4. Carbon Group

Content

Gruppe
14 or IVA

6 C	*prehistoric*
14 Si	*1824*
32 Ge	*1886*
50 Sn	*antiquity*
82 Pb	*antiquity*
114 Fl	*1998*

„Tetreles“

4.1 Occurrence

Carbon Exists in Its Elemental (gediegen) Form as Diamond or Graphite, whilst Si, Ge, Sn and Pb Almost Exclusively Occur in Oxidic and Sulphidic Ores. (Rarely in Elemental Form)

Carbon	$C_x(sp^2)$	**Graphite**
	$C_x(sp^3)$	**Diamond**
	C_{60}, C_{70}, C_{74}	**Fullerenes (in soot)**
	$CaCO_3$	**Lime, marble, chalk**
Silicon (silex)	SiO_2	**Silica**
latin: pebble	**Silicate and alumosilicate**	
Germanium (germania)	Ag_8GeS_6	**Argyrodite**
latin: Germany	$Cu_6FeGe_2S_8$	**Germanite**
Tin (stannin)	SnO_2	**Cassiterite**
latin: Zinnkies	Cu_2FeSnS_4	**Stannite**
Lead (plumbum)	PbS	**Galena**
latin: lead	$PbCO_3$	**White lead ore**




4.2 Properties

Whereas Diamond Shows Typical Behaviour of a Pure Non-Metal, Pb Is Solely Metallic

	C	Si	Ge	Sn	Pb
Atomic Number	6	14	32	50	82
Electronic configuration	[He] $2s^2 2p^2$	[Ne] $3s^2 3p^2$	[Ar] $3d^{10} 4s^2 4p^2$	[Kr] $4d^{10} 5s^2 5p^2$	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$
Electronegativity	2.5	1.7	2.0	1.7	1.6
Ionisation energy [eV]	11.3	8.1	7.9	7.3	7.4
$E_{bonding\ enth.\ X\text{-}X}$ [kJ/mol]	330	225			
$E_{bonding\ enth.\ X\text{-}O}$ [kJ/mol]	358	465			
$E_{bonding\ enth.\ X\text{-}H}$ [kJ/mol]	416	322			

Oxidation states: +2,+ 4, -4 (C) ... +2,+ 4

The stability of the oxidation state +4 decreases with increasing atomic number, whilst the stability of the +2 state increases ⇒ increase in oxidation strength of the +4 state

CO is a reductive agent — CO_2 is stabile

PbO_2 is a oxidising agent — PbO is stabile

4.3 Allotropic Carbon Modifications

Diamond

- Cubic crystal system (zincblende type)
- sp^3-hybridisation, CN = 4
- d_{C-C} = 155 pm
- High band gap E_g = 5.4 eV, isolator
- Hardest material known
- Density = 3.51 g/cm^3
- High thermal conductivity ~ $2{\cdot}10^3$ Wm^{-1}K^{-1}

Graphite

hexagonal crystal system

sp^2-hybridisation, CN = 3

d_{C-C} = 141 pm, d_{layer} = 335 pm

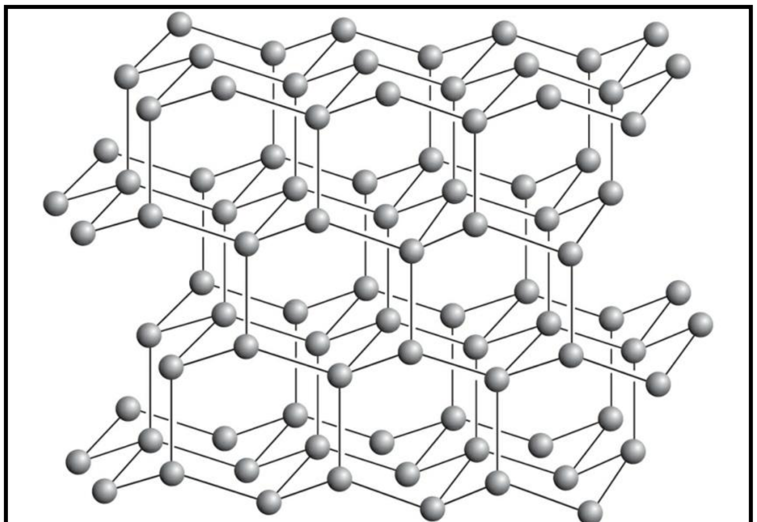
small band gap, electronic conductor

easy to cleave layers

density= 2.26 g/cm^3

good thermal conductivity

annual production 2020 ~ 10 t natural and 3000 t artificial diamond (US Geol. Survey)



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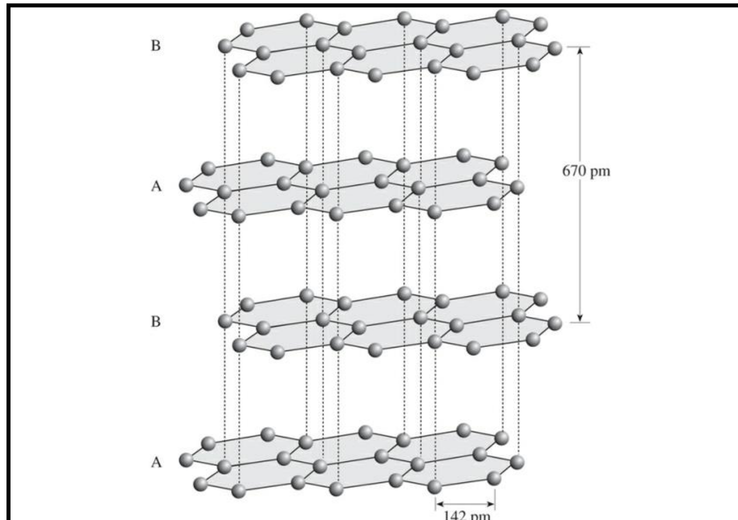

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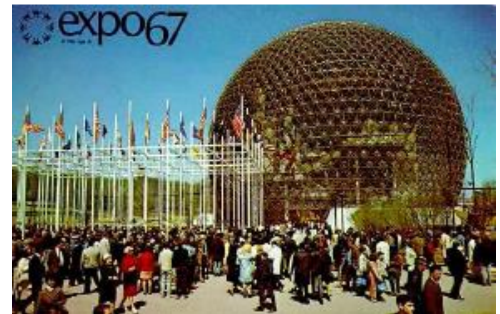
4.3 Allotropic Carbon Modifications

Fullerenes

Leonardo da Vinci (1452 -1519) was the first who constructed capped icosahedrons with 60 edges

In 1954, Richard Fuller Buckminster patented the geodetic dome as a roof construction



The so called Euro-football is made up from 20 white hexagons and 12 black pentagons

Timetable Fullerenes

1966 Postulation of carbon hollow spheres

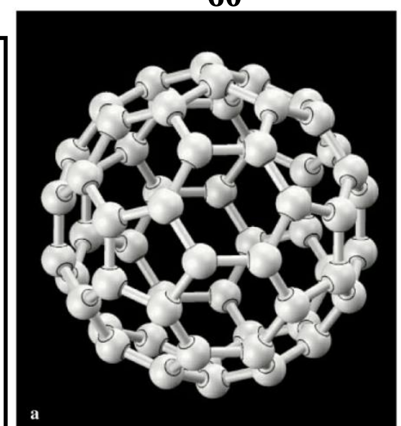
1970 Theoretical prediction of C_{60} molecule

1985 Proof of C_{60} by Laser experiments on graphite in a He-flow at 2500 °C

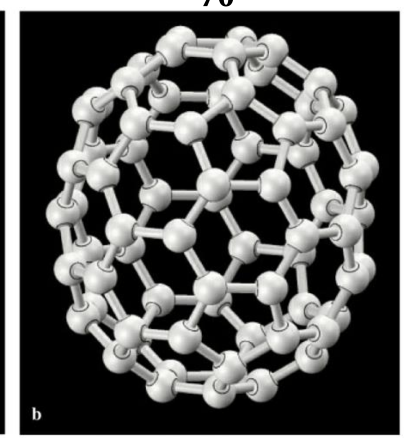
1990 Synthesis of quantitative amounts of C_{60} and C_{70}

1996 Nobel price for chemistry for the discovery

C_{60}



C_{70}



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4.4 Synthesis and Chemical Behaviour

Technical Methods for the Preparation and Behaviour Against Acids and Bases

Carbon (diamond)

- **High-pressure synthesis: 50-100 kbar, 1500-1800 °C, Fe/Co/Ni-catalyst**
- **Diamond and graphite are stable against non-oxidising acids and bases**

Silicon (diamond-like structure)

Synthesis:

1. **Electro-thermal reduction:** $SiO_2 + 2\,C \rightarrow Si + 2\,CO$ at 2000 °C
2. **Purification by distillation:** $Si + 3\,HCl \rightarrow HSiCl_3 + H_2 \rightarrow Si + 3\,HCl$
3. **Floating Zone Melting Process** From silica to ultra pure silicon (→ presentations)

