

14
6
C
12,01115
14
Si
28,086
32
Ge
72,59
50
Sn
118,69
52
Pb
207,19
114
Uuq
[285]

‘The Tetrels’

The chemistry of Group 14

Occurrence & Isolation

14	C	350 ppm
12	Si	Silicis (lat.) – flint (a type of rock), 272 000 ppm Impure Si – reduction of SiO_2 with C or CaC_2 ; purified by zone melting process
32	Ge	Germania (lat.) = Germany, 1.5 ppm As a by-product in Zn extraction, also purified by zone melting
50	Sn	2.1 ppm Reduction of SnO_2 (cassiterite) with C
52	Pb	13 ppm Conversion of PbS to PbO , then reduction of PbO with C

Crude elements Sn and Pb can be purified electrolytically

Oxidation numbers

Ox. Number(s)

14
C
12.01115
14
Si
28.086
32
Ge
72.59
50
Sn
118.69
52
Pb
207.19

-4 (CH₄), -2 (CH₃Cl), 0 (CH₂Cl₂).... +4 (CO₂)

-4 (SiH₄), -3 (BaMg₂Si₂), -2 (CaSi).... +4 (SiO₂)

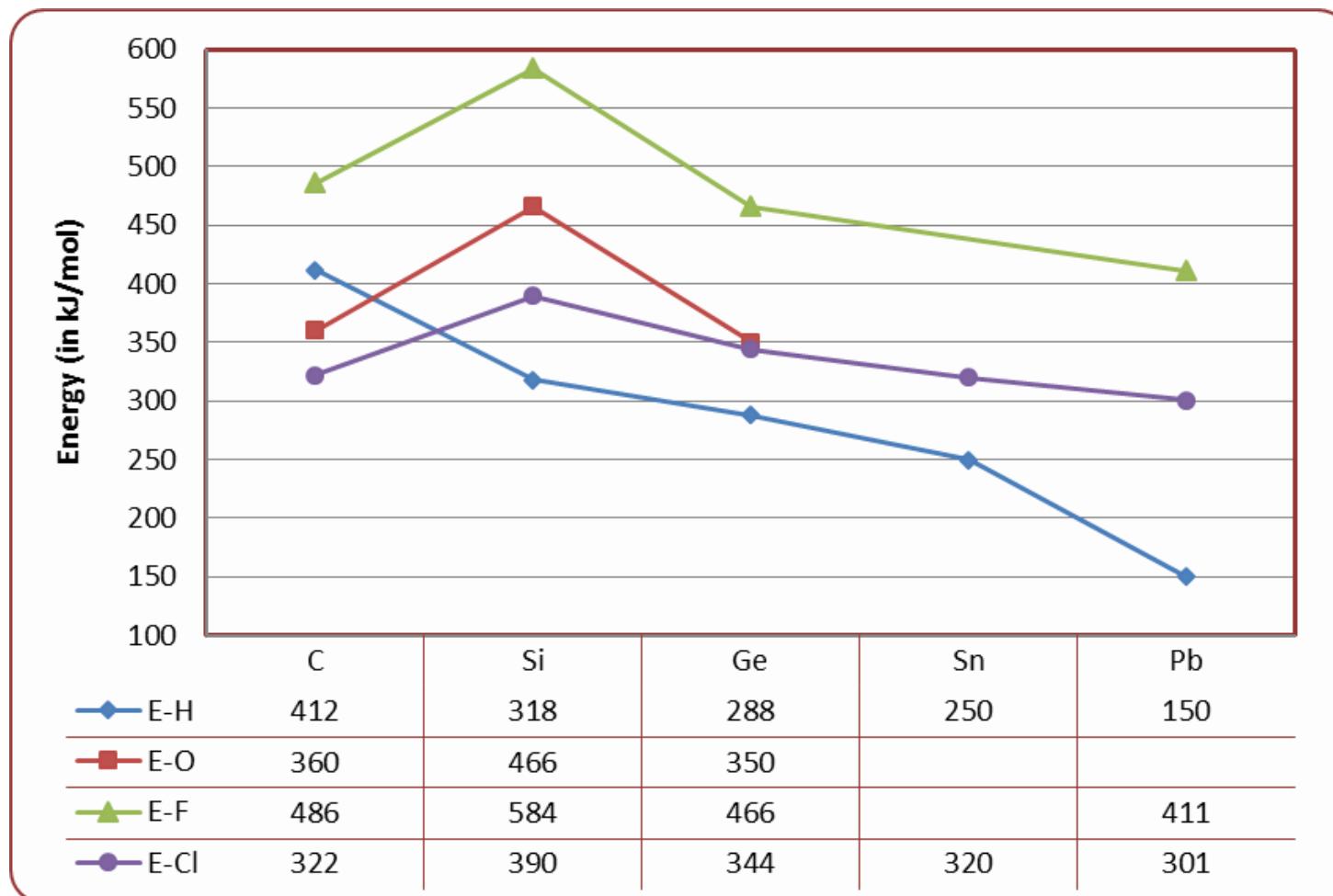
-4 (GeH₄), -2 (CaGe), +2 (GeX₂), +4 (GeF₄)

-4 (Mg₂Sn)?, +2 (SnO, SnX₂), +4 (SnO₂, SnX₄)

+2 (PbO, PbS), +4 (PbO₂)

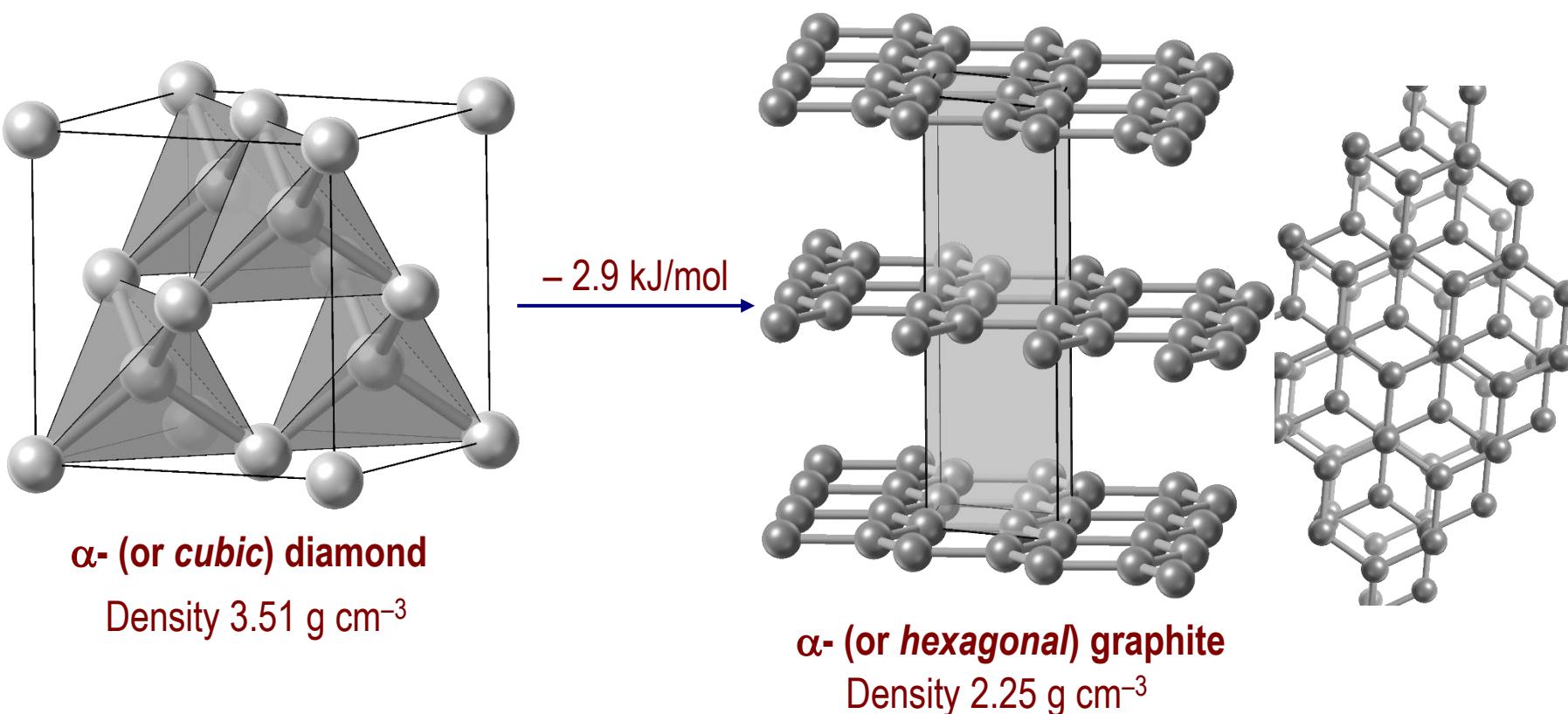
E-E and other bonds

- All bonds have a general trend: increase from C to Si then a decrease from Si to the bottom of the group, **except for E–H!**

