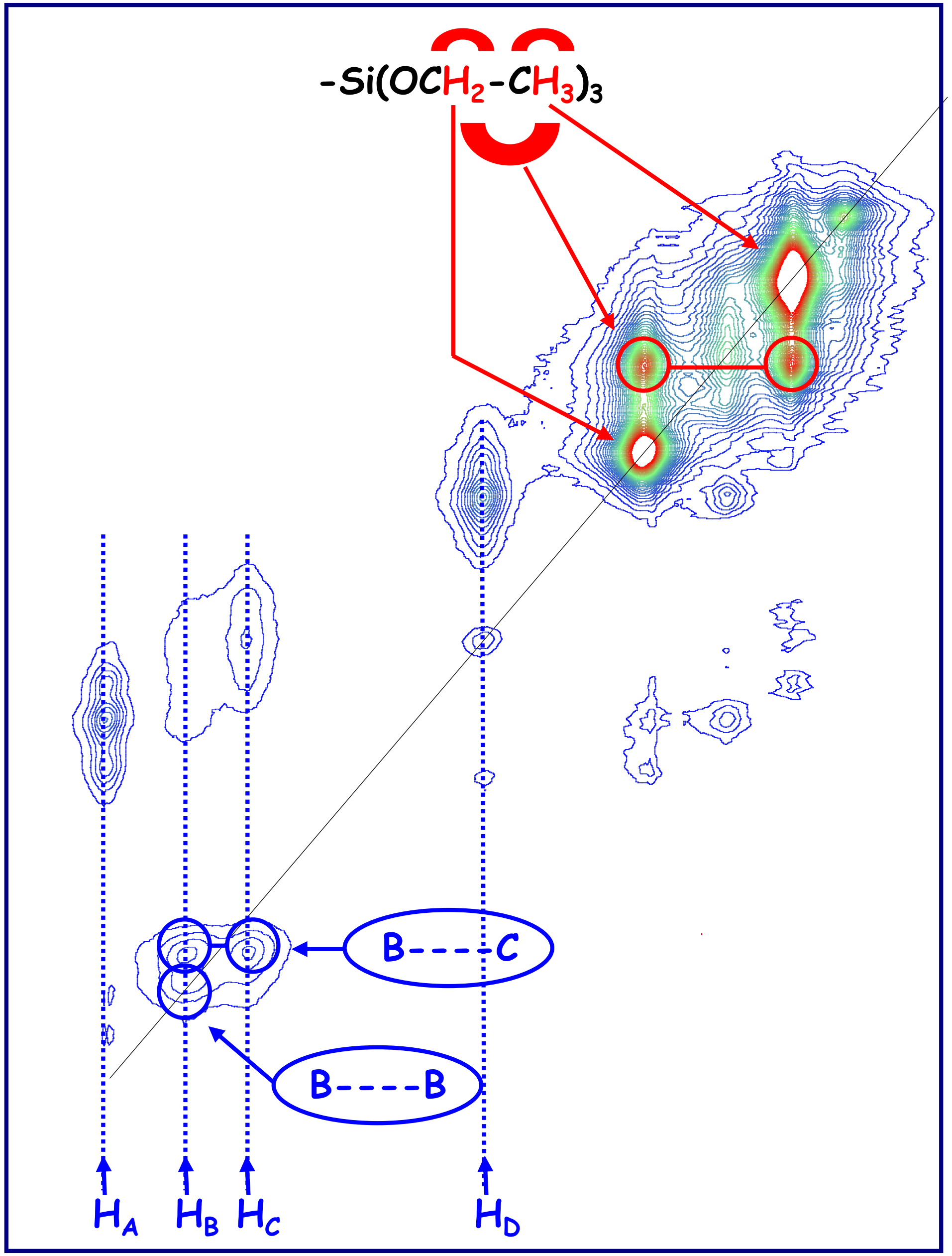
selectivity



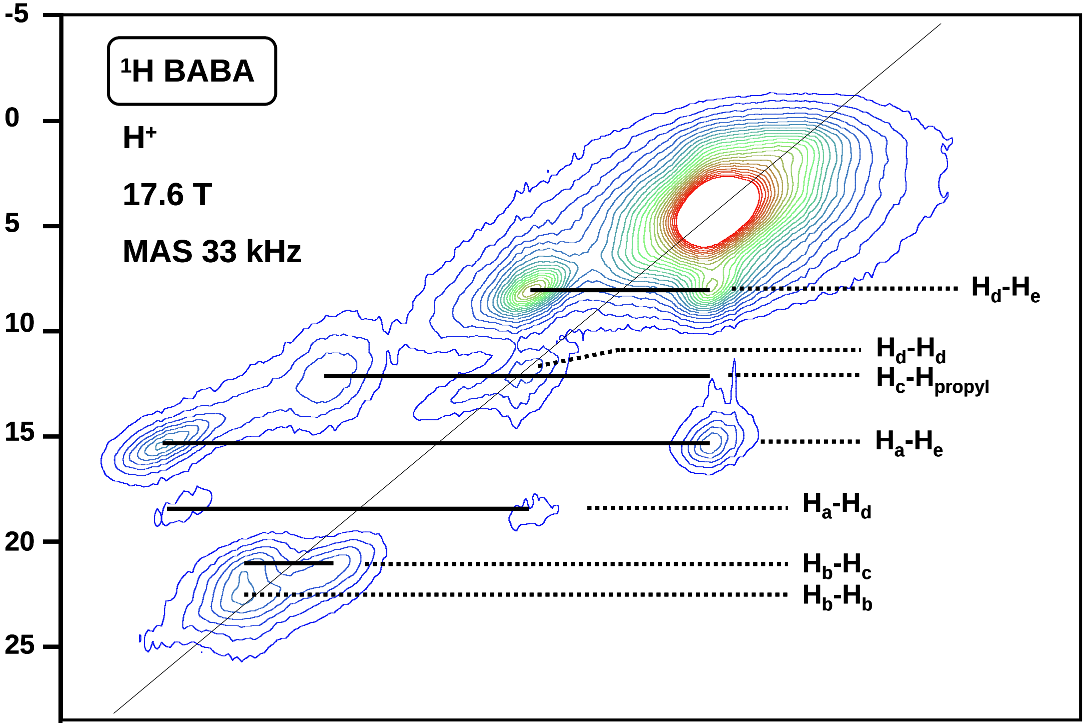
$\delta_{iso.}$: ultra fast MAS, high B_0 field!