Properties

- $Si + 2\,NaOH + H_2O \rightarrow Na_2SiO_3 + 2\,H_2$
- **Does not react with acids (despite its negative standard potential) ⇒ passivation**

4.4 Synthesis and Chemical Behaviour

Technical Methods for the Synthesis and Behaviour Against Acids and Bases

Germanium (diamond-like structure)

Synthesis:
1. $GeO_2 + 4\ HCl \rightarrow GeCl_4 + 2\ H_2O$
2. $GeCl_4 + 2\ H_2O \rightarrow GeO_2 + 4\ HCl$
3. $GeO_2 + 2\ H_2 \rightarrow Ge + 2\ H_2O$

Tin (grey α-modification crystallises in diamond-like structure)

Synthesis: $SnO_2 + 2\ C \rightarrow Sn + 2\ CO$

Properties: reacts with acids and bases

- $Sn + 2\ HCl \rightarrow SnCl_2 + H_2$
- $Sn + 4\ H_2O + 2\ OH^- \rightarrow [Sn(OH)_6]^{2-} + 2\ H_2$

Lead (cubic close packing)

Roast reduction process:	$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$	“Roast”
	$2\ PbO + 2\ CO \rightarrow 2\ Pb + 2\ CO_2$	“Reduction”
Roast reaction process:	$3\ PbS + 3\ O_2 \rightarrow PbS + 2\ PbO + 2\ SO_2$	“Roast”
	$PbS + 2\ PbO \rightarrow 3\ Pb + SO_2$	“Reaction”

4.5 Technical Applications

Carbon

- C_{sp}^{3} Diamond: cutting tools, jewellery, axle boxes
- C_{sp}^{2} Graphite: lubricant, electrode material, pencil

Silicon, Germanium

- Si: Semi-conductor, solar cells, photo diodes, Si chemistry (silicones)
- Ge: Semi-conductor, IR-detectors, phosphors ($Mg_2Ge_2O_{11}F_2:Mn^{4+}$), glass fibres
  Scintillators ($Bi_4Ge_3O_{12}$)

Tin, Lead

- Sn: tin plate, crockery (historical), soft solder (40 – 70% Sn, 30 - 60% Pb)
- Pb: lead pipe, lead characters, ammunition, petrol additive, anti-rust paint
  (Mennige Pb_3O_4), PVC-stabiliser
  Lead accumulators
  Cathode: $Pb + 2\ SO_4^{2-} \rightarrow PbSO_4 + 2\ e^-$
  Anode: $PbO_2 + SO_4^{2-} + 4\ H_3O^+ + 2\ e^- \rightarrow 2\ PbSO_4 + 2\ H_2O$
  Demands: 400 – 450 A over 30 s!

4.6 Inorganic Carbon Compounds

Carbides Result From a Combination of Carbon with Either Metals or Semi-Metals, whereby Carbon Is the More Electronegative Partner

Miner's lamp (Wikipedia)

Covalent carbides

Silicon carbide: $SiO_2 + 3\,C \rightarrow SiC + 2\,CO$ at 2200 °C

Boron carbide: $B_{13}C_2$

Salt-like carbides

Acetylides: $CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + H\text{-}C{\equiv}C\text{-}H$

Methanides: $Al_4C_3 + 12\,H_2O \rightarrow 4\,Al(OH)_3 + 3\,CH_4$

Allenides: $Li_4C_3 + 4\,H_2O \rightarrow 4\,LiOH + H_2C{=}C{=}CH_2$

$$CaO + 3\,C \rightarrow CaC_2 + CO$$

$$\downarrow N_2$$

$$CaCN_2 + C$$

(Nitrolime)

$$\downarrow 3\,H_2O$$

$$CaCO_3 + 2\,NH_3$$

Metallic carbides

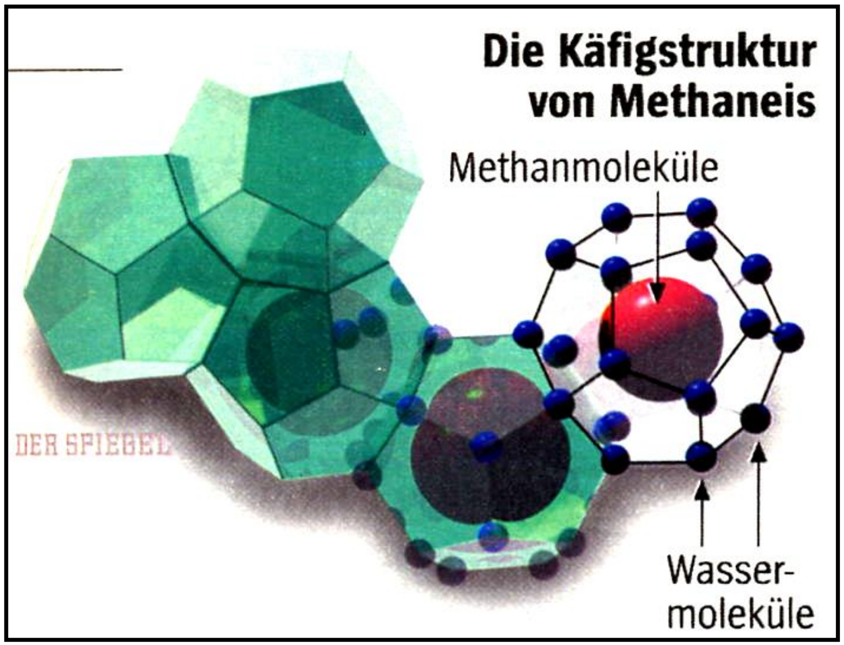
Intercalation compounds, where carbon atoms are incorporated into the crystal structure of the metal:

- Tungsten carbide WC ⇒ cutting tools
- Iron carbide (cementite) Fe_3C ⇒ micro crystals in steel

4.6 Excursion: Methane Hydrate

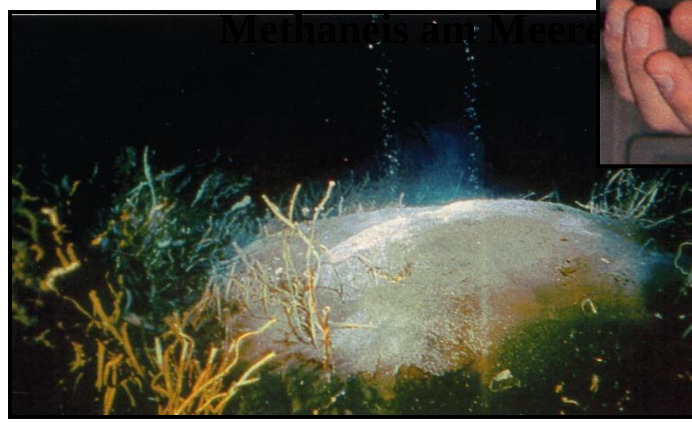
CH_4 Forms with H_2O Under High Pressure at 0 – 5 °C so-called Clathrates, whereby Methane Molecules Are Enclosed by Water Molecules (Intercalation Compounds)

⇒ In such form, ca. 10 – 15 trillions of tons of methane rest under the permafrost soils and in the deep sea (more carbon than in all fossil fuel deposits combined)



Burning chunk of methane ice

Methane ice at seabed



4.6 Inorganic Carbon Compounds

Halide and Sulphur Compounds

Compounds	CF_4	CCl_4	CBr_4	CI_4	COF_2	$COCl_2$	$COBr_2$
T_m [°C]	-187	-23	90	171(dec.)	-114	-128	
T_b [°C]	-128	77	190	-	-83	8	65
Hydrolyses to CO_2 and	*"stable"*	HCl	HBr	HI	HF	HCl	HBr

- $COCl_2$ (phosgene) has been used as war gas during WWI and is a precursor compound for a range of chemicals: acid amides, isocyanates, and so on
- Halogenated carbohydrates react explosively with alkaline metals!