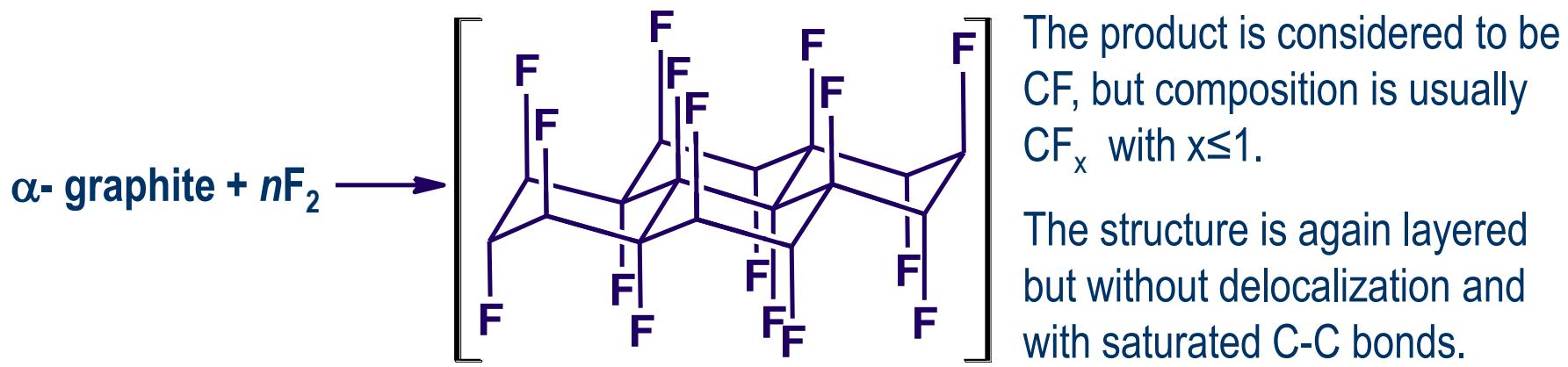


Allotropes of carbon: Diamond and Graphite

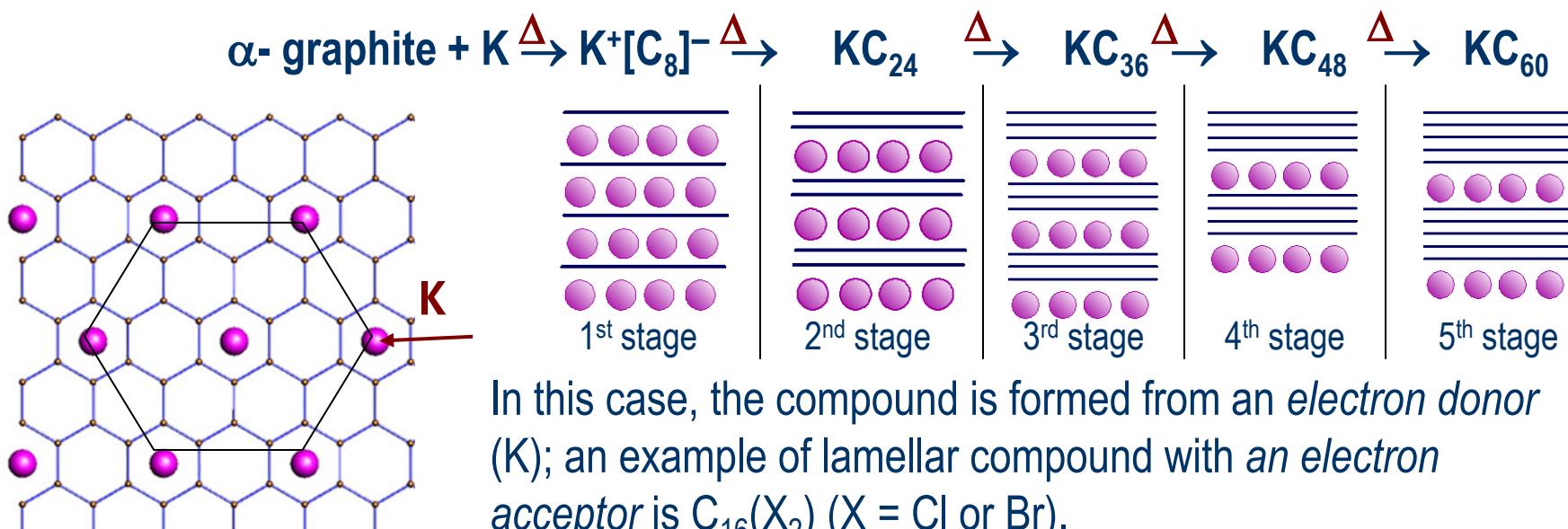
- A reminder:
 - **Allotropy**: one element can exhibit two or more different structures, each structure is a different allotrope



Chemistry of graphite

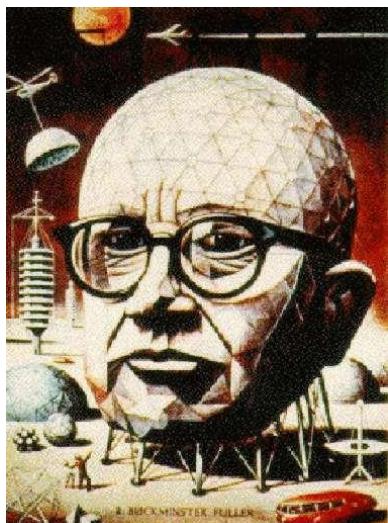


Intercalation (lamellar) compounds: an electron donor or acceptor is inserted between graphite layer with simultaneous charge transfer:



Allotropes of carbon: Fullerenes

- Fullerenes are *molecular* allotropes of carbon: they contain discrete molecules and not network of bonded atoms like diamond and/or graphite.
- Fullerenes is a common name for a series of cluster molecules comprising of fused pentagonal and hexagonal C rings with a general formula C_n (n is an even number between 30 and ~600).
 - Most stable are $n = 60, 70, 76, 78, 80$ and 90 .
- Fullerenes can be prepared by vaporizing graphite at high temperatures and rapid cooling of the produced vapor followed by chromatography to separate the various molecules.

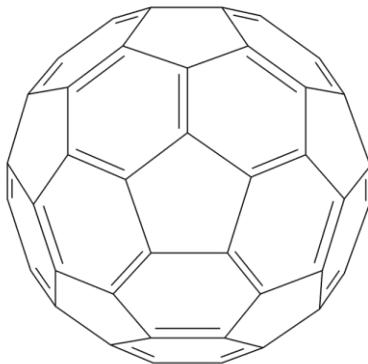
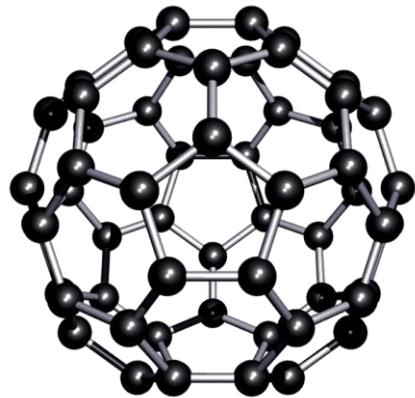


Richard Buckminster Fuller (cover of *Time* magazine, Jan. 10 1964)

The Eden Project geodesic domes panorama

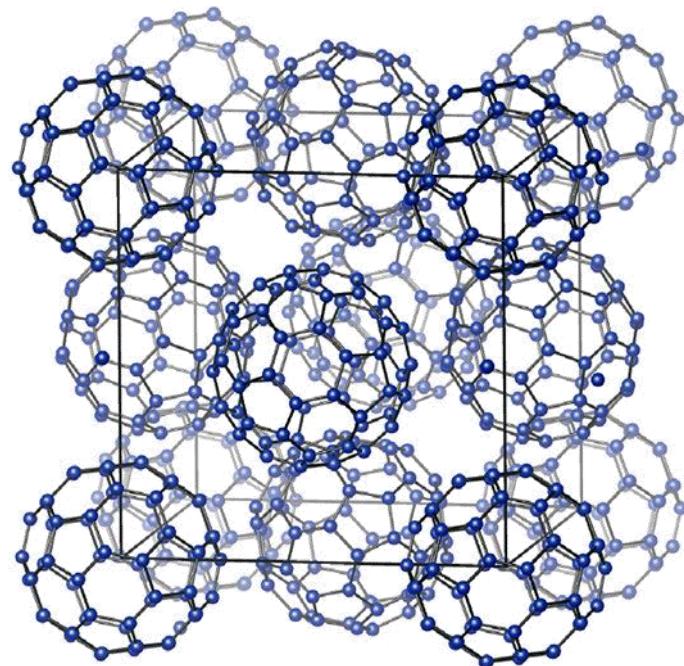
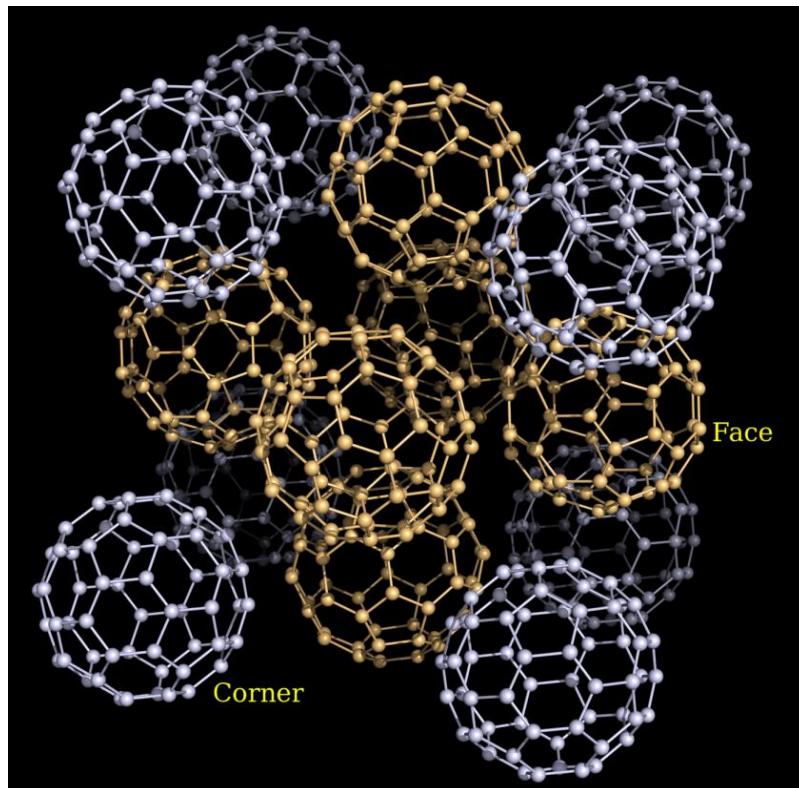


Buckminsterfullerenes or Fullerene-C₆₀



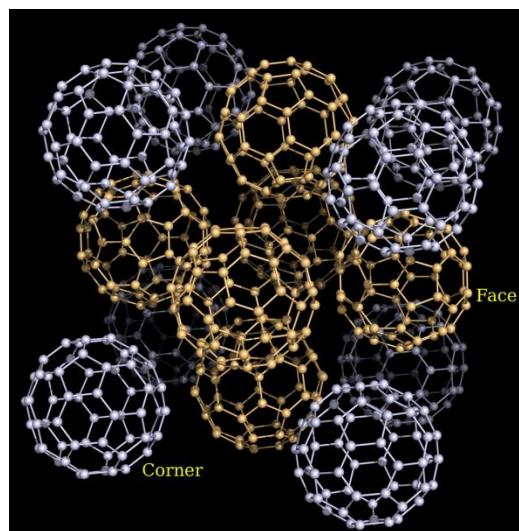
The C-C bonds are not significantly delocalized, rather alternating C=C and C-C bonds are present. Consequently fullerene-C₆₀ undergoes typical addition reactions.