Ureidopyrimidinone derivatives: ^{1}H DQ spectroscopy

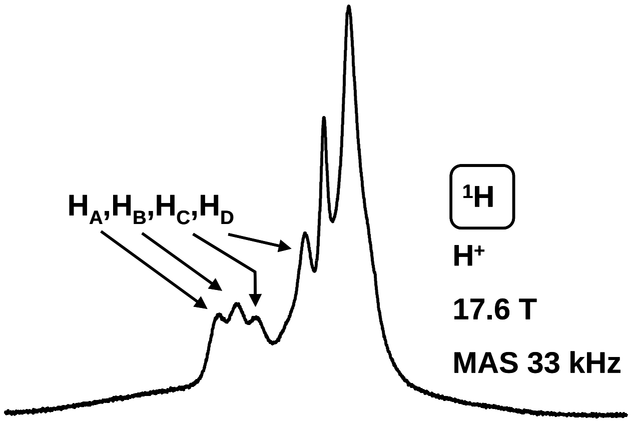


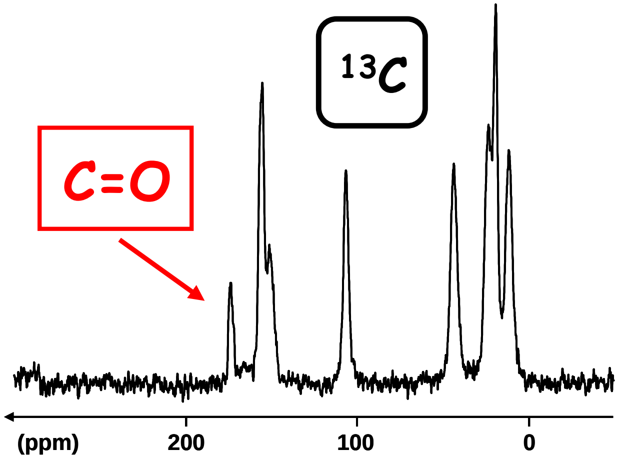


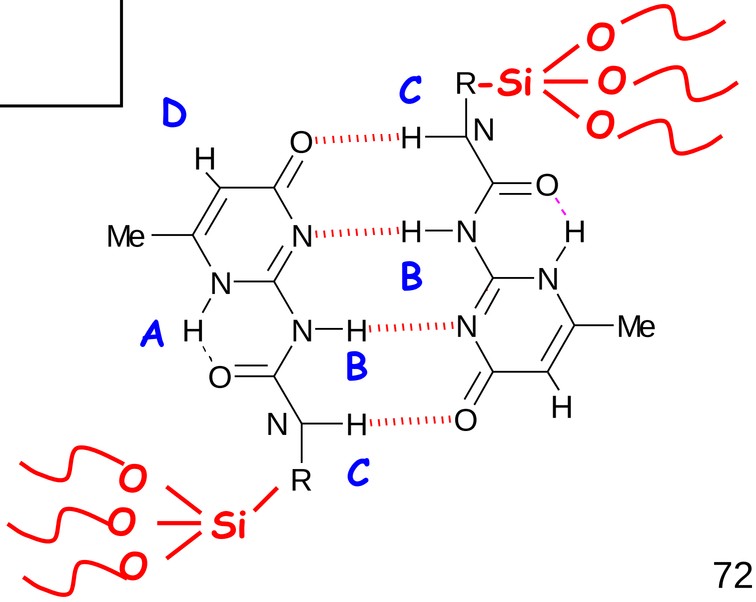
Ureidopyrimidinone derived materials



hydrolysis / condensation





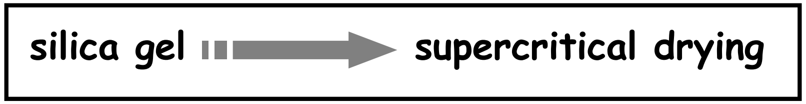


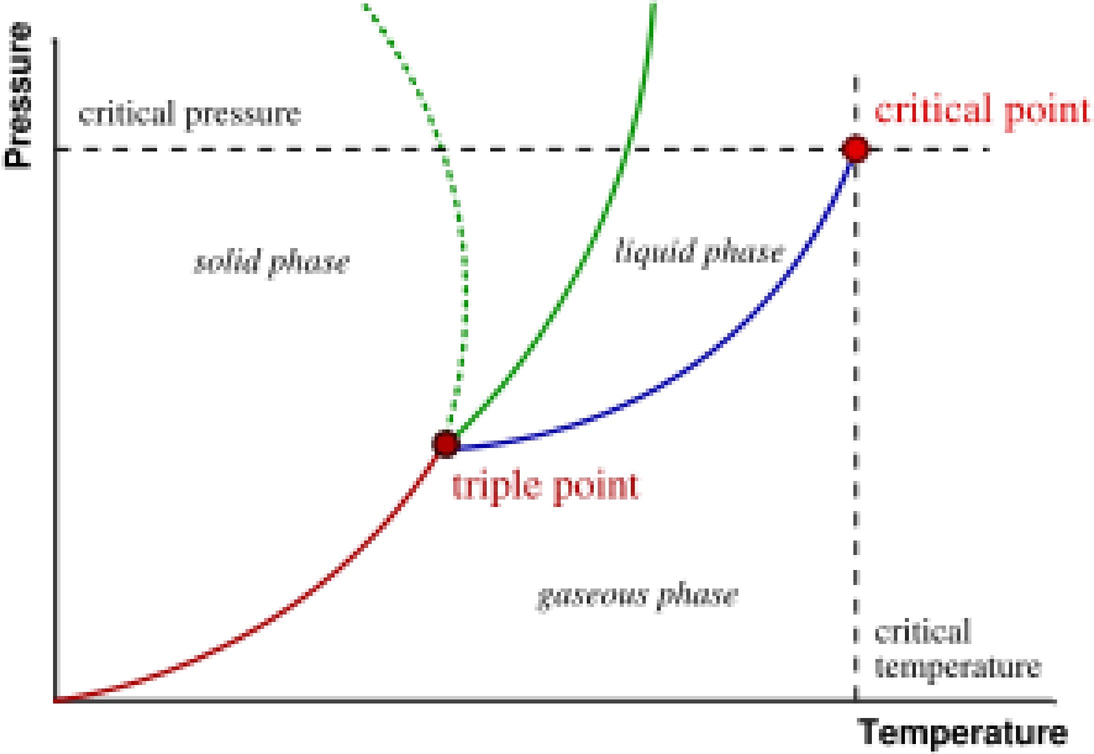
Silica aerogel – supercritical drying

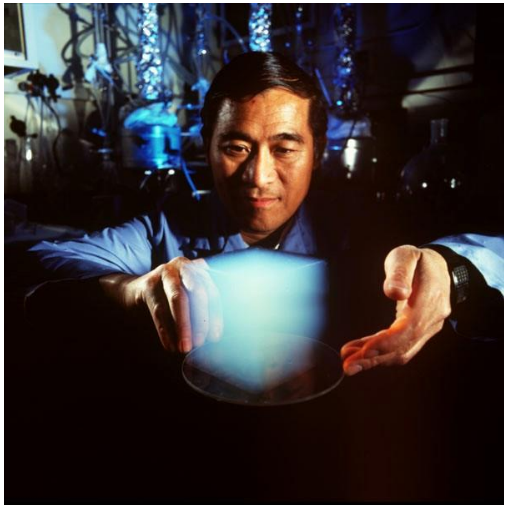
an old idea: S. Kistler 1931!

99.8 % air!

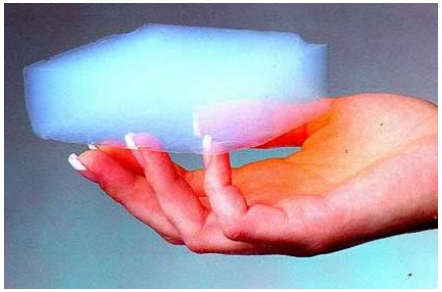
ρ = 3 mg/cm³!


silica gel → supercritical drying





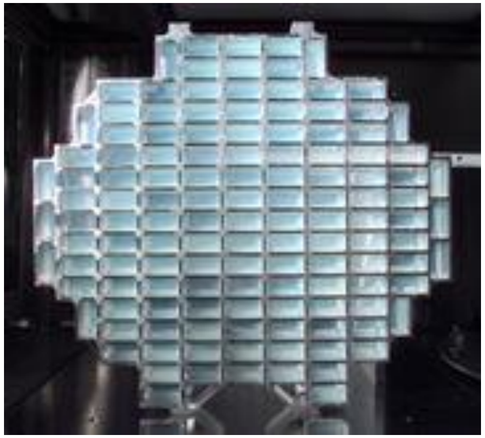
P. Tsou - NASA



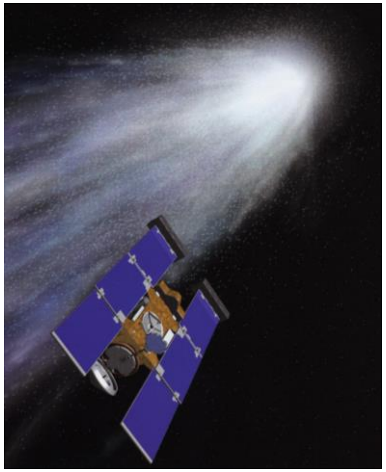
Aerogels: remarkable properties

heat insulator

mechanical properties

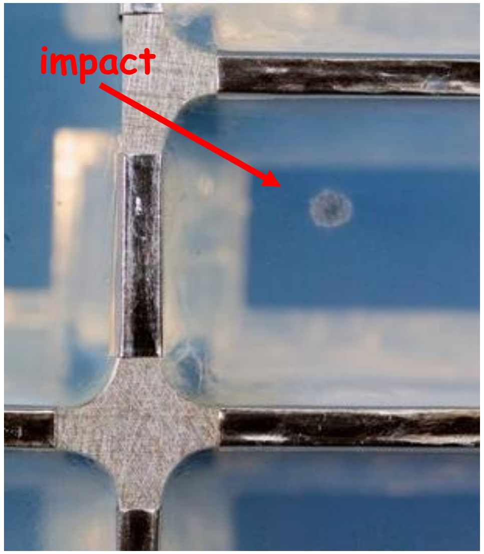


Stardust



Stardust

Wild-2 comet



Silica gel

US patent: W.A. Patrick (1919)

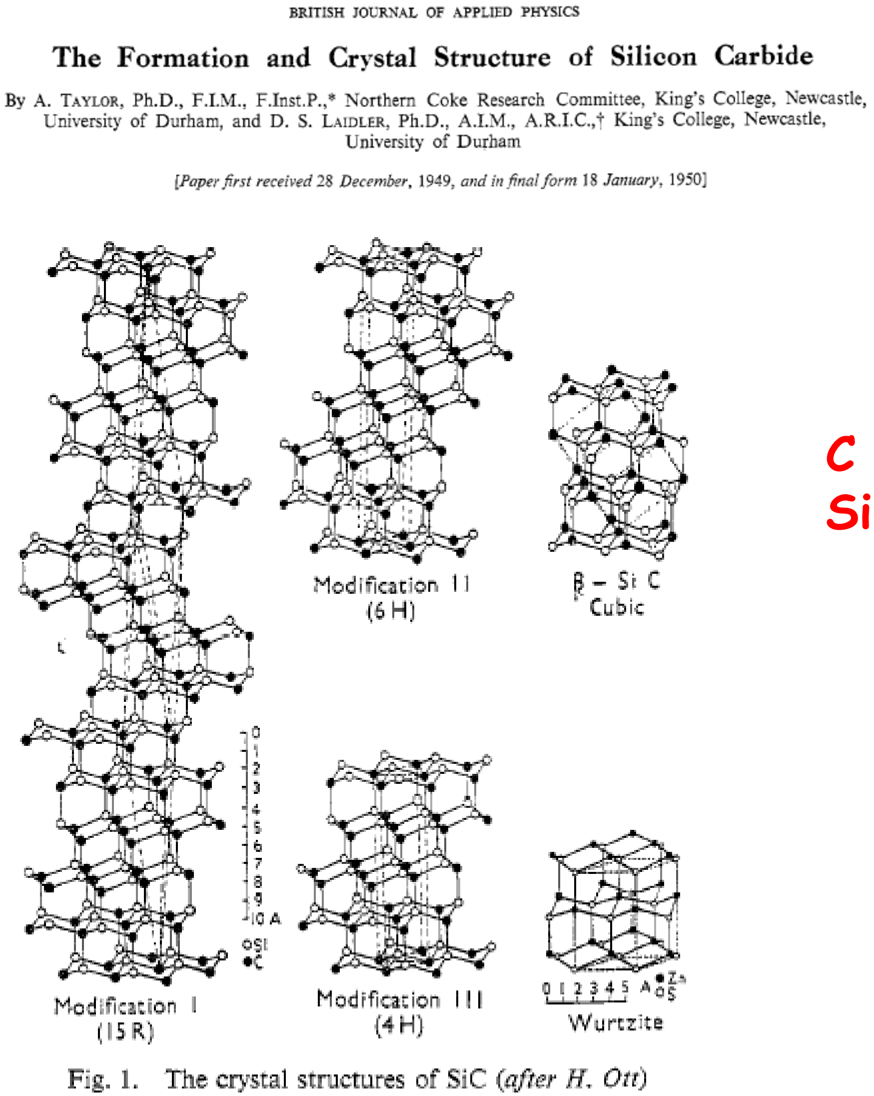
- S = 800 m^2/g
- desiccant
- can be regenerated

$CoCl_2$ (anhydrous)

$CoCl_2$ (hydrated)

Silicon carbide: outstanding properties!