<u>Carbon disulphide</u>

Synthesis:

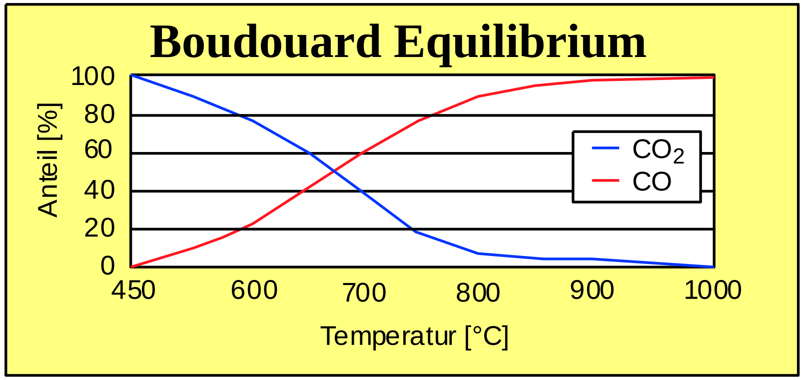
$C(s) + S(g) \rightarrow CS_2(g)$

Properties:

- Good solvent for fats, oils, sulphur and phosphor, transparent, highly toxic
- Oxidation: $CS_2(g) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g)$
- Trithio carbonate form.: $3\ CS_2(g) + 6\ NaOH(aq) \rightarrow 2\ Na_2CS_3(s) + Na_2CO_3(s) + 3\ H_2O(l)$

4.6 Inorganic Carbon Compounds

Compounds with Oxygen



CO $C + CO_2 \rightarrow 2\ CO$

$HCOOH \rightarrow H_2O + CO$ in conc. H_2SO_4

CO_2 $C + O_2 \rightarrow CO_2$ Combustion

$CaCO_3 \rightarrow CaO + CO_2$ Calcination

C_3O_2 $HOOC\text{-}CH_2\text{-}COOH \xrightarrow[-78\,°C]{P_4O_{10}} 2\ H_2O + C_3O_2$

malonic acid

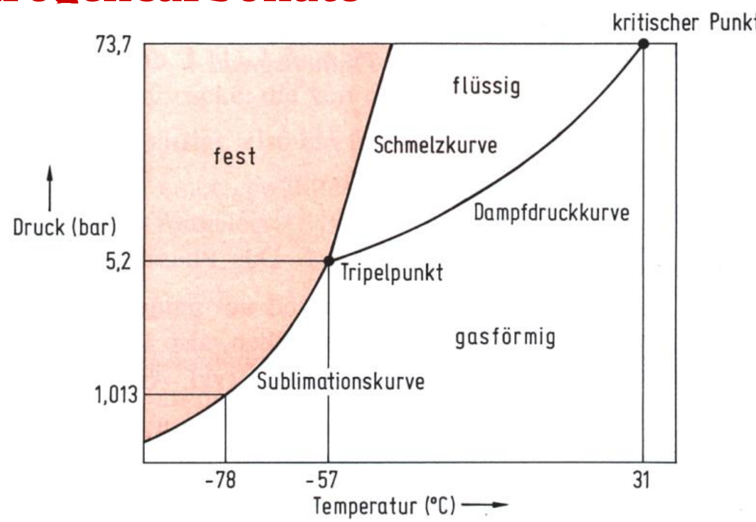
"anhydride of malonic acid"

→ polymerises at room temperature

Oxide	T_m[° C]	T_b [° C]	υ[cm^{-1}]	$d_{C\text{-}C}$ [pm]	$d_{C\text{-}O}$ [pm]
C≡O	-199	-192	2145	-	113
O=C=O	-	-78(sublimed)	1318, 2349	-	116
O=C=C=C=O	-111	7	2200, 2290	128	116

4.6 Inorganic Carbon Compounds

Carbon Dioxide, Kohlensäure, carbonates and Hydrogencarbonate



CO_2 can be liquefied easily and sublimes at normal pressure at -78 °C

At room temperature and normal pressure, 0.9 l CO_2 can be dissolved in 1 l H_2O:

$CO_2 + H_2O \rightleftharpoons CO_2{\cdot}H_2O \rightleftharpoons$ „H_2CO_3“ pK = 3.2

CO₂ hydrate → CO_2 hydrate, carbonic acid

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$ $pk_{s1} = 3.5$

hydrogen carbonate

$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$ $pk_{s2} = 10.4$

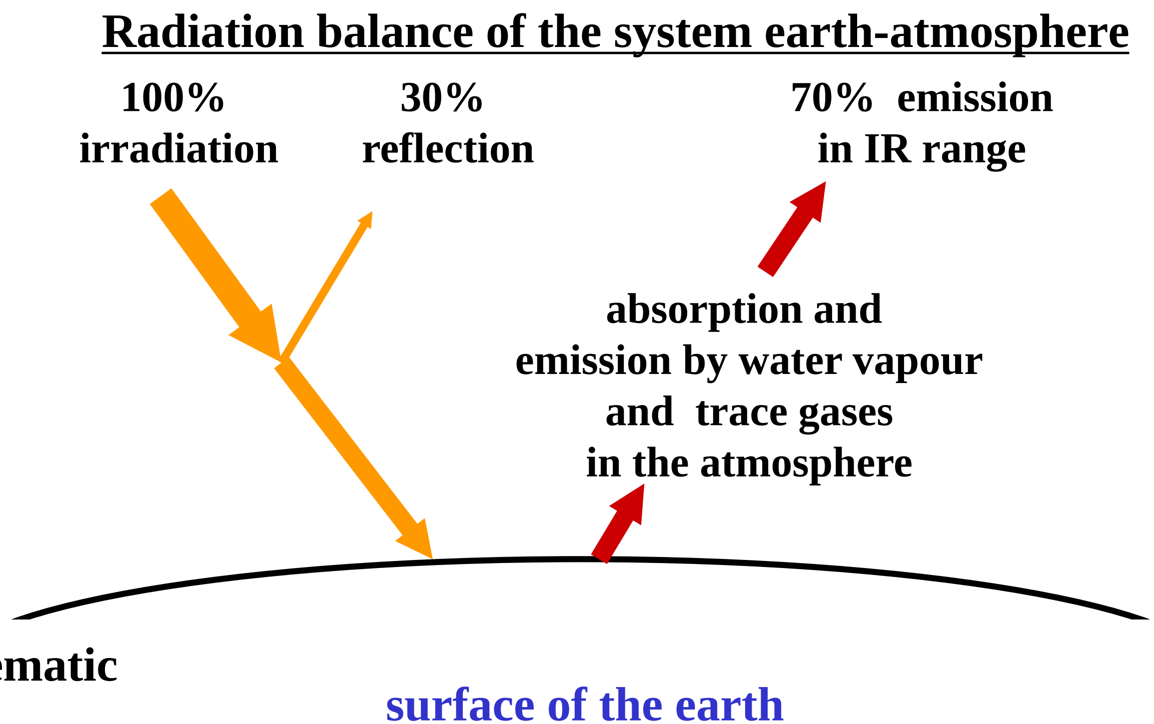
carbonates

Carbonate	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
Mineral name	magnesite	calcite, aragonite	strontianite	witherite
Decomposition at [° C]	540	908	1270	1420

4.7 Green House Effect

Green House Effect: Reabsorption of IR Radiation Emitted by Black Bodies Through Small Polyatomic Molecules (CO_2, H_2O, CH_4, N_2O, O_3, SF_6, NF_3) in the Atmosphere

	Venus	Earth	Mars
N_2 [%]	3.5	78.1	2.7
Ar [%]	< 0.001	0.93	1.6
O_2 [%]	< 0.001	20.95	0.15
H_2O [%]	< 0.001	variable	0.03
CO_2 [%]	96.5	0.040	95.3
p [bar]	92	1.0	0.007
T [° C]	482	15	-55



H_2O und CO_2 are the most problematic green house gases at the moment

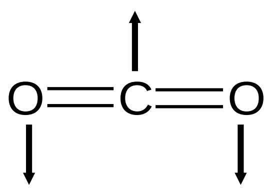
(CH_4, O_3, N_2O, CFCs ~ 10% share of green house effect)

Over the course of the history of the earth, CO_2 has been almost completely removed from atmosphere through the formation of carbonate sediments and fossil fuels!

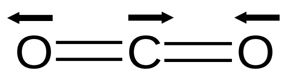
4.7 Green House Effect

Due to the Green House Effect, the Average Temperature of the Earth's Surface Is About 33 ° C Higher Than One Would Assume From the Radiation Equilibrium (-18 ° C)

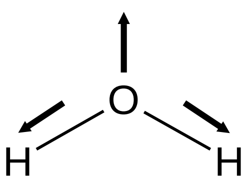
Position of the absorption bands of IR active vibrations of CO_2 and H_2O