Solid state
structure:
face centered
cubic



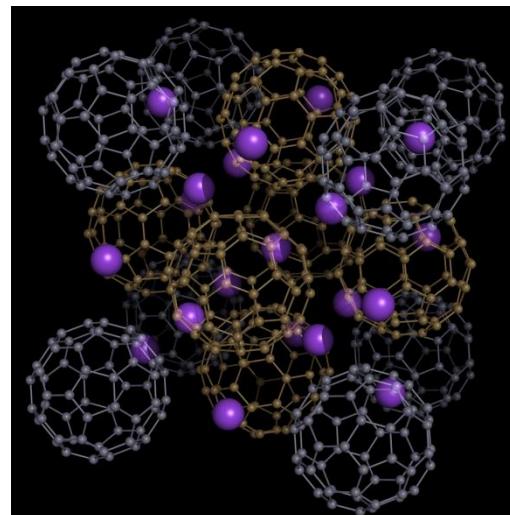
Fullerene-C₆₀ reactivity

- Like graphite, fullerene-C₆₀ can be reduced in a reaction with alkali metals to give *metal fullerides* of general formula M_nC₆₀ⁿ⁻ (n = 1 - 6).

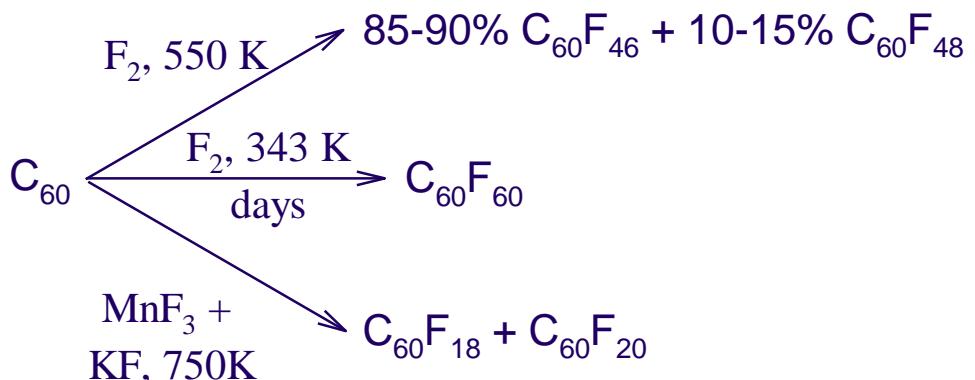


Add K⁺ in every
octahedral &
tetrahedral hole

(for n = 1- 3 the fcc
lattice of C₆₀ is
conserved, for n =
4-6, the C₆₀ lattice
changes to bcc)

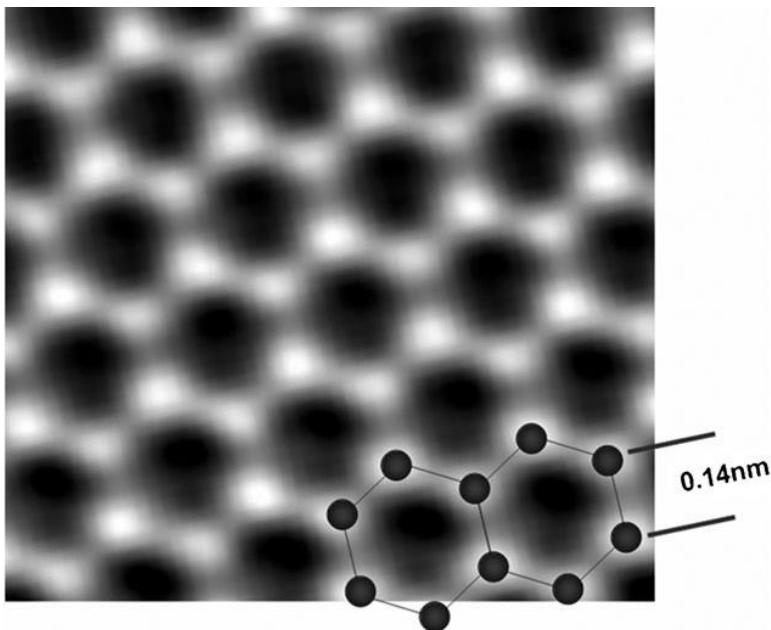


- Fullerene-C₆₀ can also be oxidized with halogens, the products depending on conditions

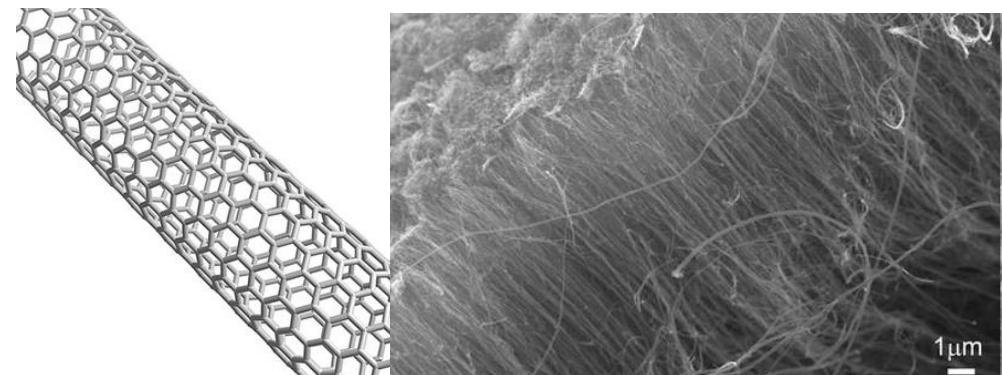


Allotropes of carbon: Graphene & Carbon Nanotubes

- Neither have been found in the Nature yet:
 - Graphene** is just one layer from graphite structure (a monolayer graphite): an ‘infinite’ aromatic molecule that can be produced large enough to be visible by a naked eye;
 - Carbon nanotubes** can be considered a ‘rolled’ graphene.



Structure of graphene as observed in transmission electron microscope (TEM)
(Image by TEAM05 at Berkeley)



Left: structure of nanotube. Right: a scanning electron microscopy (SEM) image of nanotubes



Nanobamas, each face is composed of about 150 million nanotubes

Carbides & Silicides

- **Carbides** are binary compounds with a general formula M_xC_y .
- Based on the carbide anion, carbides can be divided into those:
 - Containing an isolated C^{4-} anion (Be_2C , Al_4C_3) with carbon ON –4 (with water give CH_4 and metal hydroxide);
 - Containing C_2^{2-} (acetylide) ion (MC_2 , M_2C_2) with carbon ON –1 (with water produce $HCCH$ and $M(OH)_2/MOH$);
 - Containing $[C=C=C]^{4-}$ ion; these are rare (Li_4C_3 is one example)
 - Fullerides
 - Graphides
- Carbides can be obtained either directly from the elements, or from oxides and carbon
- **Silicides** are silicon analogues of carbides (M_xSi_y):
 - Containing isolated Si anions
 - Containing Si_2 -units
 - Containing Si_4 - units
 - Containing Si_n - chains

Binary Hydrides

- **Carbon hydrides:** too many!
- **Si hydrides (*silanes*):** $\text{Si}_n\text{H}_{2n+2}$ ($1 \leq n \leq 10$) both linear and branched.
 - Synthesis of SiH_4 :
$$3\text{SiO}_2 + 6\text{H}_2 + 4\text{Al} \rightarrow 3\text{SiH}_4 + 2\text{Al}_2\text{O}_3$$
- **Ge hydrides (*germanes*):** $\text{Ge}_n\text{H}_{2n+2}$ ($1 \leq n \leq 9$) also linear and branched.
- **Sn hydride:** SnH_4 (unstable, decomposes to Sn and H_2).
 - Synthesis of EH_4 ($E = \text{Si}, \text{Ge}, \text{Sn}$):
$$\text{ECl}_4 + \text{LiAlH}_4 \rightarrow \text{EH}_4 + \text{LiCl} + \text{AlCl}_3$$
 (in ether or THF)
- **Pb hydride (*plumbane*):** PbH_4 is stable for about 10 sec. and its existence is still questionable
 - Substituting one or more hydrogens with organic groups significantly increases the stability of Pb hydrides
- All EH_4 are *molecular* and contain tetrahedral element center (just like hydrocarbons have tetrahedral C atom!)

Selected molecular carbon halides

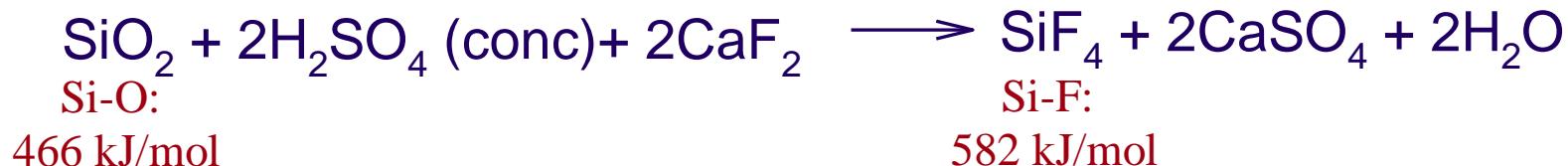
Type of halide	Fluoride	Chloride	Bromide	Iodide
CX_4 (tetrahalides) Derived from methane	CF_4 Colorless gas	CCl_4 Colorless liquid	CBr_4 Pale yellow crystals	CI_4 Deep red crystals
C_2X_6 ('trihalides') Derived from ethane	C_2F_6 Colorless gas	C_2Cl_6 Colorless crystals	C_2Br_6 Yellow crystals	-
C_2X_4 ('dihalides') Derived from ethene	C_2F_4 Colorless gas	C_2Cl_4 Colorless liquid	C_2Br_4 Pale yellow crystals	C_2I_4 Yellow crystals
C_2X_2 ('monohalides') From acetylene	C_2F_2 ^{a)}	C_2Cl_2 Colorless gas	C_2Br_2 Yellow gas	C_2I_2 Dark solid
COX_2 (oxohalides) From formaldehyde	COF_2 Colorless gas	COCl_2 Colorless gas	COBr_2 Brown solid	-

^{a)} Several molecular 'monofluorides' are known: C_6F_6 , $\text{C}_{60}\text{F}_{60}$ etc

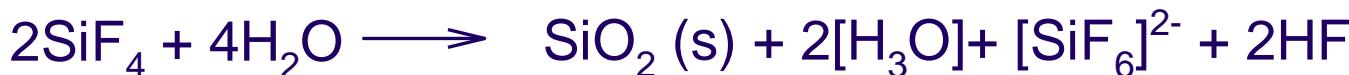
Halides – Silicon, SiX₄

- All Si halides are known and can be prepared directly from the elements
 - SiF₄ is more conveniently prepared from SiO₂ and HF (note the differences in Si-F and Si-O bond strengths!)