SiC *a unique natural example: meteor impact in Canyon Diablo!*



BRITISH JOURNAL OF APPLIED PHYSICS

The Formation and Crystal Structure of Silicon Carbide

By A. Taylor, Ph.D., F.I.M., F.Inst.P.,* Northern Coke Research Committee, King's College, Newcastle, University of Durham, and D. S. Laidler, Ph.D., A.I.M., A.R.I.C.,† King's College, Newcastle, University of Durham

[Paper first received 28 December, 1949, and in final form 18 January, 1950]

Fig. 1. The crystal structures of SiC (*after H. Ott*)

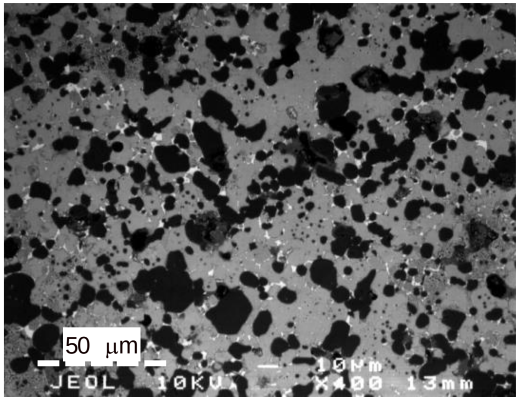
Arizona

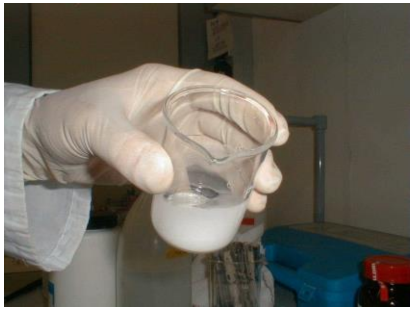
$$\left.\begin{matrix}C\\SiO_2\end{matrix}\right\}\xrightarrow{\Delta T \quad \text{electric furnace}} SiC$$

- ◇ abrasive (carborundum)
- ◇ hardness (Mohs: 9.6!)
- ◇ refractory
- ◇ thermal schock resistance

The role of precursors

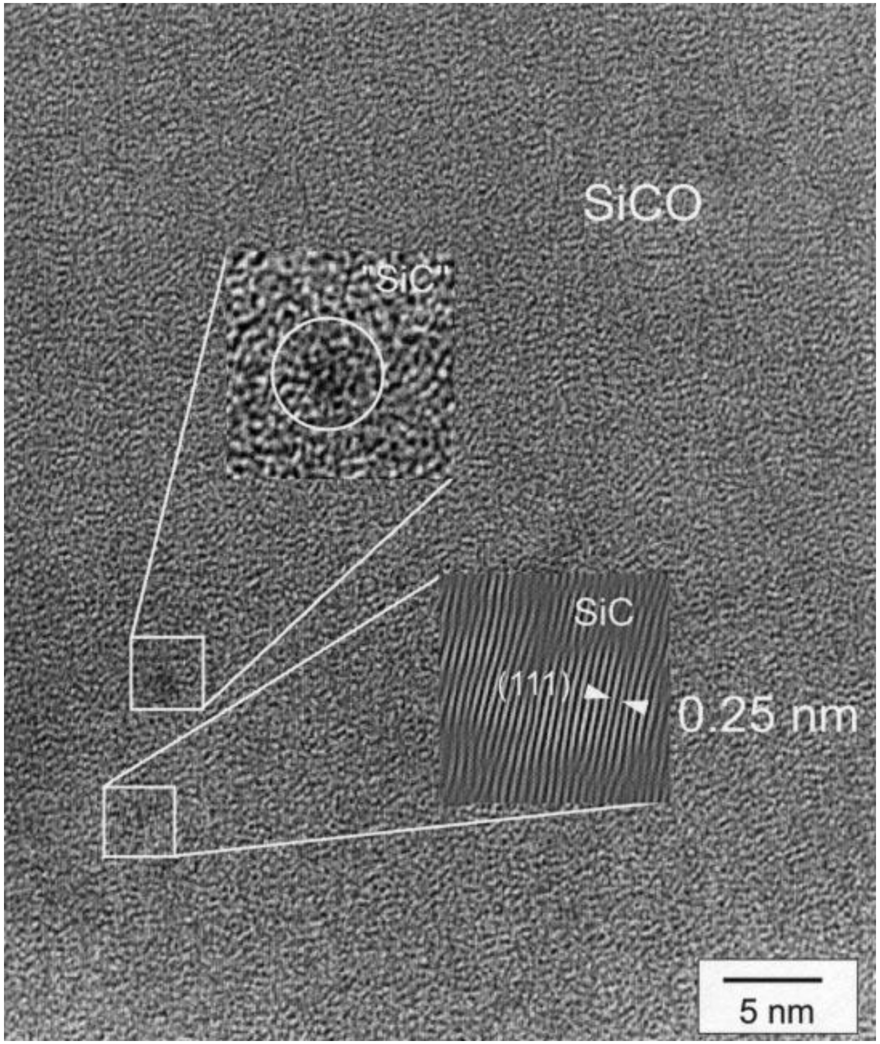
traditional ceramics





polymeric precursors

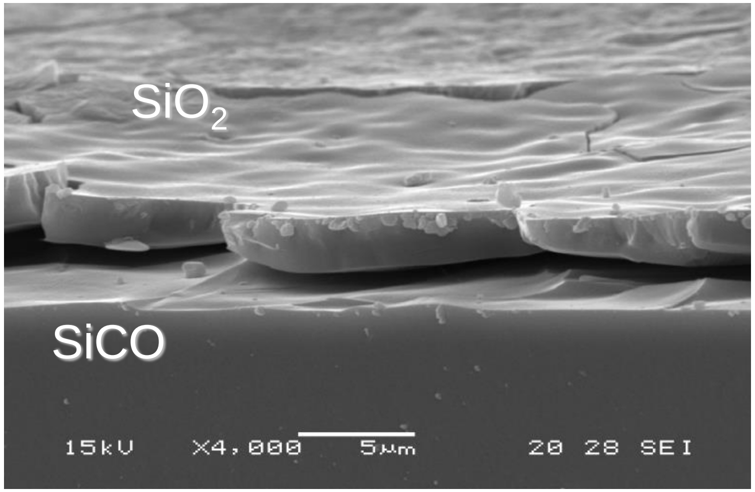
nanostructured SiCO phase



G. D. Soraru, Trento (Italy)

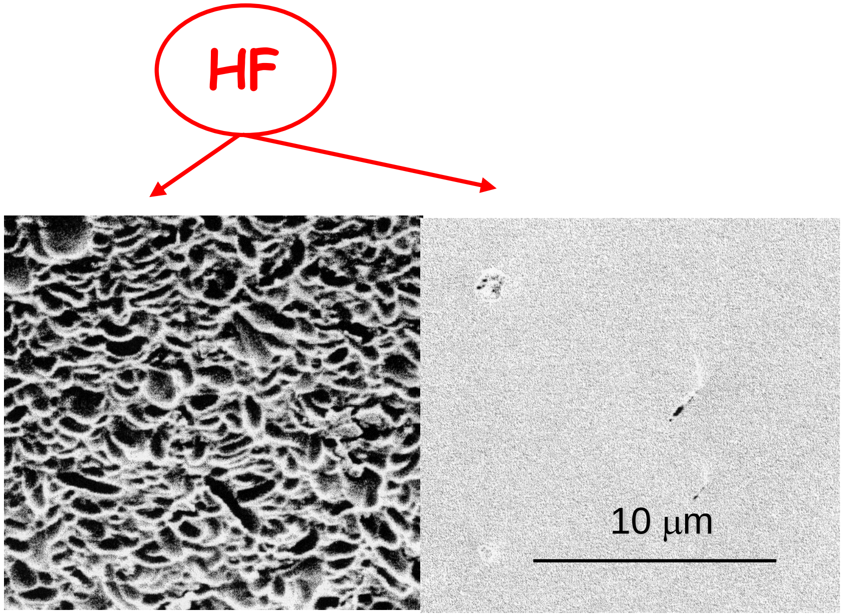
Oxidation and chemical resistance

T = 1350 °C, 100h



$SiCO + O_2 \longrightarrow SiO_2 + CO$

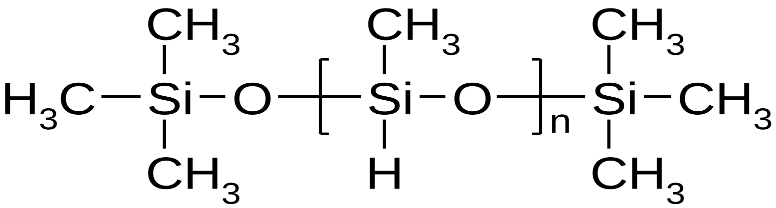
Modena, J. Am. Ceram. Soc.



SiO_2 SiCO

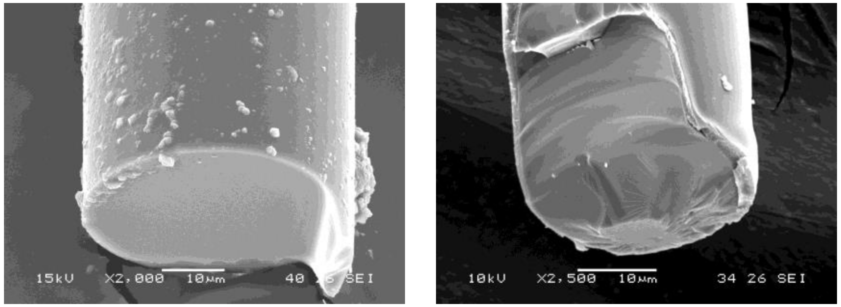
Soraru, J. Am. Ceram. Soc., 2002

Fibers



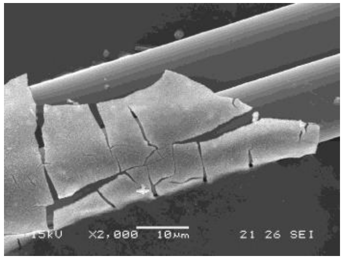
$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{H}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

SiOC fiber obtained at 1000 °C

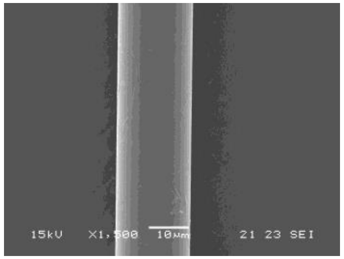


$$\sigma > 1.5\,GPa$$

base solution (Portland cement)