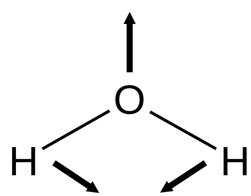
15.00 µm



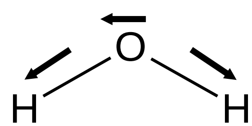
4.30 µm



2.73 µm

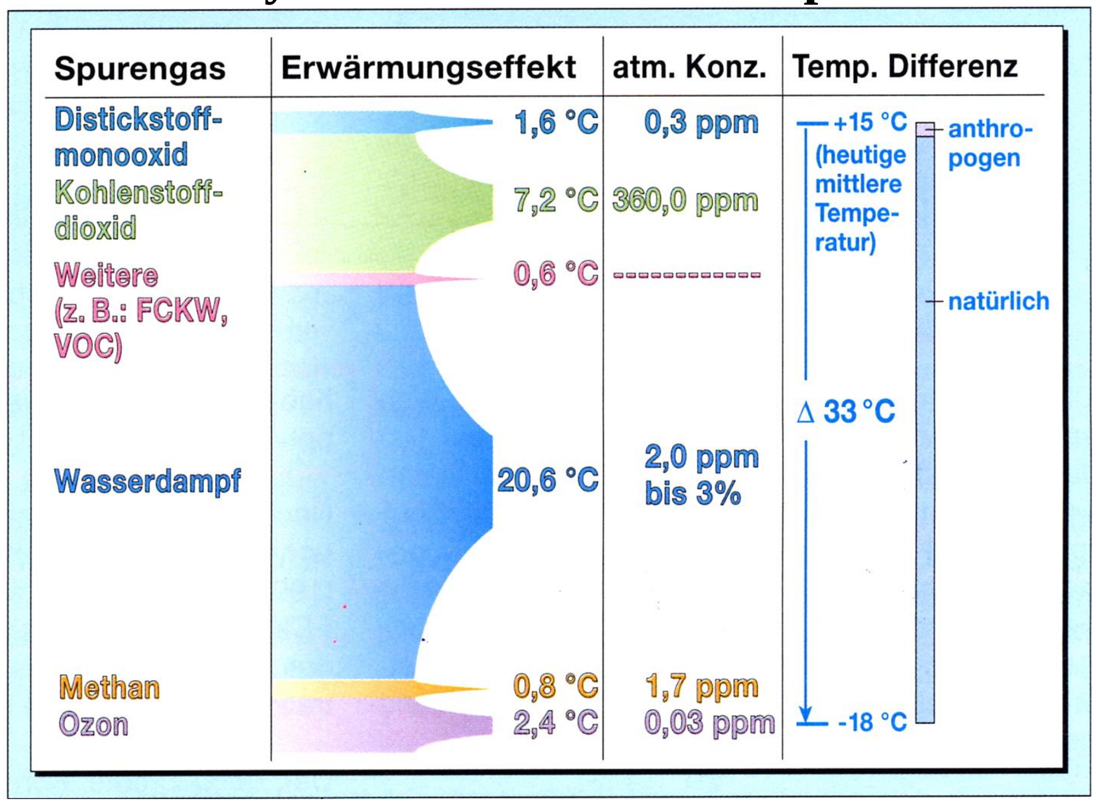


6.30 µm



2.66 µm

Green house gases relevant for the climate sorted by their effect on the temperature



4.8 Silicon Compounds

The Polymerisation of Silenes Can Only Be Prevented by Sterical Means, since the Formation Energy of a Si/Si Double Bond Is Lower Than That of Two Si/Si Single Bonds

Si/H-hydrogen compounds: silanes (and silenes)

SiH_4	Monosilane
Si_2H_6	Disilane
Si_3H_8	Trisilane
Si_4H_{10}	Tetrasilane, isotetrasilane
Si_nH_{2n+2} (n = 1-15)	Acyclic silanes
Si_nH_{2n} (n = 5, 6)	Cyclic silanes

Synthesis

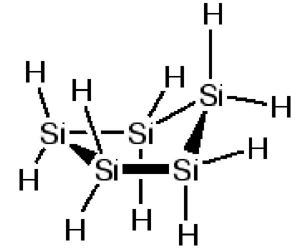
$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiAlCl_4$

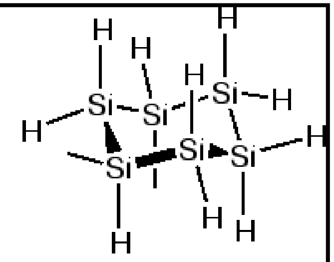
$2\ Si_2Cl_6 + 3\ LiAlH_4 \rightarrow 2\ Si_2H_6 + 3\ LiAlCl_4$

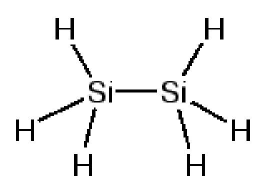
Decomposition

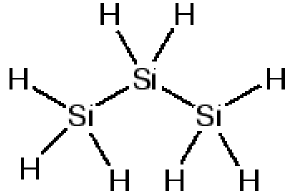
Thermal: $SiH_4 \rightarrow Si + 2\ H_2$

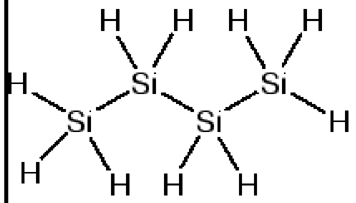
Hydrolysis: $SiH_4 + 4\ H_2O \rightarrow Si(OH)_4 + 4\ H_2$

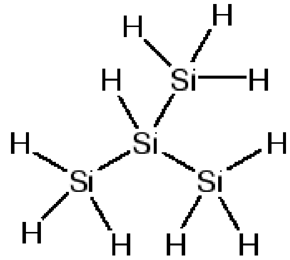

Cyclopentasilan Si_5H_{10}


Cyclohexasilan Si_6H_{12}


Disilan Si_2H_6

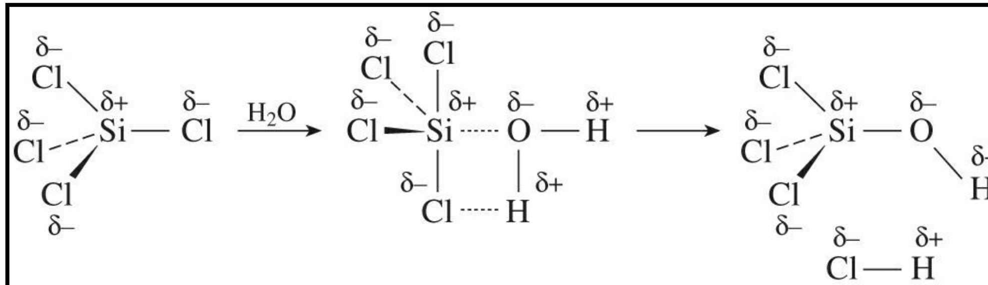

Trisilan Si_3H_8


Tetrasilan n-Si_4H_{10}


Isotetrasilan i-Si_4H_{10}

4.8 Silicon Compounds

Compounds of Silicon with Halides or Sulphur



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Silicon tetrahalide SiX_4

Synthesis: $Si + 2\ X_2 \rightarrow SiX_4$

Structure: tetrahedral

Properties:

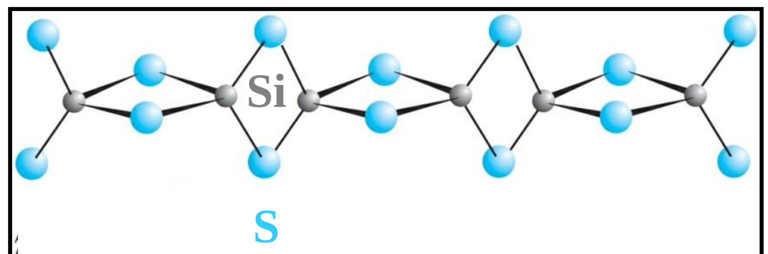
	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
T_m [°C]	-90 (1.75 bar)	-70	5	121
T_b [°C]	-96 (sublimed)	58	153	288

In contrary to carbon tetrahalides are all silicon halides subject to hydrolysis :

$SiX_4 + 2\ H_2O \rightarrow SiO_2 + 4\ HX \Rightarrow$ **Hydrolysis is enabled by empty d-orbitals**

$SiF_4 + 2\ HF \rightarrow$ „H_2SiF_6" $\Rightarrow$ **Hexafluorosilicates are stable and forms salts, e.g. $BaSiF_6$**

Silicon disulphide SiS_2



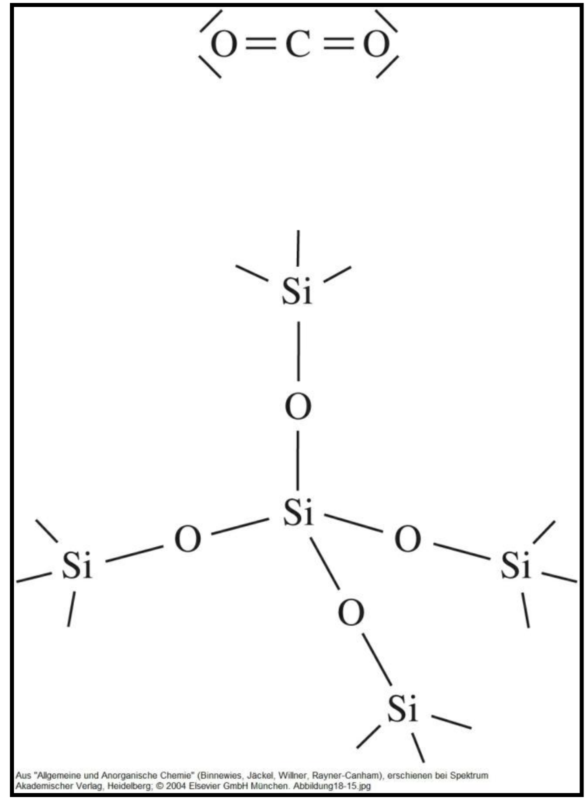
Structure: In contrary to CS_2 polymer $\Rightarrow$

Hydrolysis: $SiS_2 + 2\ H_2O \rightarrow SiO_2 + 2\ H_2S$

4.9 Silica SiO_2

Unlike in the Case of CO_2 No Double Bonds Are Formed, Due to the High Formation Energy of Si-O Single Bonds (465 kJ/mol)

⇒ SiO_2 Exists As a Extremely Stable "Polymer"