$$pK_{a_2} = 1.92 \quad pK_a(\text{HF}) = 2.95$$



- SiF₄ can react as a Lewis acid with F⁻ (a Lewis base) to produce hexafluorosilicate, [SiF₆]²⁻.
- Reactivities with H₂O



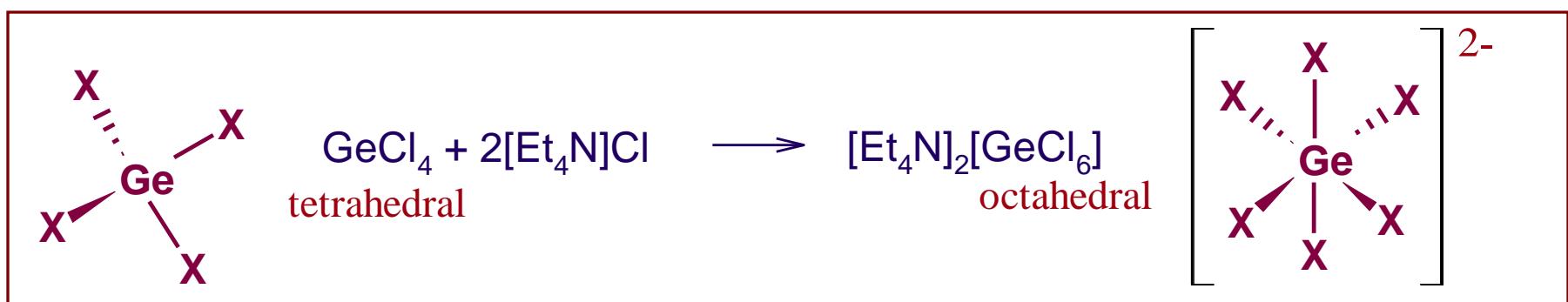
- There are also Si₂X₆ and monomeric SiF₂ and SiCl₂

Halides – GeX_4 & SnX_4

- GeX_4 and SnX_4 are prepared from elements (i.e. $\text{E} + 2\text{X}_2 \rightarrow \text{EX}_4$), all readily hydrolyze with water:



- GeX_4 and SnX_4 are strong Lewis acids (Sn stronger than Ge) and have a pronounced affinity towards halides (X^-):



- For both GeX_4 and SnX_4 Lewis acidity follows expected order:
$$\text{EF}_4 > \text{ECI}_4 > \text{EBr}_4 > \text{EI}_4.$$
 - The Lewis acidity explained by the presence of empty nd orbitals on Ge and Sn ($n = 4$ for Ge, $n = 5$ for Sn) but the increase in atomic size also plays an important role

Halides – Pb and EX₂

- For Pb, ON +2 is more stable than +4 thus all PbX₄ are unstable.
- Lead(II) halides are insoluble in water and are used in analytical chemistry.
- On going from Pb *up* in the group (towards Si), the ON +2 decreases in stability, thus: PbX₂ > SnX₂ > GeX₂ > SiX₂ >> CX₂ (as discrete, molecular CX₂!!)
- Consequently, this trend is observed:
 - SnX₂: mild reducing agents (X = Cl is often used), do not react with water, good Lewis acids, obtained from SnO + HX
 - GeX₂: reduction of GeX₄ with Ge, easily decompose back to GeX₄ and Ge, strong reductants
 - SiX₂ and X₃Si-SiX₃: very strong reducing agents, unstable and can decompose very fast

Selected Carbon Oxides

- Many oxides exist but the most important are the following anhydrides:



Carbon monoxide

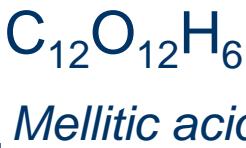
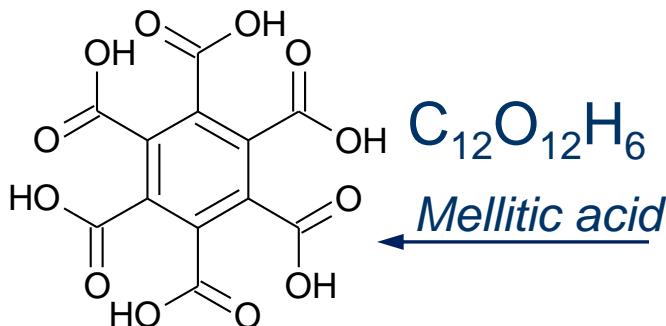


Carbon dioxide



Malonic acid

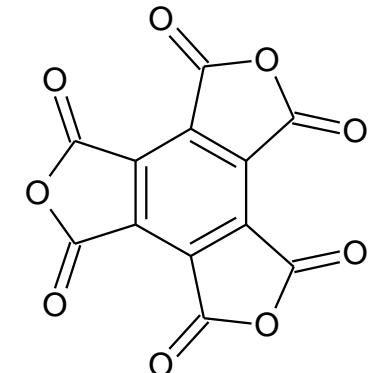
Carbon suboxide



Mellitic acid



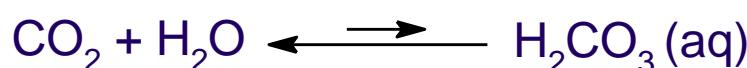
*Mellitic acid
anhydride*



- CO:** reducing agent, poison, product of incomplete combustion of fossil fuels (and organic material in general), for other synthesis see *Hydrogen* lecture.
- CO₂:** has no redox-properties, product of complete combustion of carbohydrates, not a poison; for other synthesis see *Hydrogen* lecture.
- C₃O₂:** good reducing agent, unstable and easily polymerizes.

Carbonic acid, H₂CO₃

- Carbonic acid is formed when CO₂ is dissolved in water.
- It is a dibasic (diprotic), mild acid that forms two series of salts: carbonates (CO₃²⁻) and hydrocarbonates (HCO₃⁻)



K ~ 1.7 x 10⁻³ (only ~ 0.2% of CO₂ reacts with water to give the acid!)

salts:
hydrocarbonates



$pK_{a_1} = 6.35$ 'apparent pKa' - assumes that all CO₂ is converted to acid
 $pK_{a_1} = 3.88$ real pKa - takes into account real conc. of acid

salts:
carbonates



- CO₂ is a major source of acid rain in the environment.

Carbonates, $[\text{CO}_3]^{2-}$

- Majority are insoluble in water (important minerals)
 - The exceptions are Group 1 carbonates: Na, K, Rb, Cs which are soluble and are good bases due to hydrolysis.
- Thermal stability: group 2 carbonates decompose at higher temperatures, i.e.



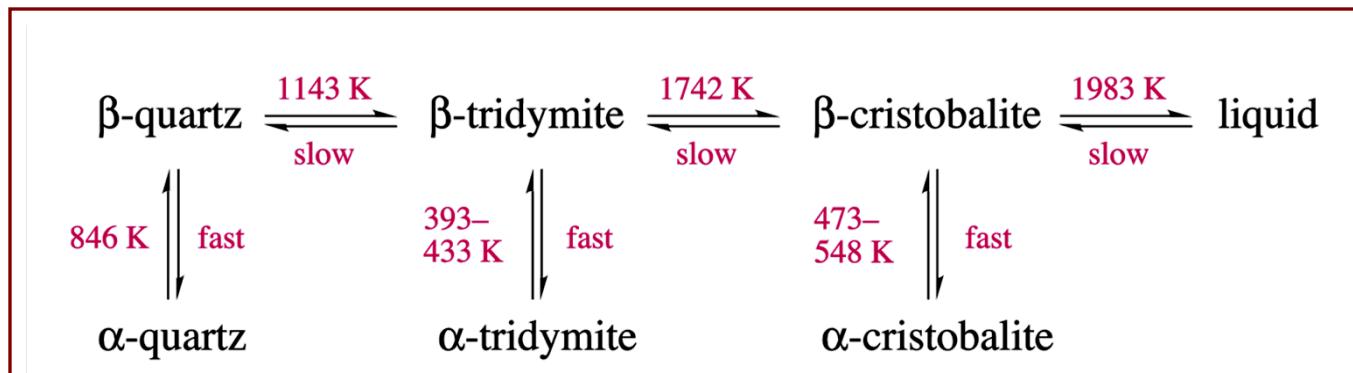
	MgCO_3	CaCO_3	SrCO_3	BaCO_3
$\Delta_r H / \text{kJmol}^{-1}$	+100.6	+178.3	+234.6	+269.6
$\Delta_r S / \text{Jmol}^{-1}\text{K}^{-1}$	+175.0	+160.6	+171.0	+172.1
Decomp. Temp.	305 °C/578 K	840 °C/1113 K	1100 °C/1373 K	1300 °C/1573 K

Note: The Group 1 carbonates (except Li) are thermally stable

- The decomposition temperature increases with increasing radius of M^{2+} : a consequence of the ability of large cations to stabilize large anions in the lattice

Oxides of silicon

- Unlike C, all other Group 14 elements give solid oxides
- SiO_2 (silica) most commonly found in nature as α -quartz, it is a basic raw material for glass industry



- SiO_2 is an acidic oxide but corresponding acid – H_4SiO_4 (or better Si(OH)_4) – is not known in free state.
- However, its salts, the silicates, are well-established and are the most common minerals in Earth's crust (about 80%)
- Important are esters of this acid, siloxanes Si(OR)_4 , which are obtained from SiCl_4 and alcohols.