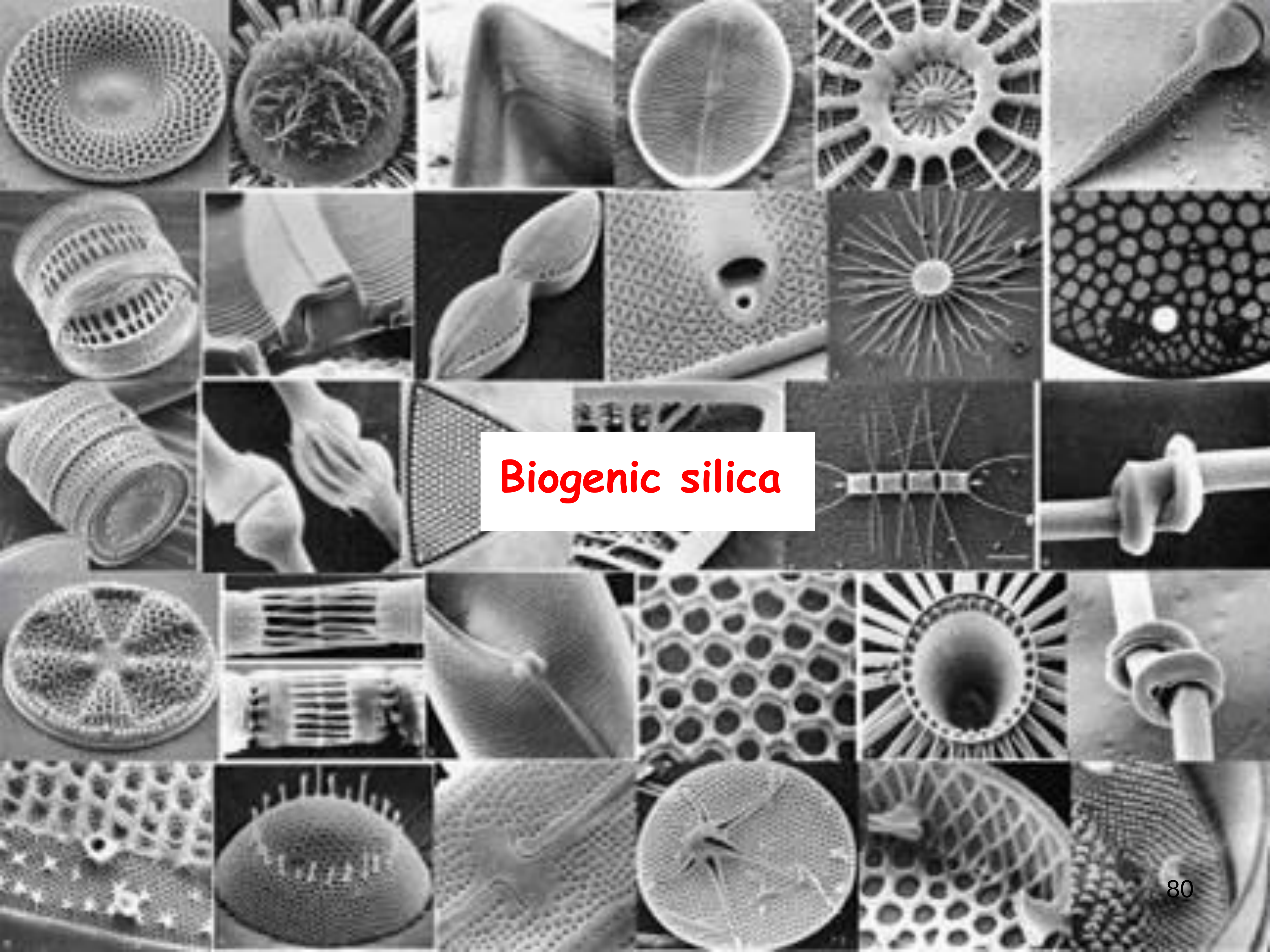


SiO_2



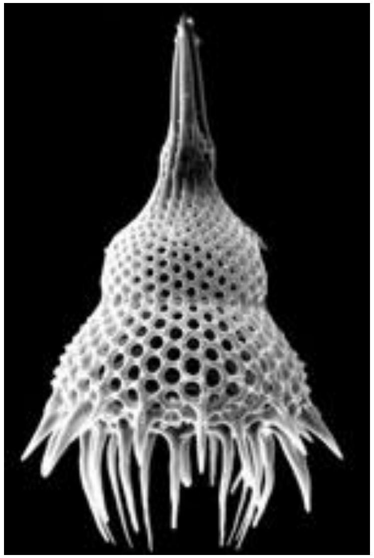
SiCO

G.D. Sorarù, S. Dirè. A. Berlinghieri, “Procedimento per la produzione di fibre di ossicarburo di silicio”, Domanda Italiana di Brevetto per Invenzione Industriale, N. TO2002A000887, 2002.

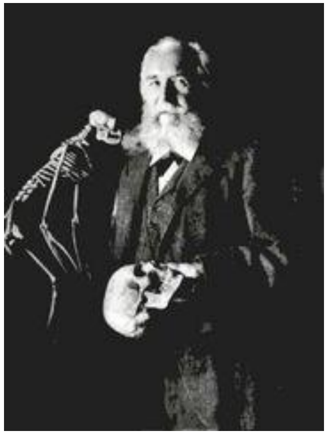


Biogenic silica

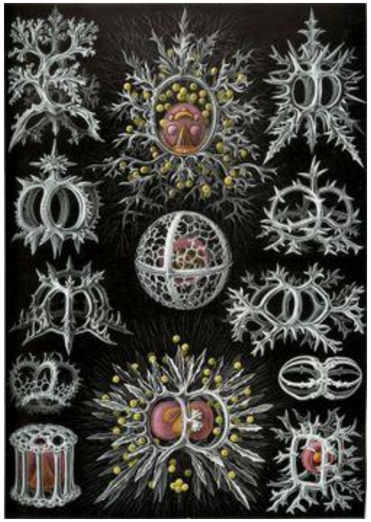
Radiolaria



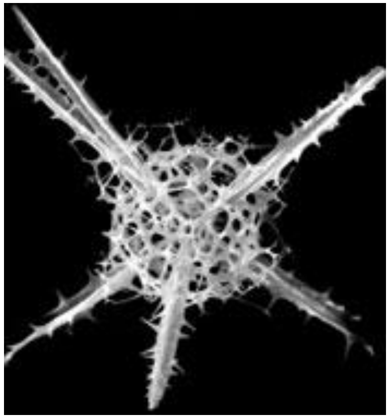
Lamprocyclas maritalis



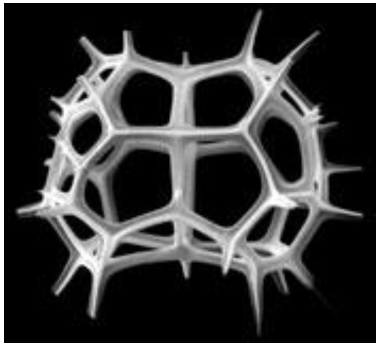
E. Haekel (1834-1919)



Kunstformen der Natur (1904)



Rhizoplegma boreale

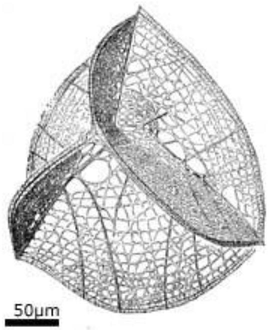


Lophospyris pentagona

protozoa {
- cell
- siliceous skeleton

⇒ radial symmetry

Shapes



Callimitra agnesae

(V,E,F)

(12,30,20)

icosaedron

Platon
427-348 av. JC

(4,6,4)

tetraedron

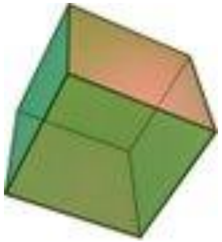
(20,30,12)

dodecaedron

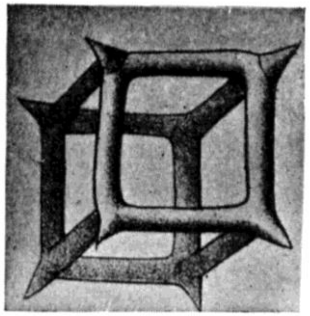
(6,12,8)

octaedron

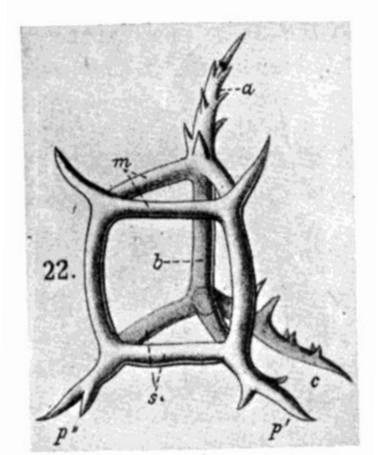
(8,12,6)