Occurrence of SiO_2 (quartz): in rocks + as a mineral

Quarzvarietät	Colour	Colour/Scattering centre
Rock crystal	transparent	-
Smoky quartz	brown	AlO_4^{4-}
Citrine	yellow-brown	Fe_2O_3 particle
Amethyst	violet	Fe^{2+}
Rose quartz	rose	Ti^{3+} + TiO_2-needles
Blue quartz	grey-blue	TiO_2-needles

Production of artificial quartz crystals of high purity

By hydrothermal synthesis at low temperatures

$$SiO_2(s) \underset{380\,^\circ C}{\overset{400\,^\circ C}{\rightleftharpoons}} SiO_2(aq)$$ in autoclave (temperature gradient)

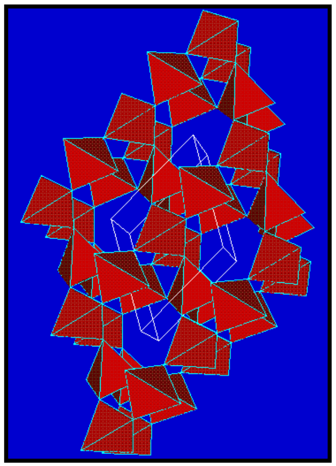
4.9 Silica SiO_2

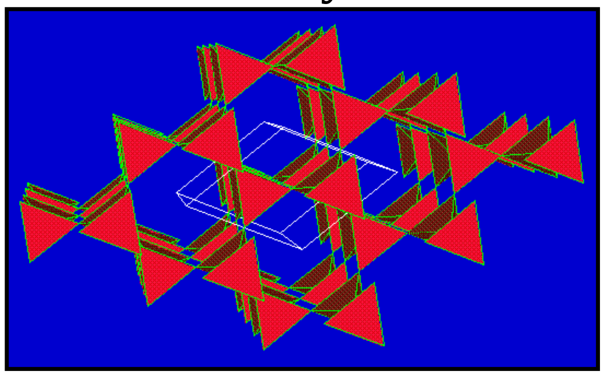
Crystalline Modifications (Polymorphism) of SiO_2

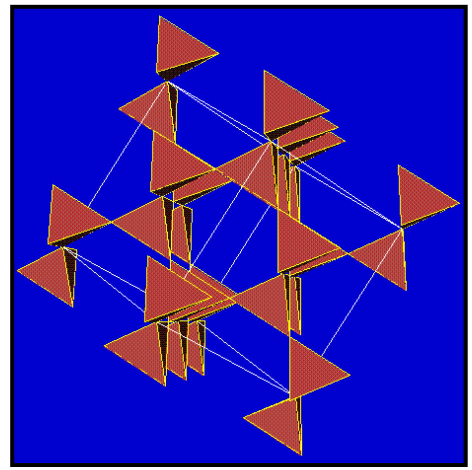
α-quartz ⇄ (573 °C) ß-quartz ⇄ (870 °C) ß-tridymite ⇄ (1470 °C) ß-cristobalite ⇄ (1725 °C) melt

ß-tridymite ⇅ (120 °C) α-tridymite

ß-cristobalite ⇅ (270 °C) α-cristobalite







trigonal — helical formation of tetrahedrons

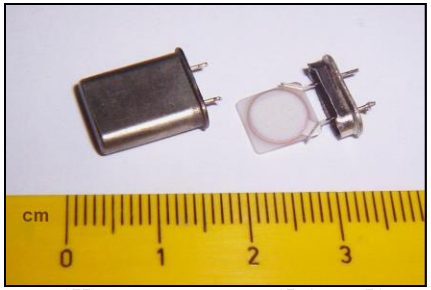
hexagonal

hexagonal (ice) — sequence of layers ABABAB

cubic (diamond) — sequence of layers ABCABCABC

4.9 Silica SiO_2

Properties and Applications



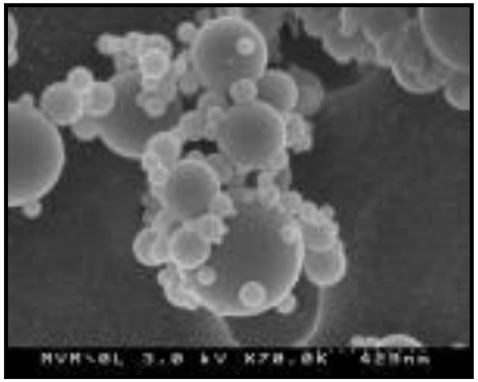
Oscill. quartz (Wikipedia)

Quartz

- Wide band gap ~ 8.8 eV (145 nm)
  ⇒ as UV-transparent quartz glass for optical components (UV lamps)
- Piezoelectric, i.e. mechanical vibrations are generated in a electromagnetic alternating field ⇒ as vibrating quartz or clock generator in watches, radios and computers

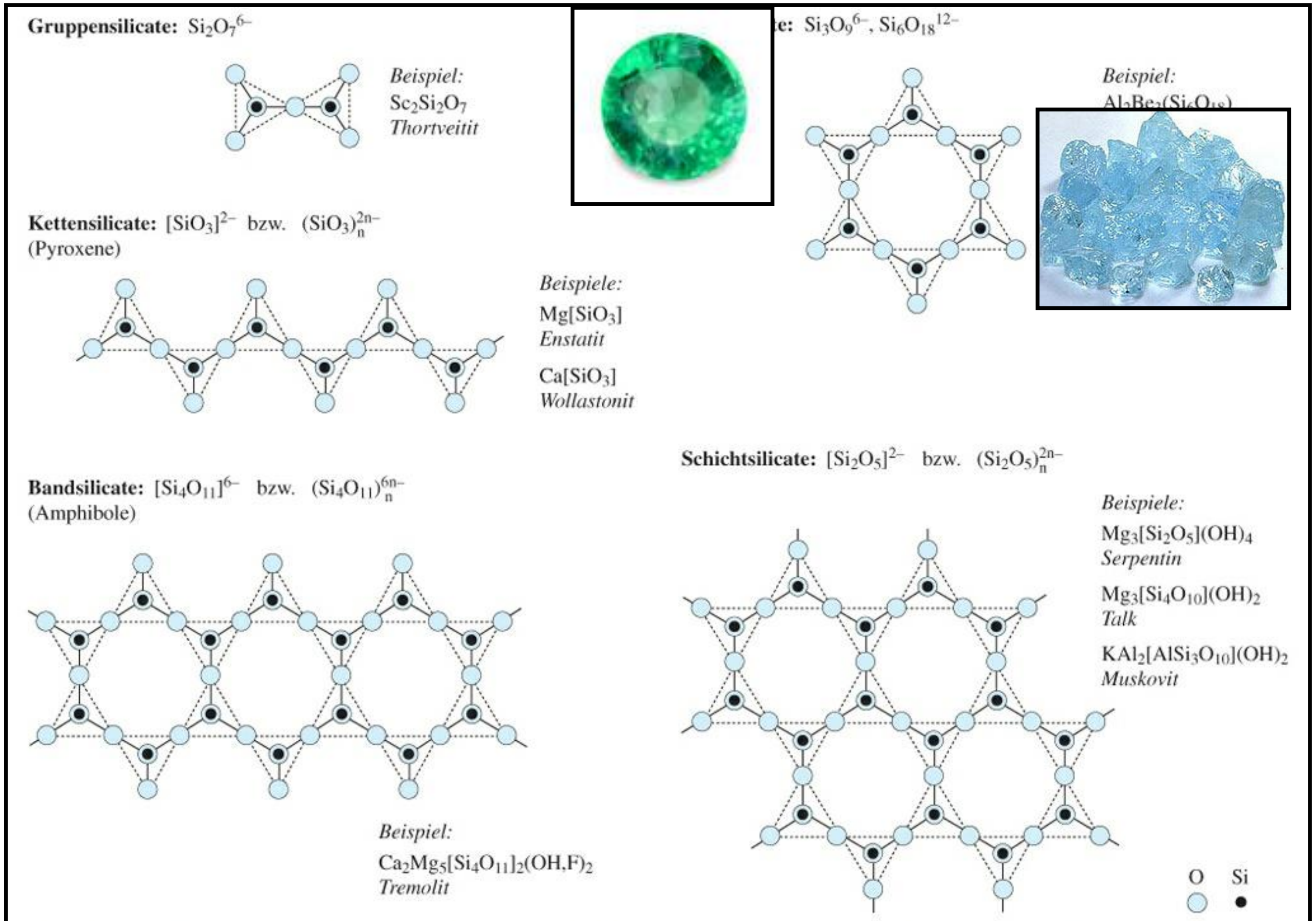
Amorphous SiO_2

- Large surface (~ 700 m^2/g) as micro-porous silicagel ($SiO_2 \cdot x\ H_2O$)
  ⇒ as desiccant
- Reactive surface through formation of hydrogen bonds between the OH groups
  ⇒ additive in suspensions and thixotropic lacquer (aerosiles)
  Synthesis via flame pyrolysis at about 1000 °C
  $2\ H_2 + O_2 + SiCl_4 \rightarrow SiO_2 + 4\ HCl$