Oxides of Ge, Sn and Pb

- Two things to consider: increase in metallic character and increase in stability of +2 ON
- **Germanium:**
 - GeO: a reducing agent, easily decomposes to GeO_2 and Ge, amphoteric: Ge(OH)_2 and $[\text{Ge(OH)}_4]^{2-}$ (germanate(II))
 - GeO_2 : well-characterized, acidic, gives a variety of germanates(IV) – compare with silicon
- **Tin:**
 - SnO : stable, amphoteric with basic properties more pronounced, mild reducing agent
 - SnO_2 stable, amphoteric with pronounced acidic properties, gives stannates(IV)
- **Lead:**
 - PbO : very stable, predominantly basic
 - PbO_2 : strong oxidizing agent, acidic – plumbates(VI)
 - Mixed oxidation state oxides (i.e. Pb_3O_4) are common for lead

Silicates and Carbonates in Nature

- **A mineral** is naturally occurring solid with a highly ordered atomic arrangement and a definite (but not fixed) chemical composition. It is usually formed by inorganic processes.
- **A rock** is a solid material composed of minerals (usually called ‘rock-forming minerals’)

Mineral Classes (simplified, according to Strunz)

1. Native elements (C, Au..)	6. Borates (borax)
2. Sulfides & sulfosalts	7. sulfates
3. Halides (NaCl, KCl)	8. Phosphates
4. Oxides & hydroxydes (Al_2O_3)	10. Silicates
5. Carbonates & nitrates	

Carbonates - families

Calcite Group

Calcite – CaCO_3

Magnezite – MgCO_3

Siderite – FeCO_3

Rhodochrosite – MnCO_3

Smithsonite – ZnCO_3

Aragonite Group

Aragonite – CaCO_3

Witherite – BaCO_3

Strontianite – SrCO_3

Cerussite – PbCO_3

Dolomite group

Dolomite – $(\text{Mg}, \text{Ca})(\text{CO}_3)_2$ (Mg:Ca close but not always 1:1)

Ankerite – $\text{CaFe}(\text{CO}_3)_2$

Basic carbonates (contain OH group):

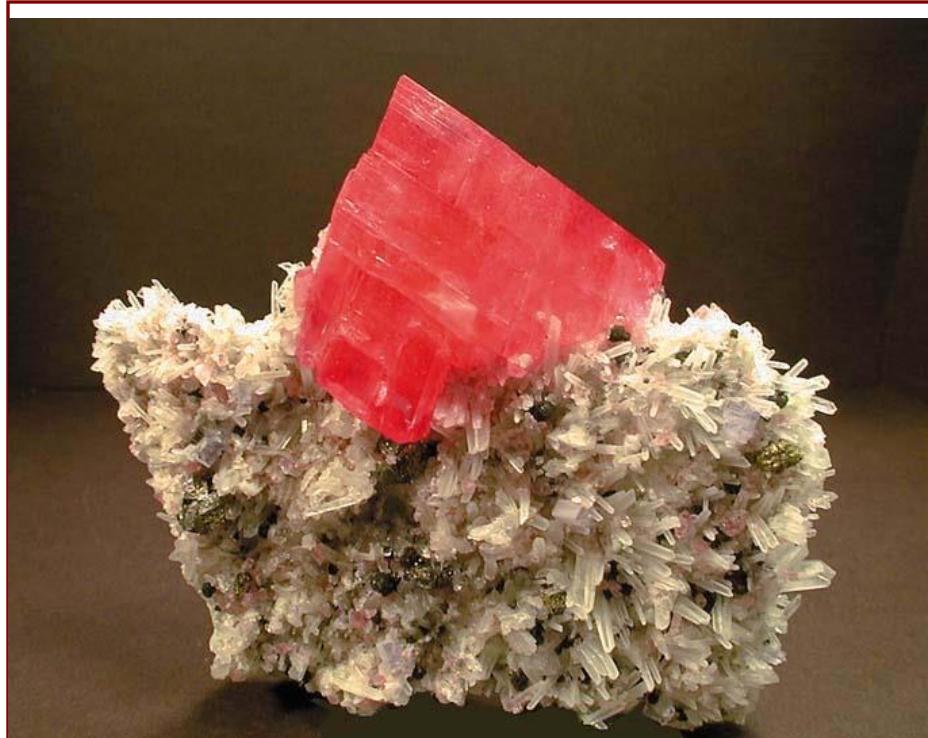
Malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$

Azurite $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$

Carbonates - examples



azurite, $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ (blue)
with malachite, $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
(green)



rhodochrosite, MnCO_3 (red,
large crystal) with quartz, SiO_2
(white-ish prisms) &
chalcopyrite, CuFeS_2 (golden)

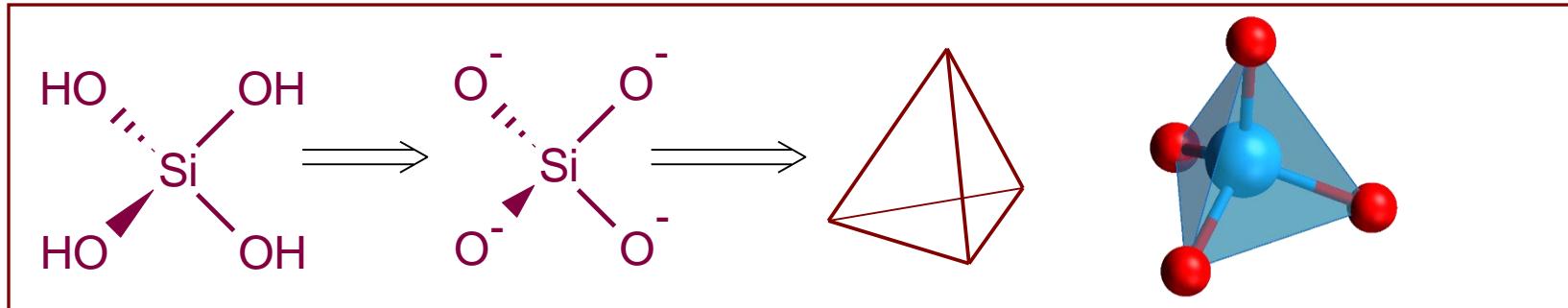
Silicates

- Most important rock-forming minerals
- They are grouped in 7 families according to structure of silicate anion (linking of SiO_4 -tetrahedra)

Family	Structure of silicate anion
Nesosilicates	Isolated SiO_4^{4-} tetrahedra
Sorosilicates	Two SiO_4 tetrahedra share a corner, $(\text{Si}_2\text{O}_7)^{6-}$
Cyclosilicates	3, 4 & 6-member rings, $(\text{Si}_x\text{O}_{3x})$
Inosilicates	<i>Piroxenes</i> : Single chains, $(\text{Si}_2\text{O}_6)^{4-}$
	<i>Amphiboles</i> : Double chains, $(\text{Si}_4\text{O}_{11})^{6-}$
Phyllosilicates	Sheets, $(\text{Si}_2\text{O}_5)^{2-}$
Tectosilicates	A net of corner sharing tetrahedra

Nesosilicate family

- Discrete $(\text{SiO}_4)^{4-}$ tetrahedra found in the structure



Garnet group

Pyralspite subgroup

Pyrope $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$

Almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$

Spessartine $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$

Ugrandite subgroup

Uvarovite $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$

Grossular $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$

Andradite $\text{Ca}_3\text{Fe}^{(III)}_2(\text{SiO}_4)_3$

Olivine Group

Forsterite, Mg_2SiO_4 ; olivine $(\text{Mg},\text{Fe})_2\text{SiO}_4$; fayalite Fe_2SiO_4

Nesosilicates - examples

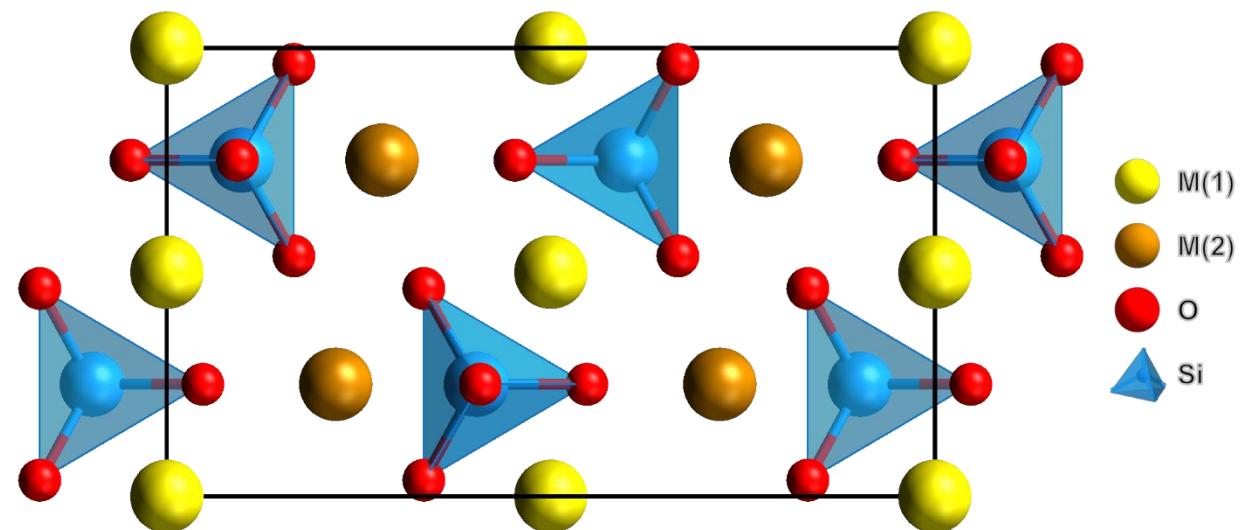
Pyrope,
 $Mg_3Al_2(SiO_4)_3$
("pyropos" – fiery-red), also known as
"Bohemian garnet"



Olivine,
 $(Mg,Fe)(SiO_4)$
(peridot variety)

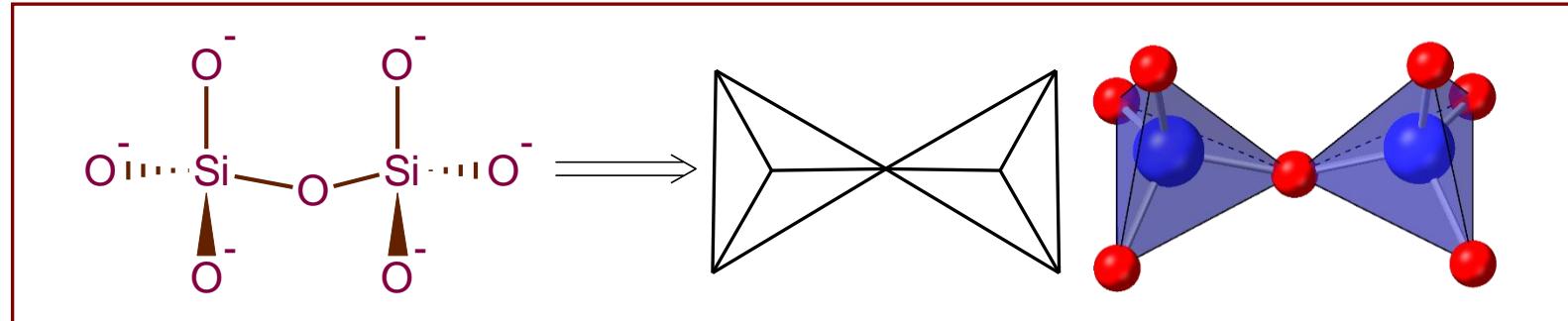


Orthorhombic cell of olivine showing isolated SiO_4 tetrahedral. The distribution of M(1) and M(2) is random