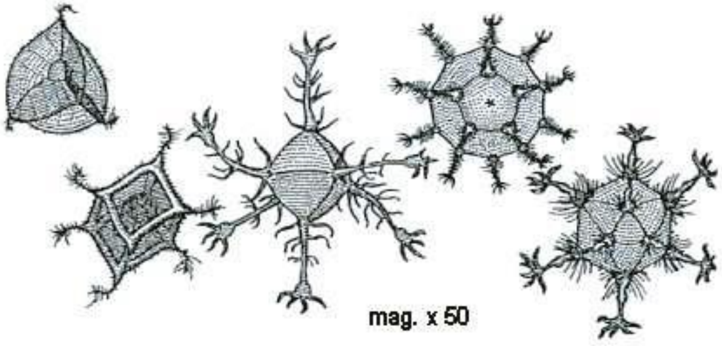
cube



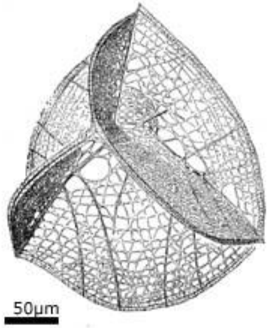
Lithocubus geometricus



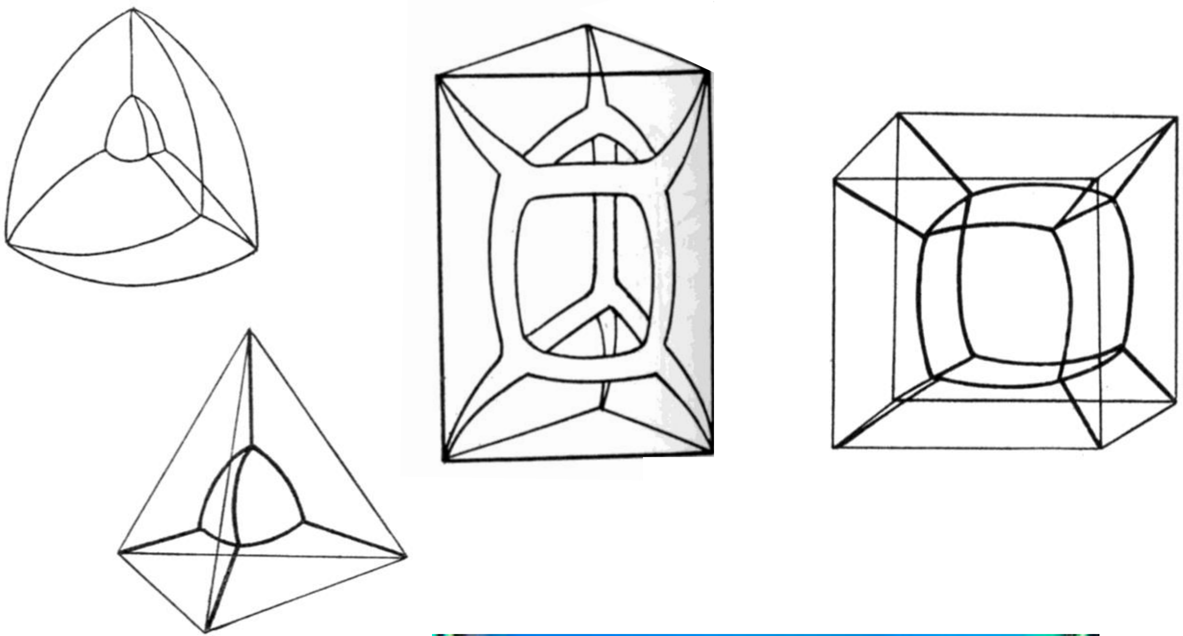
Prismatium tripodium

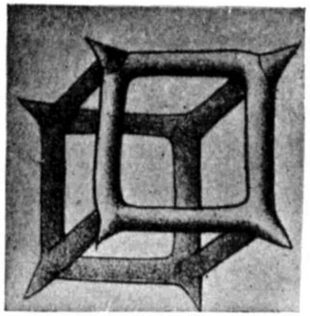


Shapes and soap bubbles

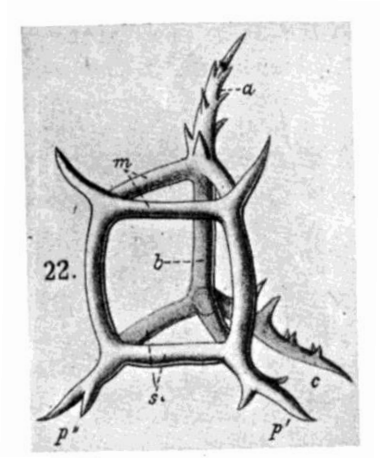


Callimitra agnesae

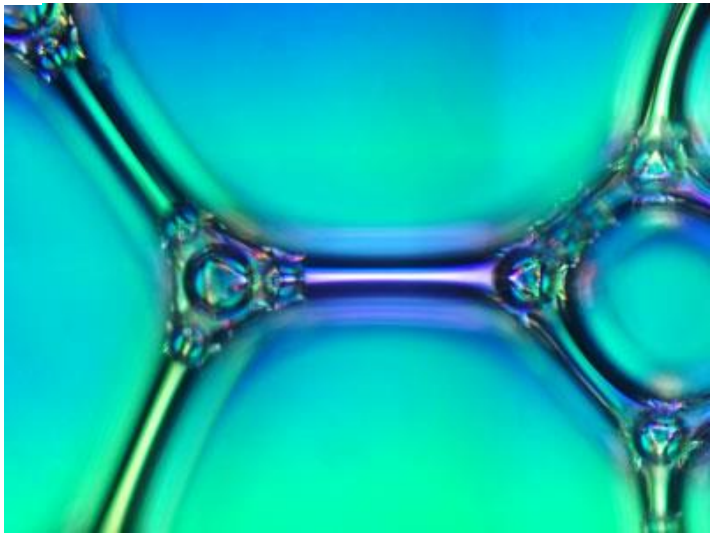




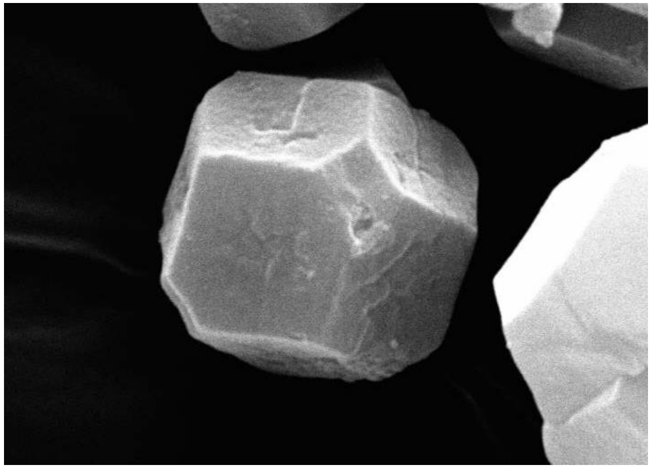
Lithocubus geometricus

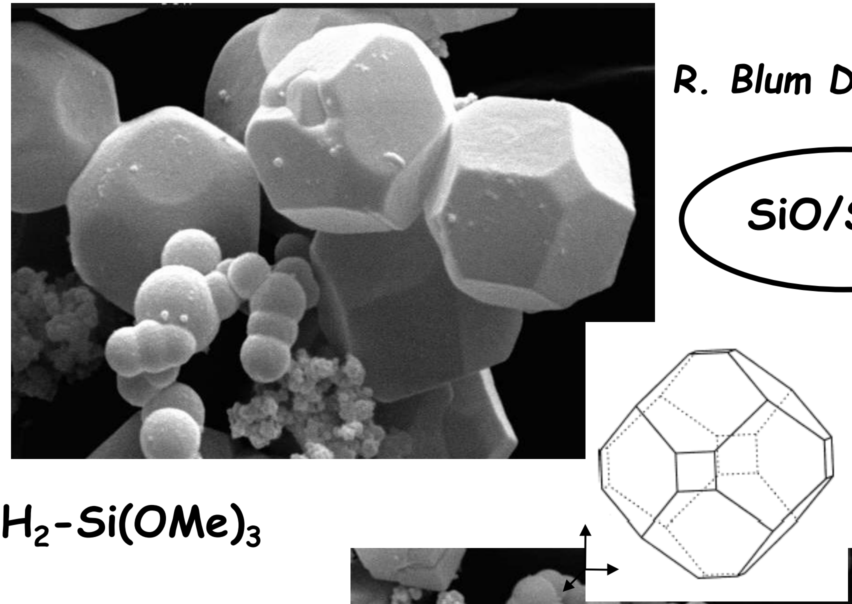


Prismatium tripodium



Silicon oxycarbide



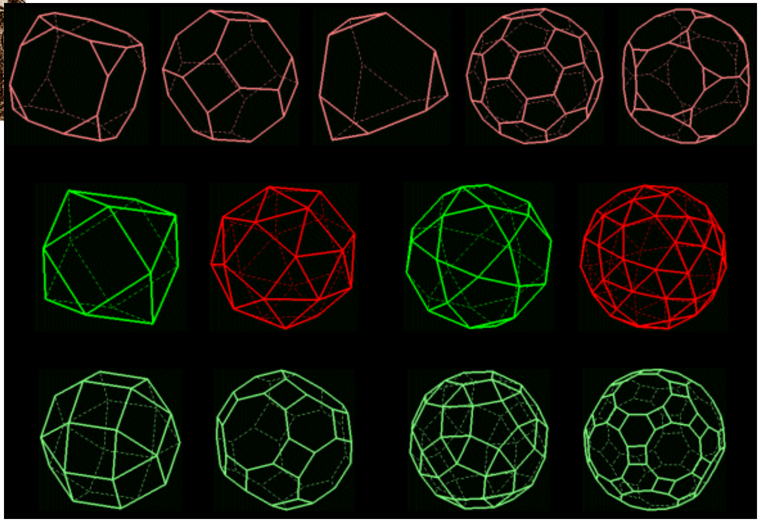


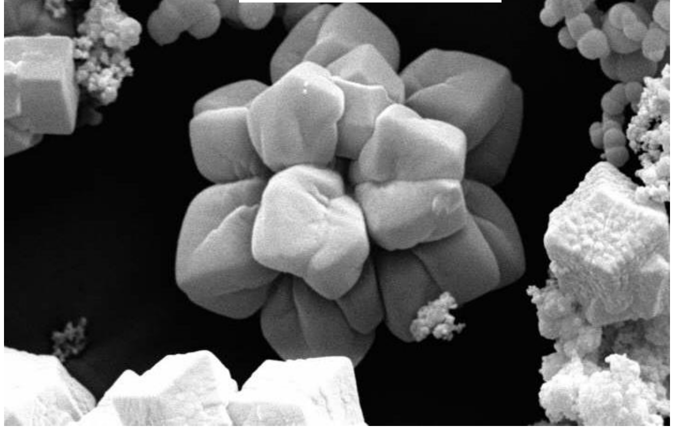
R. Blum DEA Paris 6

SiO/SiC

$(MeO)_3Si-CH_2CH_2-Si(OMe)_3$

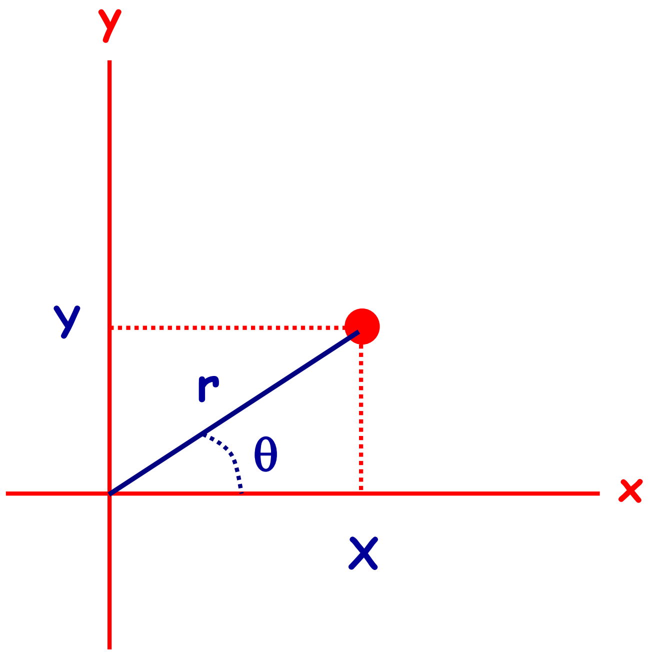
CTAC





~ 1μm (10^{-6} m)

Towards mathematics!



parametrization

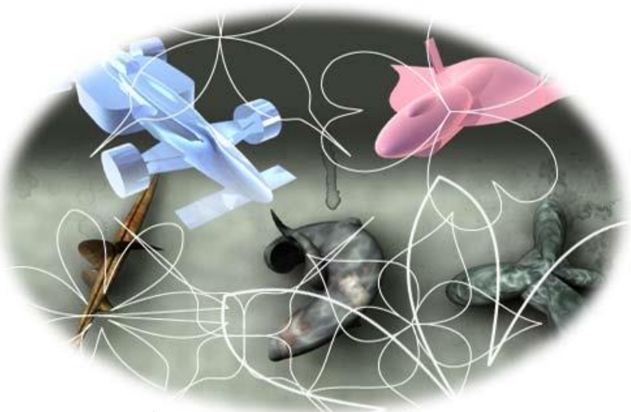
↓

r(θ)

