

EPSc 352: Lecture Overview for Part 6, Systematic Mineralogy

Systematic Mineralogy

Have looked at basic compositional and structural properties of minerals, as well as some ways to infer these properties (XRD, electron microprobe, Raman spectroscopy)

We'll examine examples from some of the major mineral groups, in order to understand the themes of composition, structure, physical properties (hand-sample and optical), occurrence, and usages.

Begin with non-silicates. Unfortunately, often lumped together as if they were a fairly homogeneous group (not!).

Non-silicates include:

- Most metallic ores (sulfides, oxides, hydroxides, carbonates)
- Many "industrial [non-metallic] minerals" (sulfates, carbonates, phosphates, halides)
- Many environmentally important phases
 - biominerals: phosphates, oxides, carbonates
 - acid-drainage products: sulfides, sulfates, oxides, hydroxides
 - remediation aids: carbonates, phosphates, silicates

Non-silicate minerals form in many cases from aqueous solutions, including hydrothermal (hot water) solutions.

Their compositions are a reminder of dissolved constituents in natural waters, which can react and precipitate. E.g., introduce ions, change oxygen pressure or pH or temperature or some combination of parameters, cause precipitation.

- Minerals become the dumping grounds of elements
- Minerals become the source of our needed elements

Can organize such minerals by property or usage (e.g., classification for scarce metals)

- precious/noble metals (e.g., Ag, Au, Pt)
- base metals (e.g., Cu, Zn, Sn)
- ferrous or ferro-alloy metals (e.g., Mn, Co, W, Ti)
- special metals (e.g., gallium, tantalum, zirconium)

Use of iron accounts for 95 wt.% of all metals consumed. Large proportion of remaining 5 wt.% is used to alloy with iron to make steel.

Look over hand-outs concerning the types of minerals from which we derive useful materials.

Look briefly at the metals, because they will be the focus of the first "minerals" that we study. Major carriers of metals we use daily are **native metals**, **sulfides**, **oxides**; lesser amounts of **carbonates** and **hydroxides** (increasingly used); minor use of silicates as metal sources.

Geological groupings of the metals – in part, for mineralogic reasons. Group by crustal abundance:

geochemically abundant ≥ 0.1 wt. % of crust: Si, Al, Fe, Mn, Mg, Ti

geochemically scarce ≤ 0.1 wt. % of crust: e.g., Cu, Zn, Pb, Au, Ag, Pt, Ga, La

Abundant metals tend to form large, numerous ore deposits; often form their own minerals, rather than piggy-backing via solid solution.

*** ESSENTIAL:

👉 Read indicated parts of textbook chapters 15, 16, and 17.

👉 Structures of Non-Silicate Minerals

Usually classify minerals based on dominant anion or anionic group (e.g., carbonate, sulfide, halide): similar chemical and physical properties, similar geologic occurrence. **See Klein and Dutrow, list on p. 332 and Table 15.1 on p. 333.**

****Themes to recall** and keep in mind as you study the mineral groups:

elements of structure, e.g., CCP, HCP, BCC
kinds of sites, e.g., tetrahedral and octahedral
electrovalency considerations
structural and compositional analogs

⇒ **Native Elements: metals, semimetals, non-metals (Chapter 15)**
Au, Pt, Fe As, Bi, Sb S, C

Metals: want to give up electrons. Simple structures with high (cubic) symmetry.

Au and Pt group: FCC lattice (CCP of atoms). Closest packing layers along {111}.

Fe group: BCC packing. I-lattice. Each Fe has 8 nearest neighbors.

Semimetals: will either donate or accept electrons; semiconductor industry.
As, Sb, Bi all isostructural.

Structure type is Rhombohedral $\bar{R}3m$

Not closest-packing of spheres. Each atom closer to 3 of its neighbors than to others; form pyramidal groups with covalent bonding. Layered structure along {0001}.

Non-Metals: S, C

Sulfur: 2 polymorphs, with transition temperature at 95.5 °C. 128 S atoms in unit cell. Puckered 8-fold rings, held together by van der Waals forces.