4.10 Silicates and Alumosilicates

Silicon in Silicates is Always Coordinated in a Tetrahedral Manner (CN = 4) By Four Oxygen Atoms



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Ortho silicates

Garnet $Ca_3Al_2Si_3O_{12}$

Olivine $(Fe,Mg)_2SiO_4$

Willemite Zn_2SiO_4

Zircon $ZrSiO_4$

Ring silicates

Doped variations of beryl are aquamarine (Fe^{3+}) and emerald (Cr^{3+})

Layer silicates

Kaolinite $Al_4[Si_4O_{10}](OH)_8$

In asbestos, the layers Coil up into fibres

4.10 Silicates and Alumosilicates

To What Extend the Condensation Has Been Progressed and What Kind of Links Exist Within the Material, Can Be Deduced From the Molecular Formula (Isle, Chain/Cycle, Layer, Frame)

Ortho silicates	**$[SiO_4]^{4-}$ tetrahedron, not condensed, i.e. solely terminal O-atoms**
Chain/ring silicates	**$[SiO_3]^{2-}$ every tetrahedron is linked via 2 O atoms to the next** **$\Rightarrow [SiO_2O_{2/2}]^{2-}$**
Layer silicates	**$[Si_2O_5]^{2-}$ every tetrahedron is linked via 3 O atoms to the next** **$\Rightarrow [SiOO_{3/2}]^{1-}$**
Frame silicates	**SiO_2 every tetrahedron is linked via all 4 O atoms** **$\Rightarrow [SiO_{4/2}]^0$**

4.10 Silicates and Alumosilicates

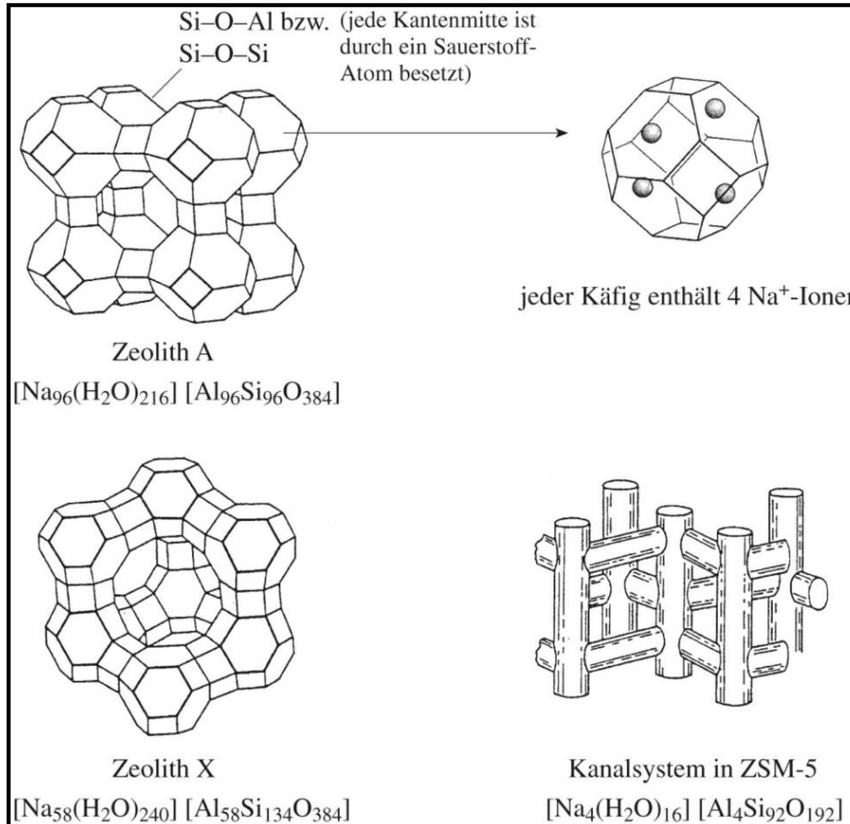
In Frame Silicates, Part of the Si^{4+}-Ions Can Be Substituted by Al^{3+}-Ions. The Charge of the Alumosilcate Frame Can Be Compensated by Alkaline or Alkaline Earth Metals in Cavities or Channels: $Me^{+}_{n}[Al_nSi_{m-n}](H_2O)_x$

⇒ Feldspars (80% the earth's crust)

Albite	$Na[AlSi_3O_8]$
Orthoklas	$K[AlSi_3O_8]$
Anorthite	$Ca[Al_2Si_2O_8]$

⇒ Zeolite (natural and artificial)

Sodalite	$Na_8[Al_6Si_6O_{24}]Cl_2$
Zeolite A	$Na_{96}[Al_{96}Si_{96}O_{384}](H_2O)_{216}$
Zeolite X (Faujasite)	$Na_{58}[Al_{58}Si_{134}O_{384}](H_2O)_{240}$



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Applications

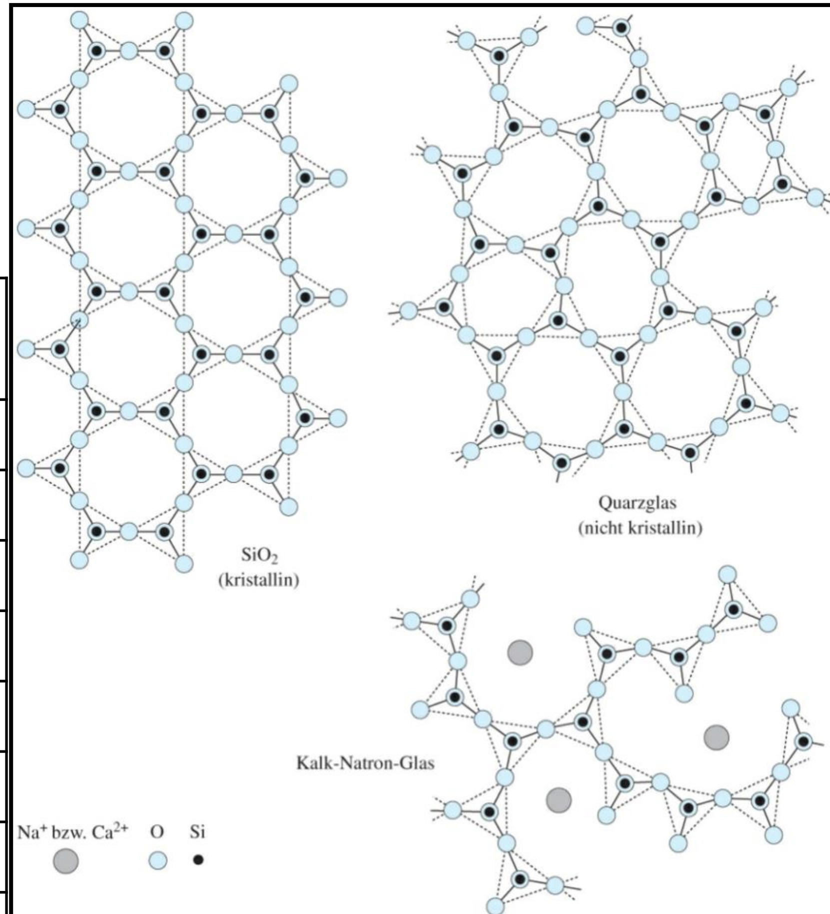
- Ion exchanger (→ presentations)
- Desiccants, filter
- Catalysts
- Latent heat accumulator

4.11 Glasses

Glasses Are Melts That Have Been Solidified Without Crystallisation (Only Close-Proximity Order, No Long-Range Order)

Basis SiO_2, T_m = 1720 ° C ⇒ Network Formers

Reduction of melting point through addition of Na_2O, K_2O, CaO etc. ⇒ Network modifiers



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<u>Composition of some glass types</u>

Component [%]	Quartz-glass	Sodium-silicate glass	Borosilicate glass	Leadsilicate glass
SiO_2	100	73	75	64
Na_2O		16	4	8
K_2O		1	2	6
CaO		5		
MgO		4		
Al_2O_3		1	1	2
PbO				20
B_2O_3			18	