J. Gielis superformula

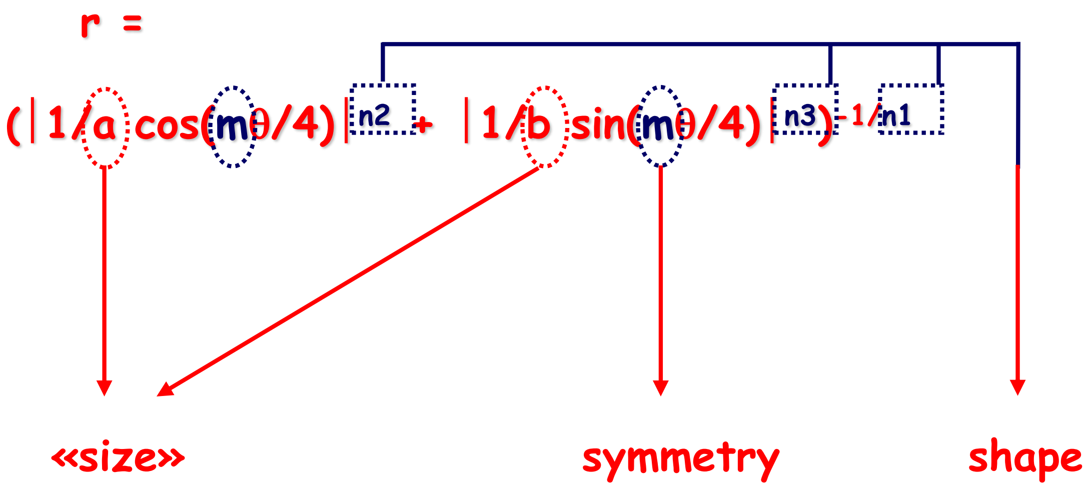
Am. J. Botany, 90, 2003, 333

... Shapes of things to come



$$r = \left(\left|\frac{1}{a}\cos(m\theta/4)\right|^{n2} + \left|\frac{1}{b}\sin(m\theta/4)\right|^{n3}\right)^{-1/n1}$$

Meaning of the parameters

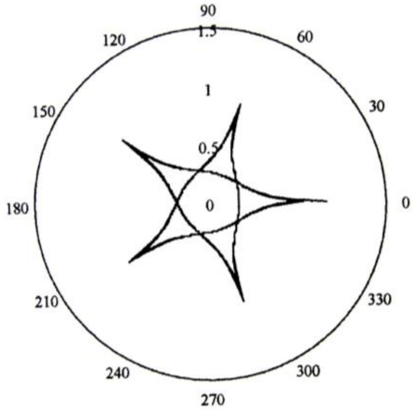


$$r = \left(\left| 1/a \cos(m\theta/4) \right|^{n2} + \left| 1/b \sin(m\theta/4) \right|^{n3} \right)^{-1/n1}$$

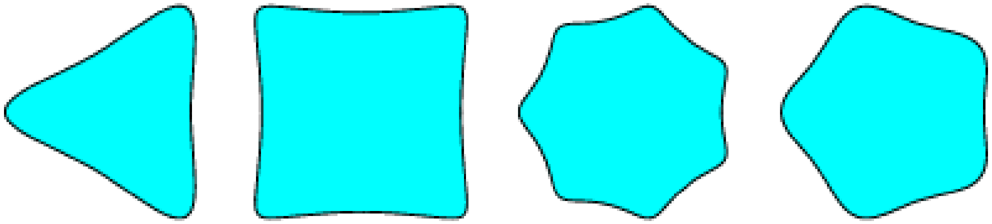
«size»

symmetry

shape

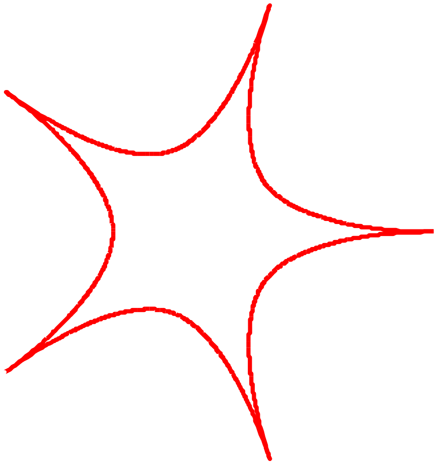


Nuphar luteum Scrophularia nodosa Equisetum raspberry



Rose sepals

m = 5

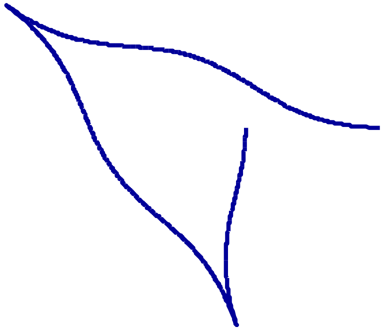


θ∈[0,2π]

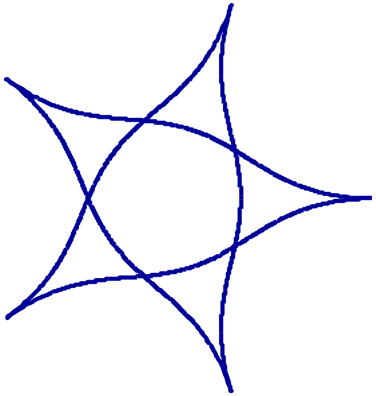
0,5 0,5 0,5

n1 n2 n3

m = 5/2

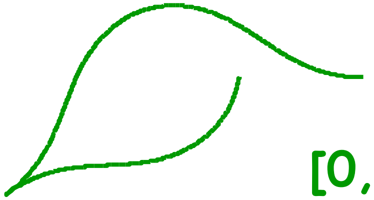


[0,2π]

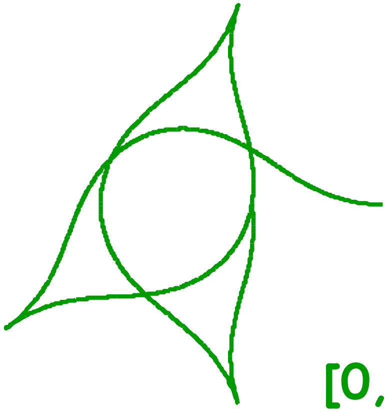


[0,4π]

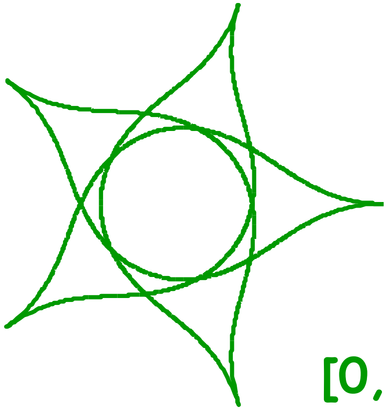
m = 5/3



[0,2π]

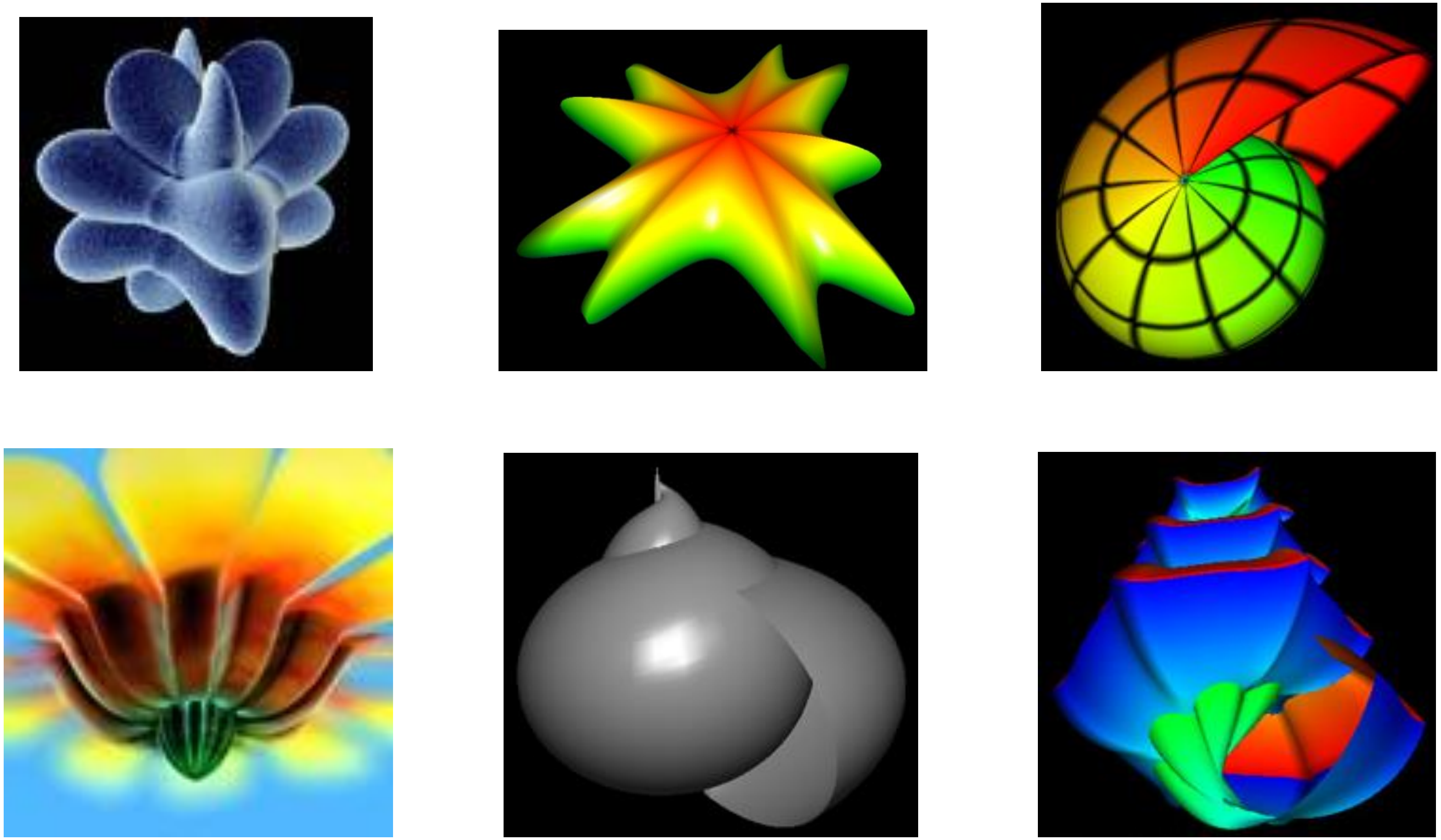


[0,4π]



[0,6π]