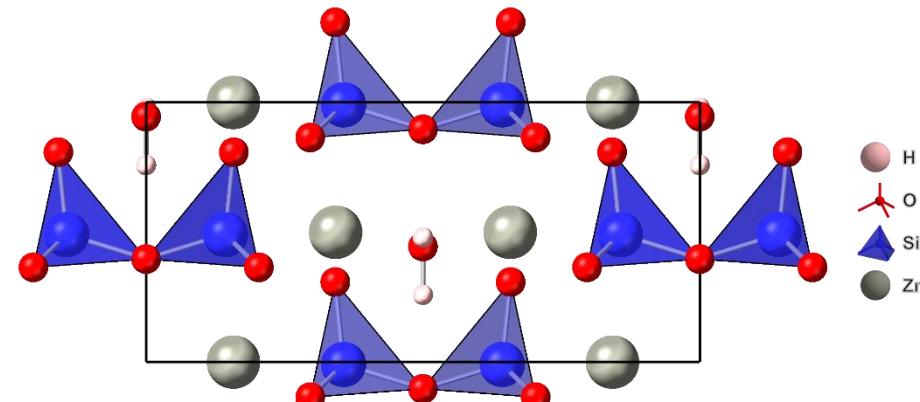


Sorosilicate family

- Sorosilicates are relatively rare, contain ‘dimer’ $(\text{Si}_2\text{O}_7)^{6-}$

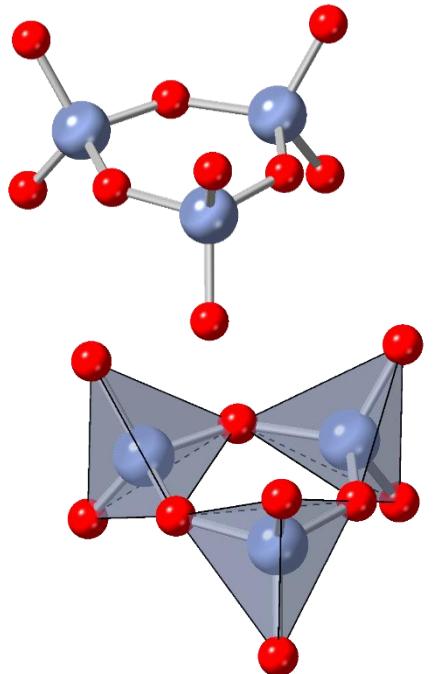
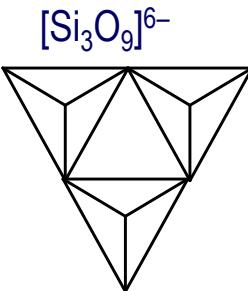


A sample of pink hemimorphite, $\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$ and its orthorhombic unit cell



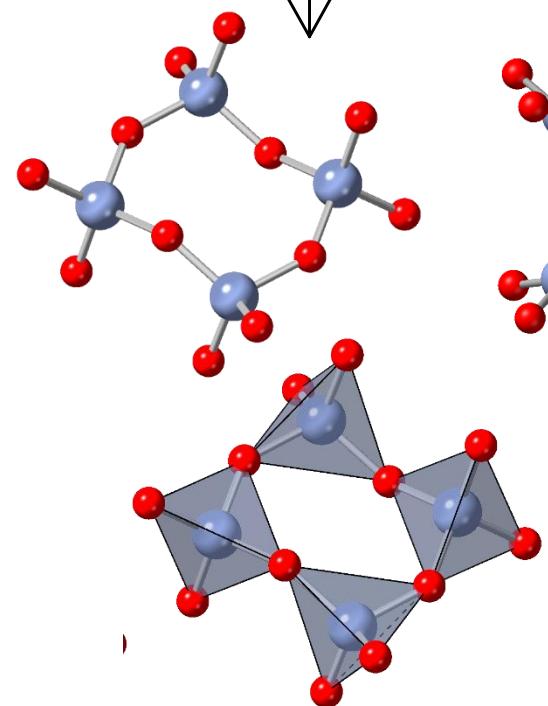
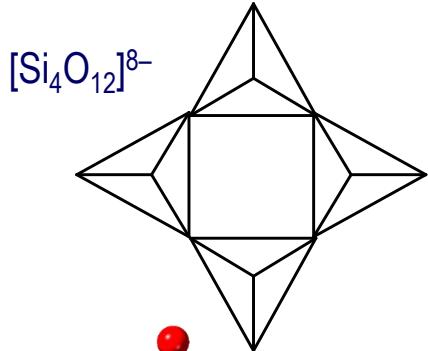
Cyclosilicate family

- Ring anion structures:



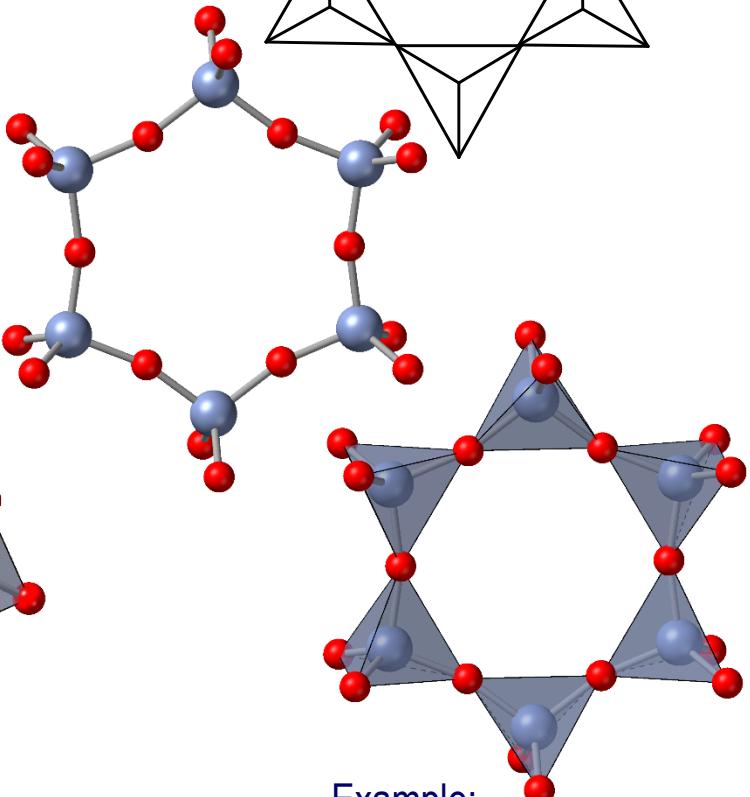
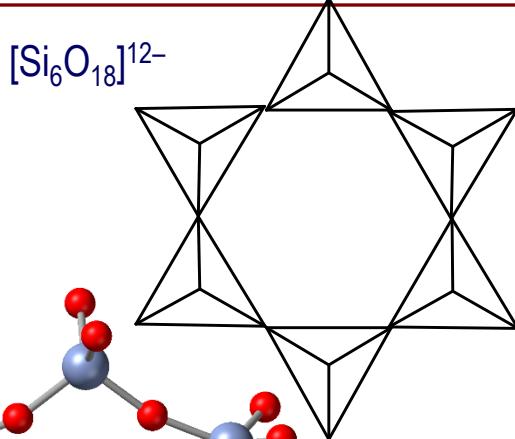
Example:

benitoite, $\text{BaTiSi}_3\text{O}_9$



Example:

papagoite, $\text{Ca}_2\text{Cu}_2\text{Al}_2\text{Si}_4\text{O}_{12}(\text{OH})_6$



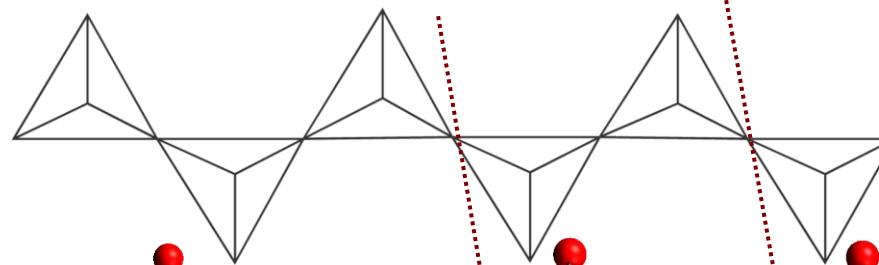
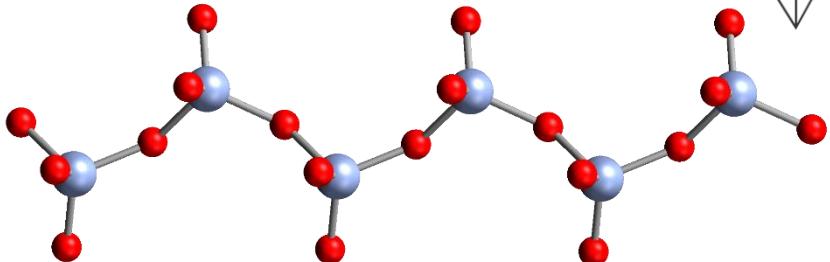
Example:

beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

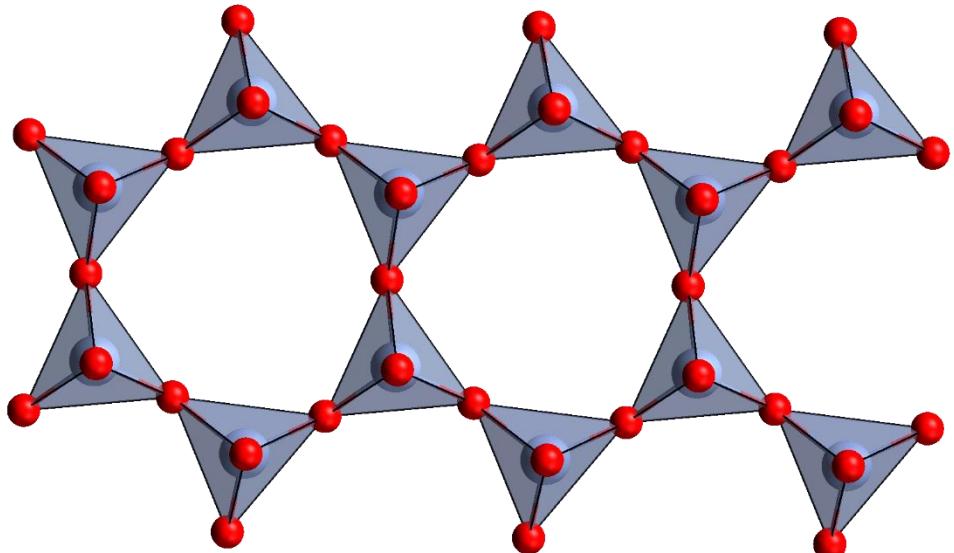
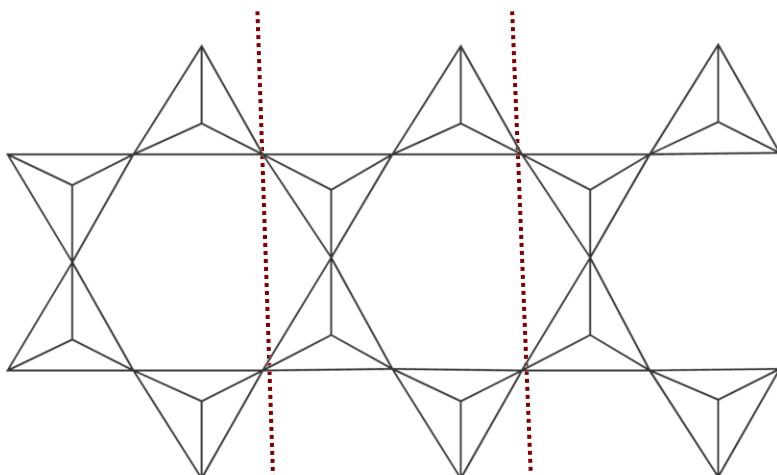
Inosilicate family

- Two sub-families:

Pyroxenes, $[\text{Si}_2\text{O}_6]^{4-}$



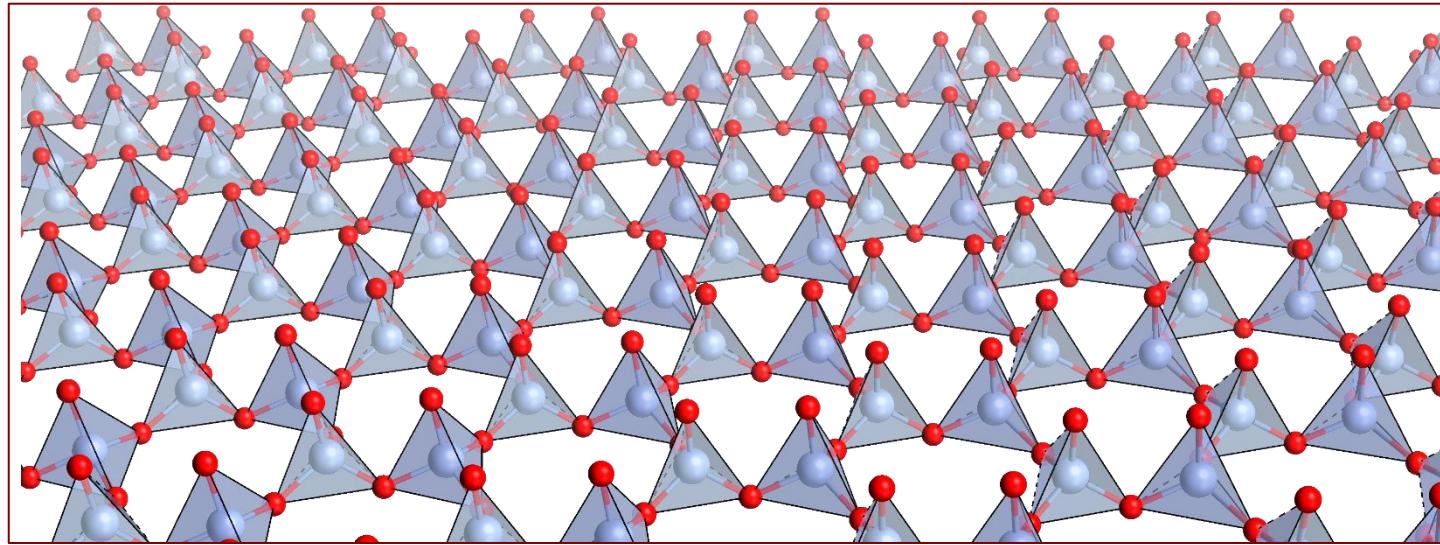
Amphiboles $[\text{Si}_4\text{O}_{11}]^{6-}$



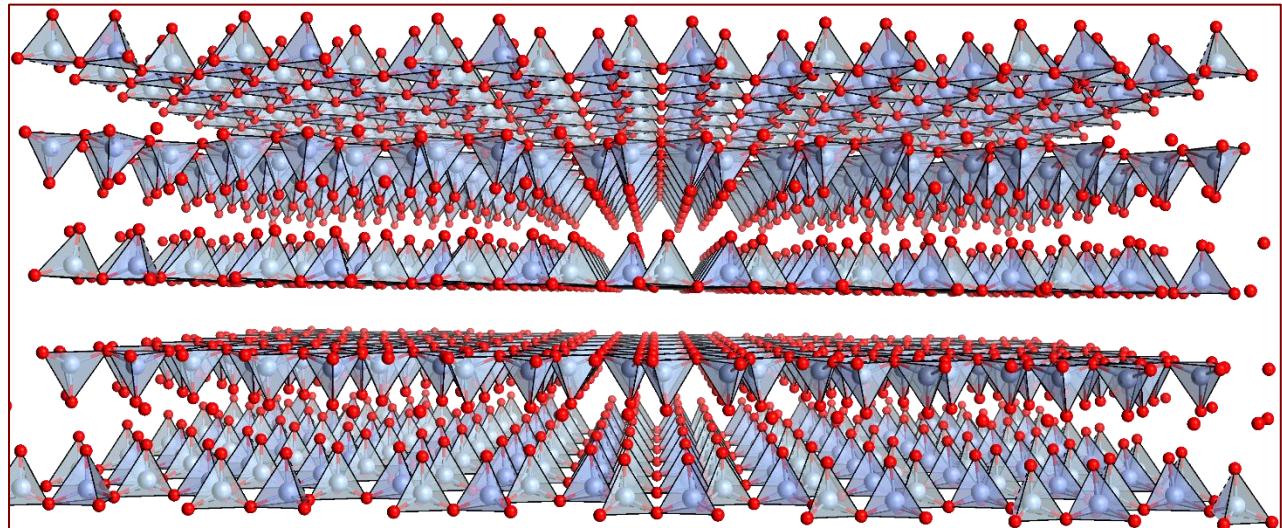
Phyllosilicate family

- Sheets (layers) of SiO_4 -tetrahedra, $[\text{Si}_2\text{O}_5]^{2-}$

One sheet of interconnected SiO_4 tetrahedra



Stacks of sheets



Tectosilicate family

- A three-dimensional framework of linked SiO_4 tetrahedra
- Quartz, SiO_2 (has 9 polymorphs!) (see lab manual for one structure)
- Replacement of $\text{Si}^{(+4)}$ with $\text{Al}^{(+3)}$ further groups:
 - If one out of four $\text{Si}^{(+4)}$ is replaced with $\text{Al}^{(+3)}$ albite ($\text{NaAlSi}_3\text{O}_8$) and orthoclase and microcline (both KAlSi_3O_8) can be formed
 - If two out of four $\text{Si}^{(+4)}$ are replaced with $\text{Al}^{(+3)}$ anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) can be formed
- A special group of tectosilicates are zeolites characterized with large channels in their structures (industrially important materials)

Overview

14	C	12,01115
14	Si	28,086
32	Ge	72,59
50	Sn	118,69
52	Pb	207,19
114	Uuq	[285]

- The elements: occurrence, isolation, oxidation numbers and trends in bond strengths
- Carbon allotropes and their reactivity
- Pb and inert pair effect
- Hydrides: syntheses, stability reactivity
- Halides: syntheses, reactivity (trends, Lewis acidity, reaction with water)
 - Keep in mind that there are two groups of halides now: EX_2 and EX_4
- Oxides: stabilities, acid-base properties
 - Keep in mind that the oxides are not limited to only expected EO_2
- Zintl anions/Wade rules
- Carbonates and silicates

Readings and problems

- Readings (both 6th and 7th ed.):
 - **Chapter 14** – “The Group 14 elements”; you can skip the following:
14.6b) and 14.6c), 14.16 and 14.17
 - Read Boxes 14.1, 14.2, 14.3, 14.4 (14.5 in 7th), 14.5 (14.6 in 7th)
- Problems:
- 6th edition:
 - Examples and Self tests: 14.1 (the example is a bit strange though), 14.2, 14.3, 14.4
 - Exercises: 14.1, 14.2, 14.3, 14.4, 14.5a) (not 14.3b), we did not cover NMR), 14.6, 14.9, 14.10, 14.11, 14.12, 14.17, 14.20
- 7th ed.
 - Examples and Self tests: 14.1, 14.2, 14.3 (the example is a bit strange though), 14.2, 14.3, 14.4, 14.5, 14.6
 - Exercises: 14.1, 14.2, 14.3, 14.4, 14.5, 14.7a) (not 14.3b), we did not cover NMR), 14.8, 14.10, 14.11, 14.12, 14.13, 14.19, 14.20, 14.21

Cyclosilicates - examples



Si_3O_9 : benitoite,
 $\text{BaTiSi}_3\text{O}_9$



Si_4O_{12} : papagoite,
 $\text{Ca}_2\text{Cu}_2\text{Al}_2\text{Si}_4\text{O}_{12}(\text{OH})_6$