4.11 Glasses

Modification of Physical Properties

- **Enhanced thermal shock resistance through**
  Addition of B_2O_3

- **Increased transparency →**
  Addition of SiO_4

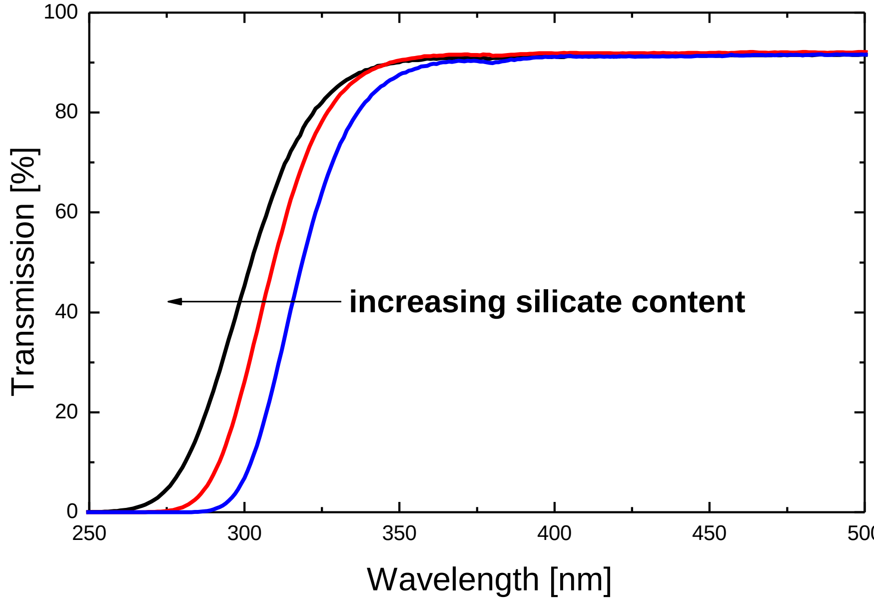
- **Higher refractive index**
  Addition of PbO/BaO/La_2O_3

- **Increased absorption of x-rays**
  Addition of BaO/SrO

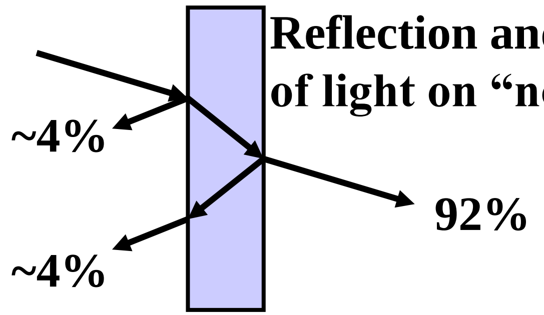
- **Colouring**
  Addition of TM-ions: V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{2+}
  Incorporation of metal clusters: Au^0, Cu^0

- **AR coating**
  Coating with nanoscale particles

Transparency of sodium silicate glasses



Reflection and transmission of light on "normal" glass



4.12 Ceramic Materials

Ceramic Materials Are Polycrystalline, Non-Metal Inorganic Materials

Clay ceramic: clay (kaolin) + quartz (SiO_2) + feldspar (→ presentations)

Glass ceramic: glasses with a well-defined amount of crystallites

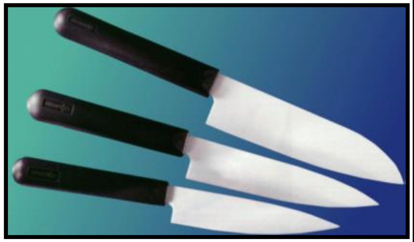
Metal ceramics: ceramics with finely distributed metal within (Co in WC-ceramics)

Ceramic components

Applications for ceramics

- Components — machines, engines, turbines (Si_3N_4)
- Electronics — capacitors, resistors ($BaTiO_3$)
- Dummy moulds — Irdengut, Steinzeug, Steingut, Porzellan (s.o.)
- Light sources — CDM-lamps (Al_2O_3)
- Tools — Knives (Al_2O_3)
- Medicine — Implants, dental filling (phosphates)

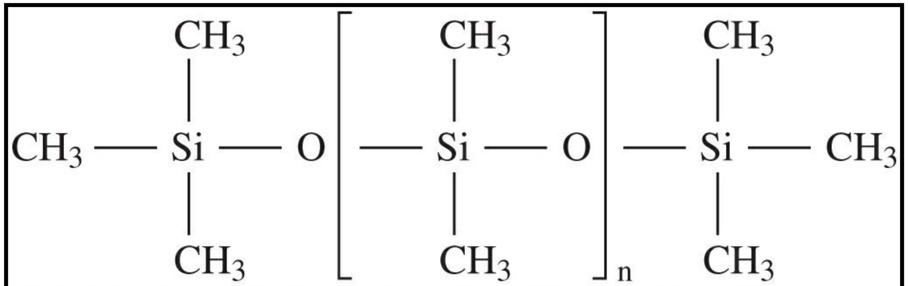
Ceramic knives



4.13 Silicones

Silicones Can Be Understood as SiO_2, Modified by Organic Functional Groups. They Are Highly Stable in Terms of Chemical and Thermal Means, since Their Si-C Bonds Are Extremely Stable

Structure



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Synthesis

Müller-Rochow-Process (→ presentations)

$$6\ RCl + 3\ Si \xrightarrow{Cu,\ 300-400\ ^\circ C} RSiCl_3 + R_2SiCl_2 + R_3SiCl \quad (R = \text{alkyl remnant } C_nH_{2n+1}\text{-})$$

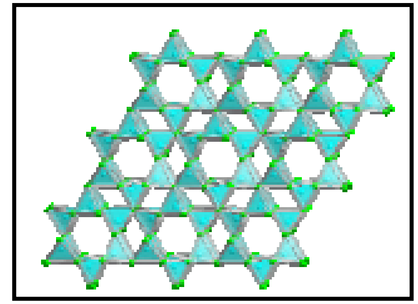
$$R_2SiCl_2 + H_2O \rightarrow R_2Si(OH)_2 + 2\ HCl \rightarrow \text{silicone} + H_2O$$

Applications

• Silicone oils	lubricants, hydraulic breaks
• Silicone rubber	tubing, gaskets, heart valves, contact lenses
• Silicone gels	implants, LEDs

4.14 Silicon Nitride and Nitridosilicates

Silicon Nitride, Si_3N_4, is an Important Ceramic Material of Low Density (ρ = 3.2 g/cm^3) But Great Hardness and is Frequently Used in Casting or Functional Ceramics



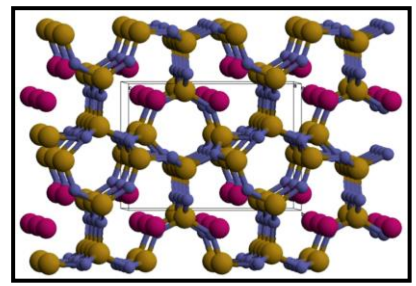
Synthesis

- **From the elements: $3\ Si + 2\ N_2 \rightarrow Si_3N_4$ at 1400 °C**
- **$3\ SiCl_4 + 4\ NH_3 \rightarrow Si_3N_4 + 12\ HCl$ at 1500 °C**
- **Carbothermal reduction: $3\ SiO_2 + 2\ N_2 + 6\ C \rightarrow Si_3N_4 + 6\ CO$**

Structure

The polymeric network structure consists of SiN_4 tetrahedrons, where every N atom links three Si atoms to one another (strong cross-linking). Nitridosilicates are derivatives of Si_3N_4:

- **$MSiN_2$ (M = Ca, Sr, Ba)**
- **$M_2Si_5N_8$ (M = Ca, Sr, Ba)** $\Rightarrow$ **structure of $Sr_2Si_5N_8$**
- **$MAlSiN_3$ (M = Ca, Sr)**
- **$MYbSi_4N_7$ (M = Sr, Ba)**



N can be terminally bound to Si or act as a linker between 2, 3 or even 4 Si atoms!

4.15 Germanium, Tin and Lead Compounds

Germanium

- **Germanes Ge_nH_{2n+2} up to n = 9 known**
- **Ge(IV) compounds are thermodynamically stable: GeO_2**
- **Ge(II) compounds are strong reducing agents but much more stable as Si(II) compounds ⇒ GeI_2, GeO, GeS and GeSe are known solids**

Tin

- **Tin(IV) compounds thermodynamically stable: SnO_2 (cassiterite)**
- **Freiberger digestion: $2\ SnO_2 + 9\ S + 2\ Na_2CO_3 \rightarrow 2\ Na_2SnS_3 + 3\ SO_2 + 2\ CO_2$**
- **Tin(II) compounds are semi-strong reducing agents:**
  $Hg^{2+} + Sn^{2+} \rightarrow Hg\downarrow + Sn^{4+}$
- **Electronic configuration: $[Kr]4d^{10}5s^2$ free non-bonding $5s^2$ pair of electrons "s^2-ion" ⇒ foundation of glow test based on the blue luminescence of $SnCl_2$:**
  $Sn^{2+}([Kr]4d^{10}5s^2) \rightarrow Sn^{2+}([Kr]4d^{10}5s5p) \rightarrow Sn^{2+}([Kr]4d^{10}5s^2) + h\nu$ (blue)
  as in phosphors, e.g. $Sr_3(PO_4)_2:Sn^{2+}$ or in metal halide lamps $SnCl_2$

4.15 Germanium, Tin and Lead Compounds

Lead

Lead(II) compounds: application as pigments in paint

- $Pb(OH)_2 \cdot 2PbCO_3$ (lead white)
- $PbCrO_4$ (chromium yellow)
- Pb_2SnO_4 (lead tin yellow)

Lead(IV) compounds: strong oxidising agents

- $PbO_2 + 4\ HCl \rightarrow PbCl_2 + Cl_2 + 2\ H_2O$
- $2\ PbO_2 \rightarrow 2\ PbO + O_2$