Extension to 3D images

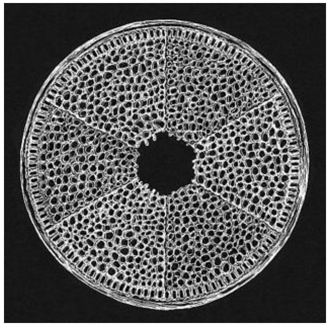


Genicap Supergraphx @

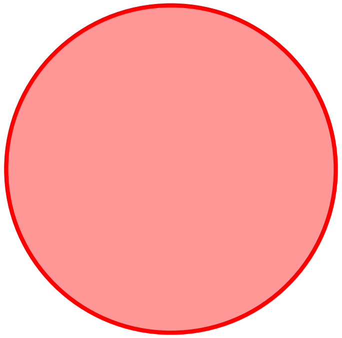
3D Shape Explorer

P. Bourke, Australia

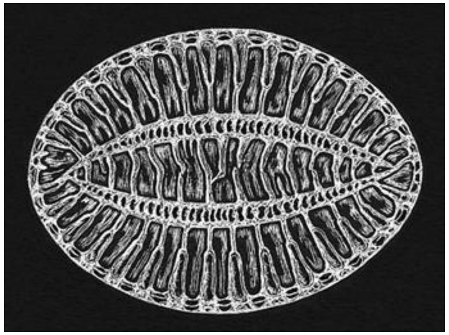
Back to sea organisms: diatoms



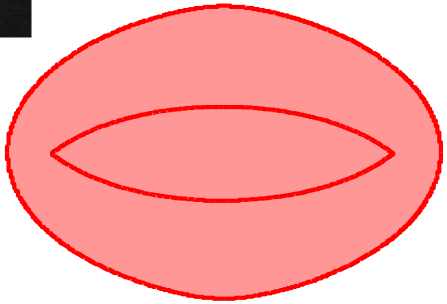
Actinotychus senarius



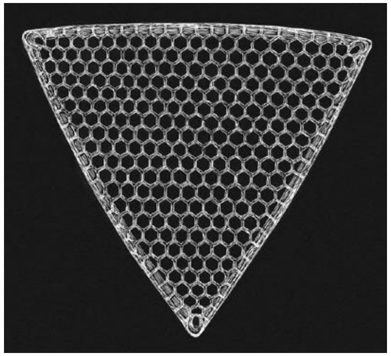
m = 0



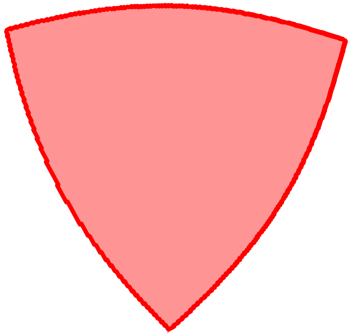
Surirella fastuosa



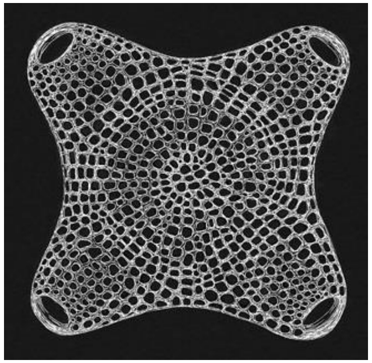
m = 2



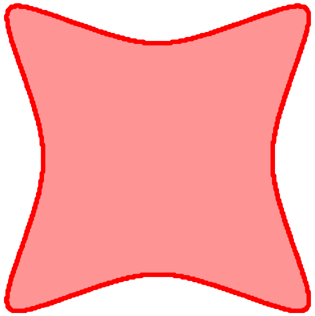
Triceratium favum



m = 3



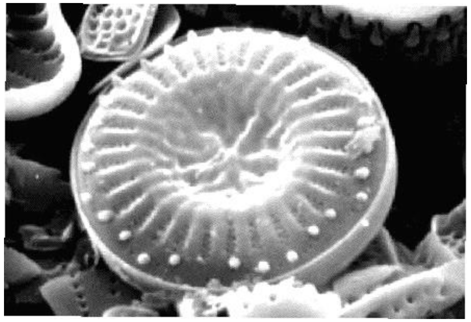
Biddulphia antediluviana



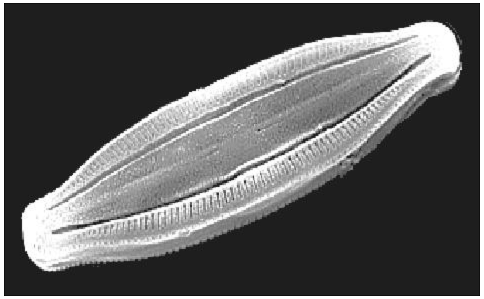
m = 4

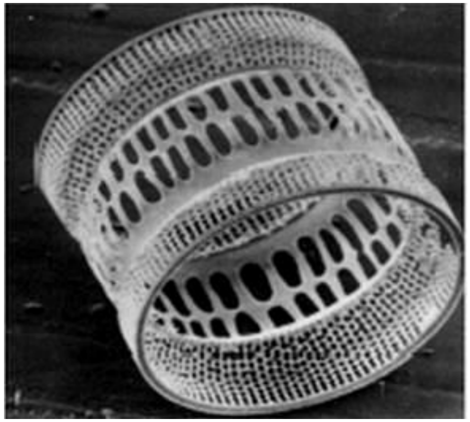
Diatoms

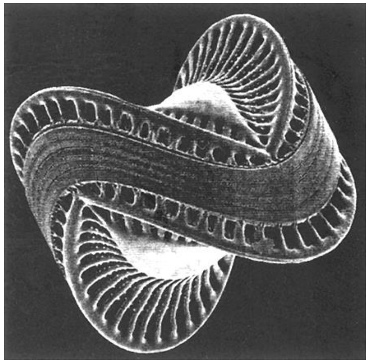
...micro-organisms living in the sea plankton.. ➡ silica glass from aqueous solution!



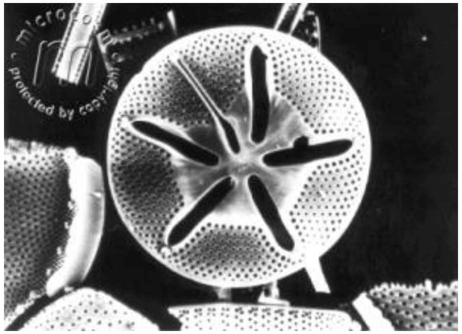
amorphous silica







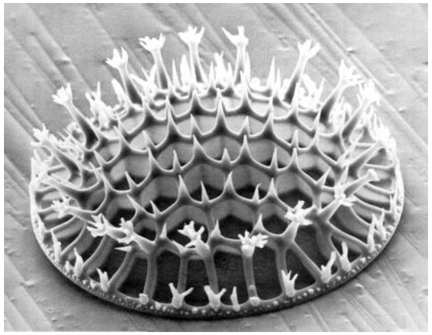
unicellular algae
in a silica cage



strong (protection)

transparent (photosynthesis)

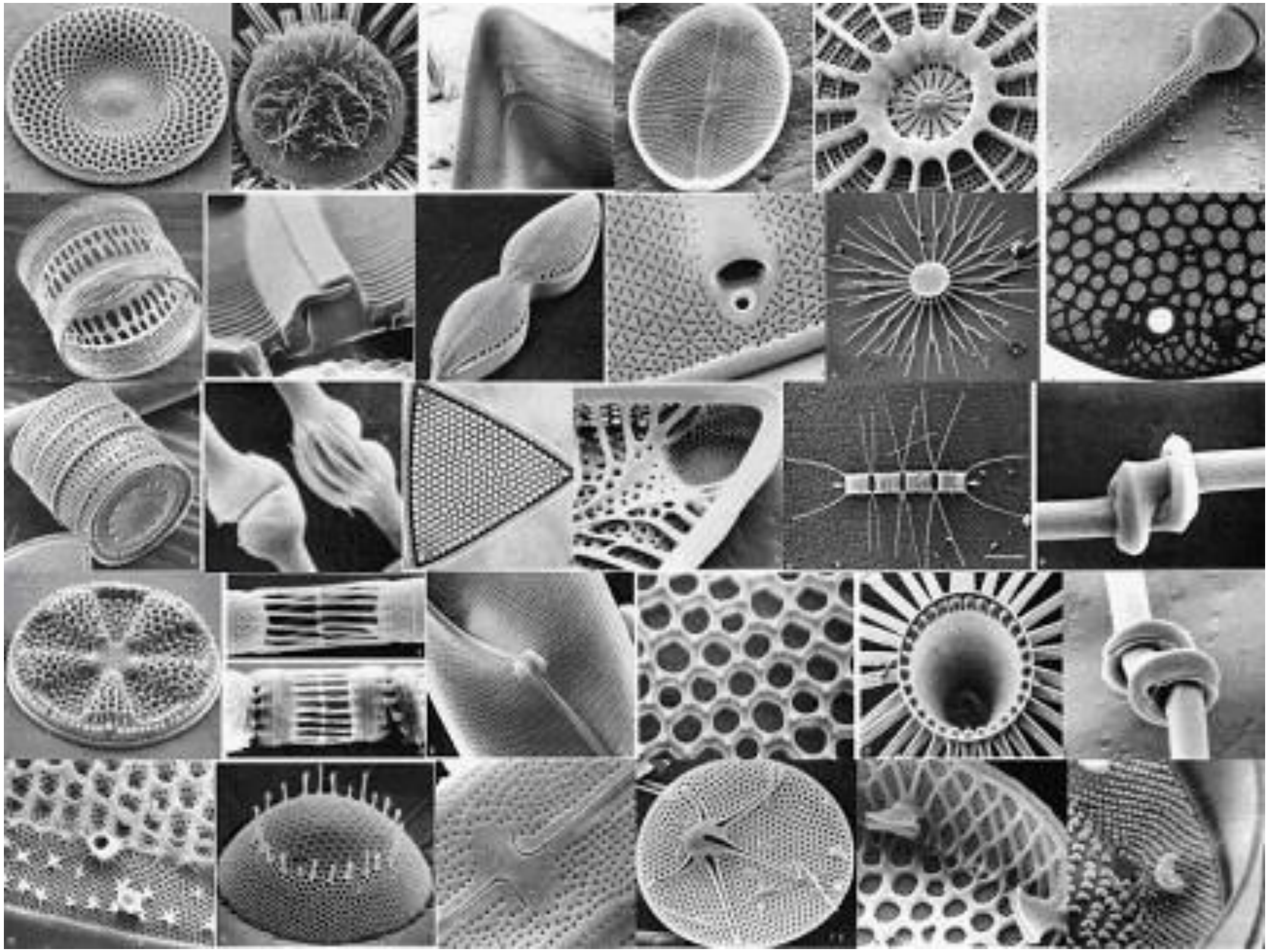
porous (metabolism)