Si_6O_{18} : beryl,

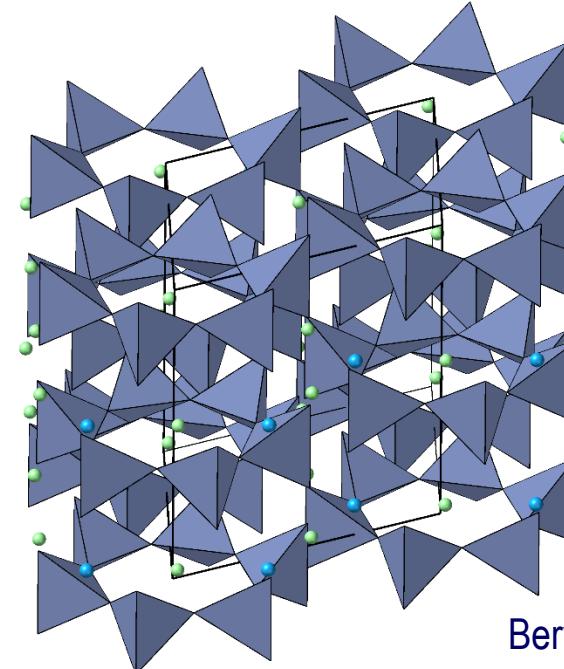
$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ (greenish prism)

Also: apatite,

$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$, pink;

Muscovite

$\text{KAl}_2(\text{Al},\text{Si}_3)\text{O}_{10}(\text{OH},\text{F})_2$

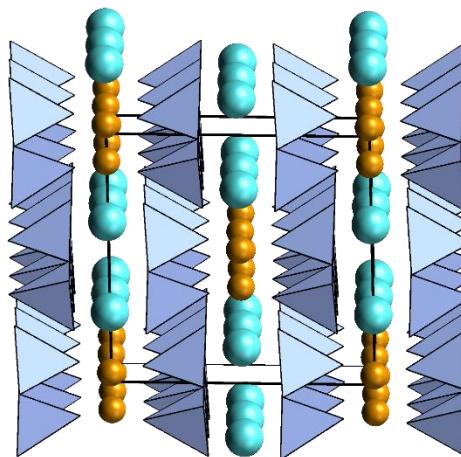


Beryl's structure

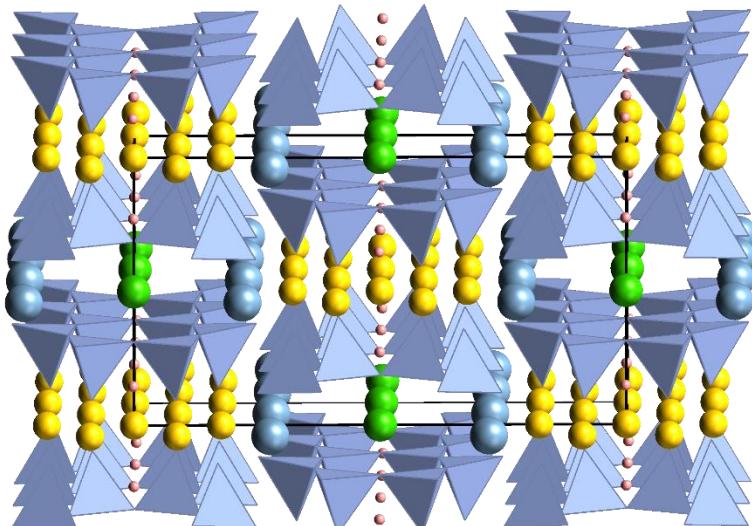
Pyroxenes - example



Hedenbergite (structure on the right side),
 $\text{CaFeSi}_2\text{O}_6$, (green prisms)
with ilvaite,
 $\text{CaFe}^{\text{II}}_2\text{Fe}^{\text{III}}\text{Si}_2\text{O}_7\text{O(OH)}$, a
sorosilicate (black)



Amphibole - example



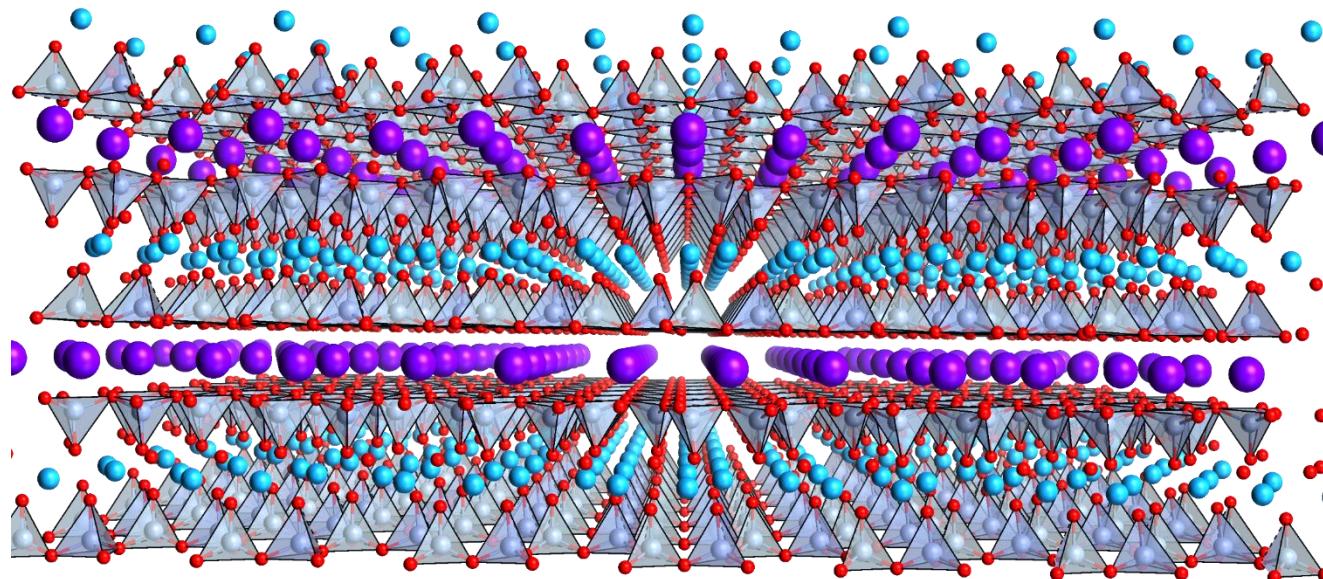
Tremolite,
 $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$
Mineral sample (far left) and the structure (right; unit cell outlined in black)

Phyllosilicate example



Muscovite, $KAl_2(Si_3Al)O_{10}(OH,F)_2$
mica group

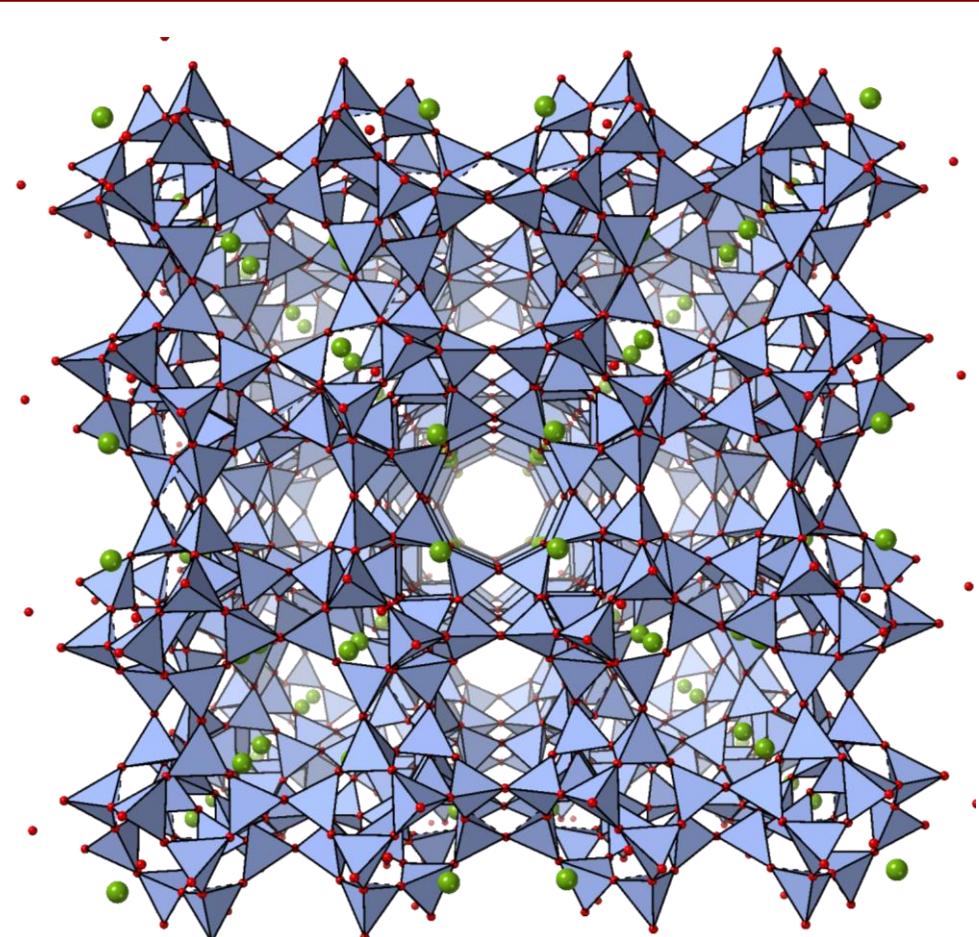
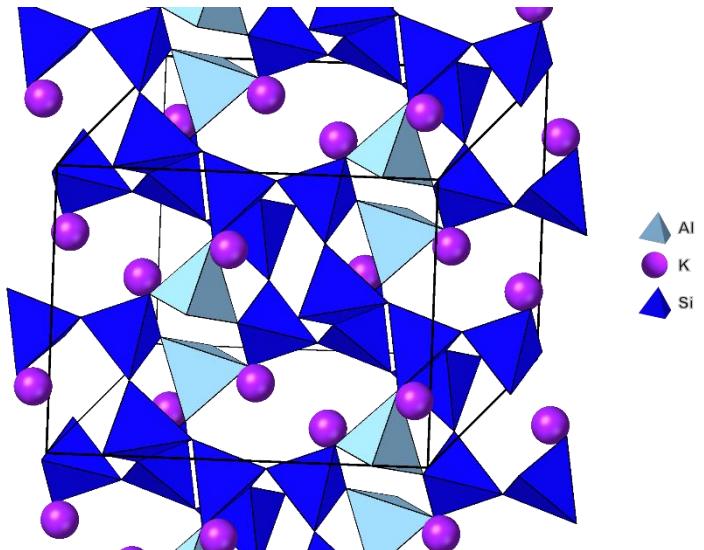
● Al ● K ● O ▲ Si



Tectosilicate family



Microcline (structure below), $KAlSi_3O_8$
(var. amazonite), green with quartz,
 SiO_2 (var. smoky quartz), black



Zeolites: structure of anhydrous natrolite, $Na_2Al_2Si_3O_{10}$