Lead(II/IV) compounds: antirust agent

- Pb_3O_4 (minium) can be described as $Pb^{II}_2[Pb^{IV}O_4]$

Organo-metallic lead compounds: fuel additives

- $(C_2H_5)_4Pb$ (tetraethyl lead)
  $4\ Na/Pb(s) + 4\ C_2H_5Cl(g) \rightarrow 4\ NaCl(s) + (C_2H_5)_4Pb$
  Nowadays replaced by methyl tert-butyl ether (MTBE)

Lead white

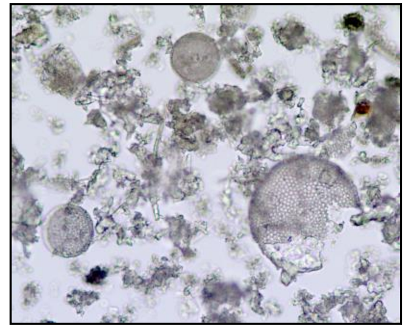
Chromium yellow

Lead tin yellow

Minium

4.16 Biological Aspects

Silicon



Copyright by Curtis Clark

- Part of skeletons of minute marine organisms (diatoms, brown algae), which consumes about 6.7 Gt Si per year
- No essential trace element
- Counters the toxic effect of Al^{3+} through formation of aluminosilicates

Tin

- Metal-organic compounds of Sn, such as $(C_4H_9)_3SnOH$ (hydroxytributyltin) are highly toxic

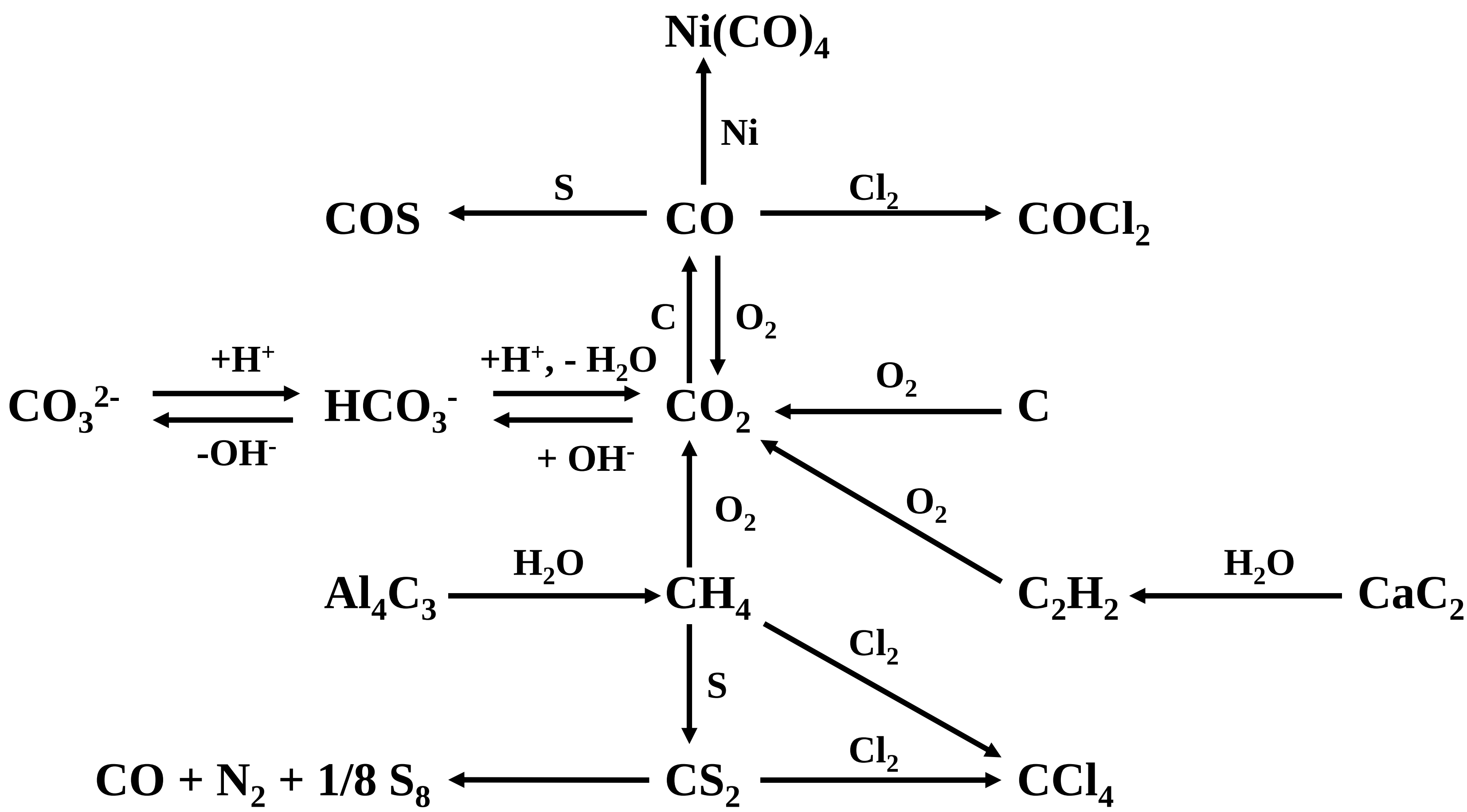
  ⇒ application as antifungals in agriculture and ships' paint

Lead

- Lead(II)-ions interfere with a number of biochemical reactions, leading to chronic symptoms of poisoning: headache, anaemia, breakdown of nervous system, sterility
- $Pb(CH_3COO)_2$ (lead acetate, lead sugar *Sapa*) ⇒ sweetener during the time of the Roman Empire
- Nowadays, lead intoxication caused by lead plumbing, leaded fuel, paints and stabilisers for PVC

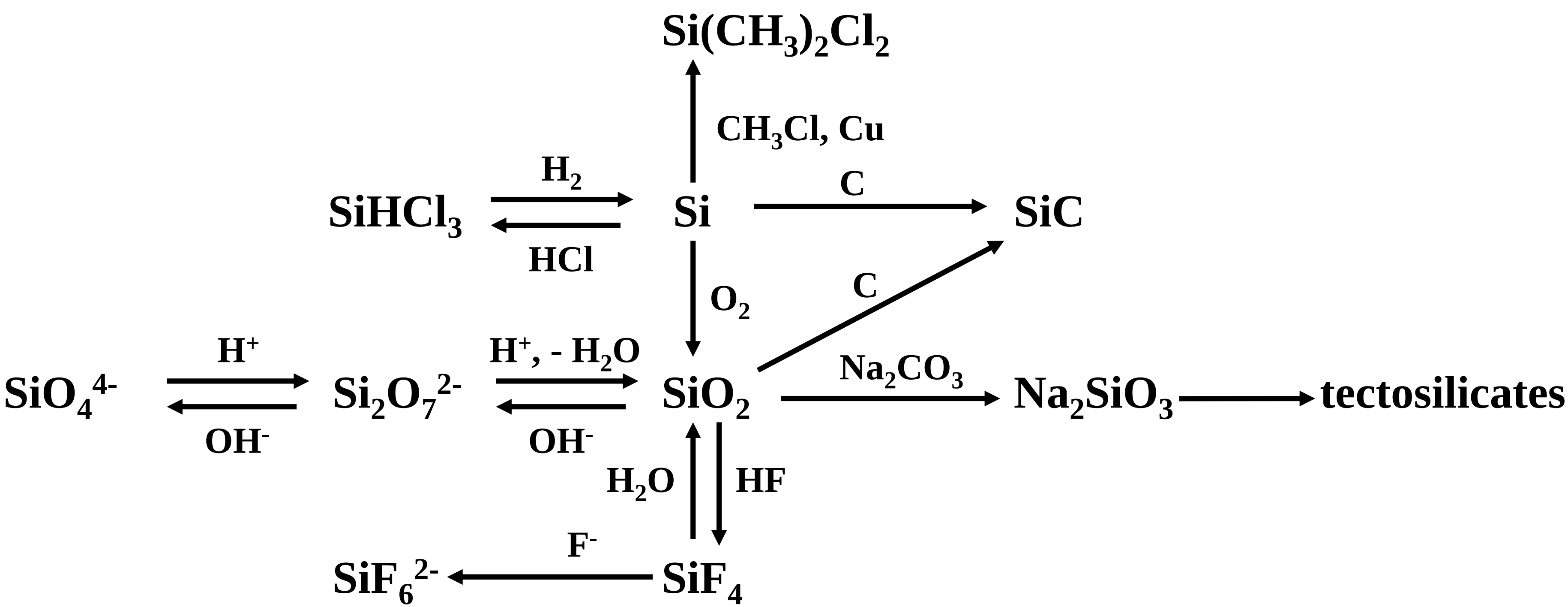
Overview Carbon Chemistry

Oxidation States: +IV, +II, 0, -I, -II, -III, -IV → Basis of organic & bio chemistry



Overview Silicon Chemistry

Oxidation States : +IV, +II, 0 → geo chemistry, crusts of planetary bodies



Overview Lead Chemistry

Oxidation States : +IV, +II, 0