J. Livage, T. Coradin

Variety of shapes

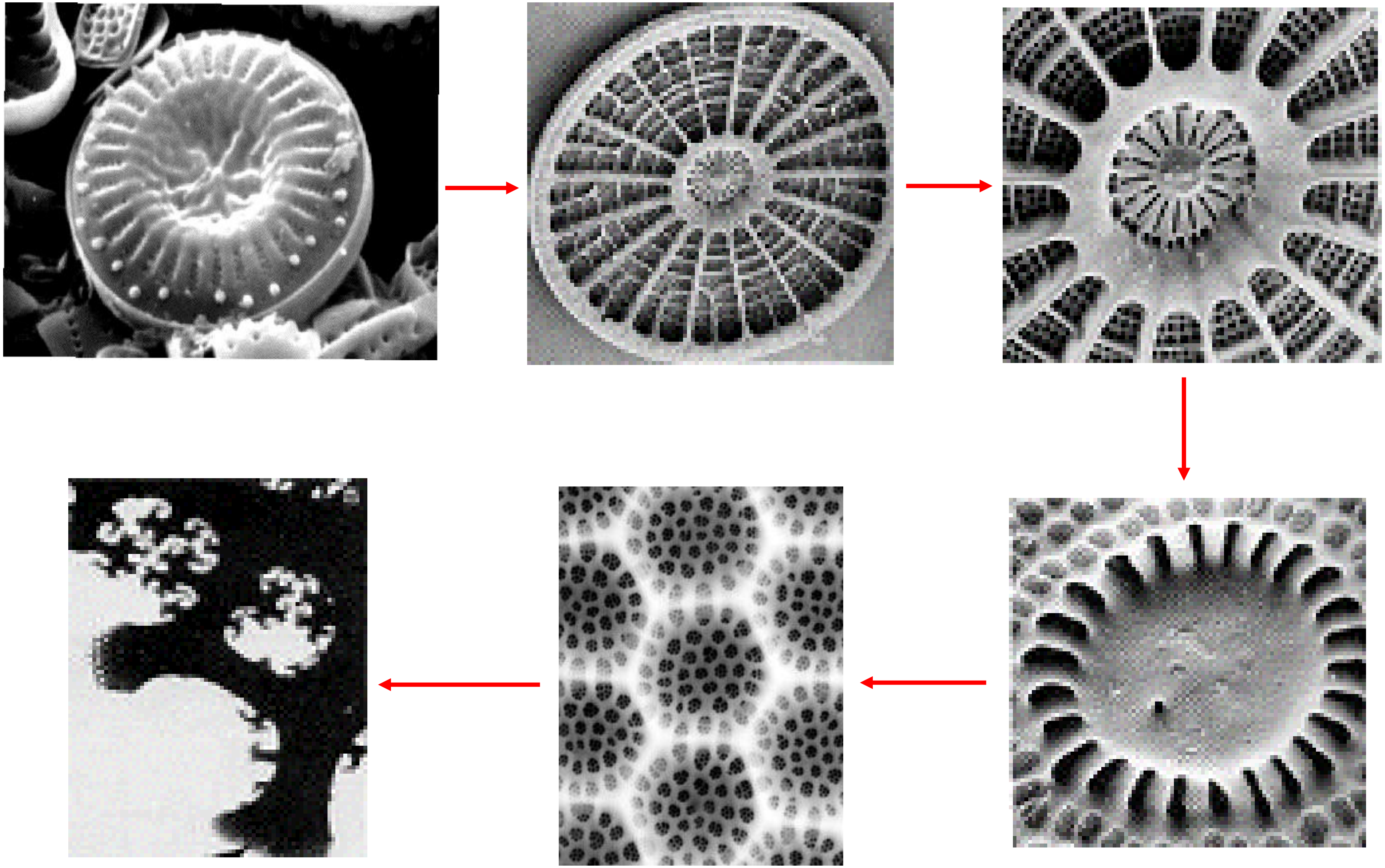
25 % of whole CO_2 via photosynthesis!



≈ 50.000 species

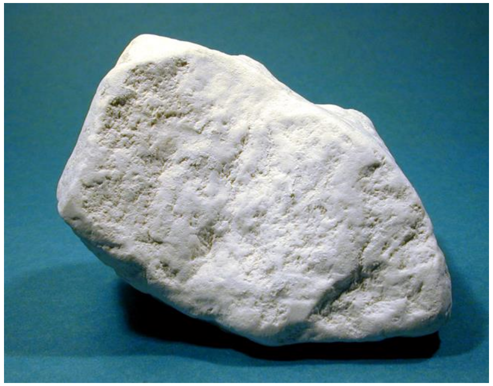
Hierarchical porous materials

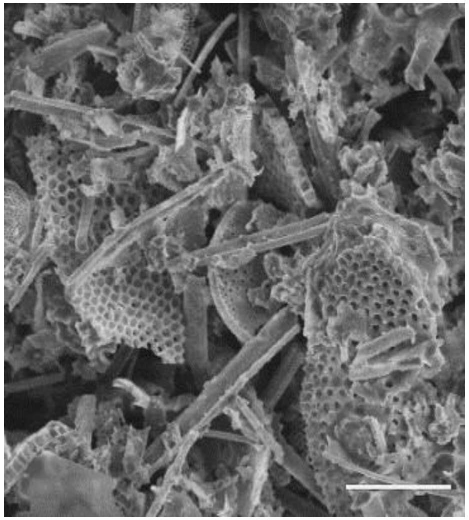
starting from µm...



...to nm range!

Diatoms as porous materials





filtration

absorption

catalysis

…

Solid phase extraction purification of DNA

US Patent Issued on April 11, 1995

Claims

What is claimed is:

1. A method for purifying DNA from solution in the absence of chaotropes which comprises:

a) adding to the solution (i) a hydrophilic surface selected from the group consisting of celite diatoms, silica polymers, magnesium silicate, silicon nitrogen compounds, aluminum silicates, silica dioxide, glass fiber and nitrocellulose, and (ii) a water soluble organic solvent selected from the group consisting of 80-100% isopropanol, 80-100% propanol, 95-100% ethanol, 100% acetonitrile, and mixtures consisting essentially of 20-80% of each of at least two alcohols selected from the group consisting of isopropanol, propanol and ethanol;

Silica in plants

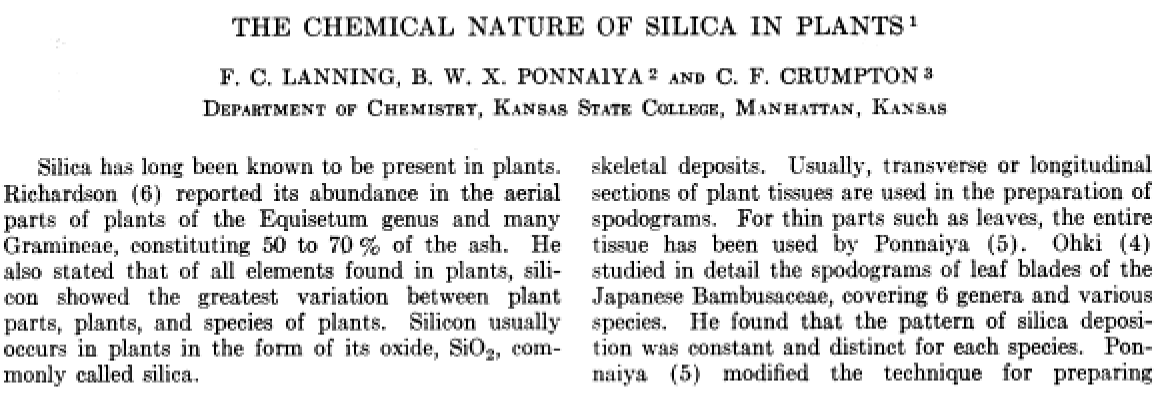
bamboo

hardness of bamboo:

combination of lignin fibers and silica (up to 5%!)

leaf (G > 1000)

Characterization of silica in plants



THE CHEMICAL NATURE OF SILICA IN PLANTS[1]

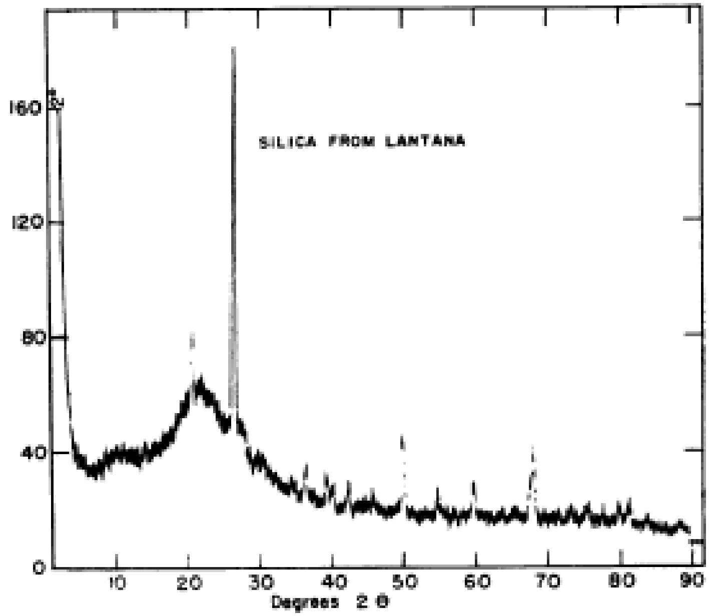
F. C. LANNING, B. W. X. PONNAIYA[2] AND C. F. CRUMPTON[3]
DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE, MANHATTAN, KANSAS

Silica has long been known to be present in plants. Richardson (6) reported its abundance in the aerial parts of plants of the Equisetum genus and many Gramineae, constituting 50 to 70 % of the ash. He also stated that of all elements found in plants, silicon showed the greatest variation between plant parts, plants, and species of plants. Silicon usually occurs in plants in the form of its oxide, SiO_2, commonly called silica.

skeletal deposits. Usually, transverse or longitudinal sections of plant tissues are used in the preparation of spodograms. For thin parts such as leaves, the entire tissue has been used by Ponnaiya (5). Ohki (4) studied in detail the spodograms of leaf blades of the Japanese Bambusaceae, covering 6 genera and various species. He found that the pattern of silica deposition was constant and distinct for each species. Ponnaiya (5) modified the technique for preparing

in: Plant Physiol. 1958

silica particles (corn leaf)



powder XRD of silica from *lantana* (leaf, stem)

Experimental – enjoy!....

spinel structure AB_2O_4 with
A: 2+ and B: 3+

normal spinels: A^{2+} (Td), B^{3+} (Oh)
inverse spinels: A^{2+} and ½ B^{3+} (Oh), ½ B^{3+} (Td)

Magnetite Fe_3O_4
($Fe^{2+}Fe^{3+}{}_2O_4$)

ferrofluid in the presence of
a magnet