Uses of sulfur: fungicides, insecticides, vulcanization of rubber, H_2SO_4

Graphite: sheets. (**See earlier notes** on covalent and hybrid bonding.) 6-member rings. 3 of carbon's valence electrons form strong, covalent sigma bonds in plane. Fourth electron wanders over sheet – forms pi bond side-to-side with adjacent carbons. Van der Waals forces between sheets: cleavage. Requires 3 sheets to define unit cell.

Diamond: each C is tetrahedrally coordinated to 4 other carbons. Very strong, directional covalent bonds, but all bonds equal in strength.

Uses of graphitic carbon: lubricant; non-reactive compound; refractory (to about 3000 °C); good electrical conductor; pencil lead; strong carbon fibers, especially in composites. Activated carbon.

Uses of diamond: grinding and polishing metals and other hard objects; synthetic diamond films to create robust surface on materials.

⇒ **Sulfides** Difficult to organize/classify (Chapter 15)

Can exhibit metallic, ionic, and covalent bonding – even within same mineral!

In many cases, get regular tetrahedral and octahedral coordination of metal atoms by sulfur, but distorted polyhedra are also common.

In simpler sulfides, can view both ways: metal atom coordinated by sulfurs AND sulfur atom coordinated by metals.

Sphalerite, ZnS . Has diamond structure in which C's replaced by Zn's and S's in 1:1 ratio.

Symmetry thus drops from $4/m\bar{3}2/m$ to $4\bar{3}m$ (both are cubic).

Sphalerite illustrates derivative structures:

The (more chemically complex) sphalerite structure is a derivative of the (less chemically complex) diamond structure, by the above replacement

Chalcopyrite, CuFeS_2 , is derived from sphalerite structure by substituting 1:1 of Cu:Fe for Zn.

Symmetry then drops to $42m$ (tetragonal)

Pyrite, FeS_2 . Also cubic, but only $2/m\bar{3}$ symmetry. S's are covalently bonded dumbbells (go back to your lab #2). Also consider this structure as a derivative of NaCl structure, only with separate Fe and S_2 groups. Structurally different from **marcasite**.

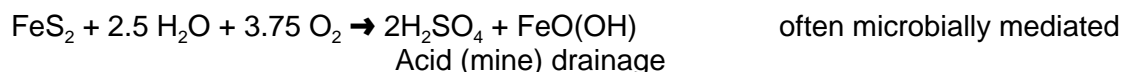
Arsenopyrite is a derivative of the marcasite structure.

Galena, PbS . Exactly the same as the NaCl structure.

Some sulfides have very complex structures and stoichiometries; combinations of bonding types.

Uses of sulfides: sources of many metals, e.g., Cu, Co, Pb, Zn.

Problems of sulfides: smelting of them releases sulfurous gases to the atmosphere (highly reactive, acidic). Oxidation of pyrite occurs readily and ubiquitously in the natural and disturbed environment. Grinding of sulfides makes them especially reactive:



⇒ Oxides (Chapter 16)

Tend to be refractory (high melting temp.) and hard. Usually as accessory phases. Bonding is mostly ionic in character.

Can be concentrated geologically, as by precipitating from a melt or hydrothermal fluid.

Basic types [distinguish between different 1) crystallographic sites and 2) valences of atoms that may fill those sites]

simple oxides = M_xO_y One type of metal site E.g., M_2O , MO , M_2O_3
Discount ice and quartz

multiple oxides = multiple sites E.g., XY_2O_4 Where X and Y typically are
A and B sites: tetrahedral (IV) and octahedral (VI) ions of different valences

Hematite group: example of simple oxide

hematite (Fe_2O_3) ilmenite (FeTiO_3) corundum (Al_2O_3)

HCP of oxygens (so, produces 12 tetr and 6 oct sites for cations)

In hematite, Fe^{3+} in oct sites: Some octahedral sites vacant, due to charge balance; i.e., hematite is Fe_2O_3 NOT Fe_3O_3 . One out of every 3 octahedral sites is empty. NOTE: The same is true for the octahedral layer in the clays you worked with, because Al ions also have +3 charge.

Rutile, TiO_2 , another simple oxide

Oxide used as opaquing agent in paints and on paper. Titanium metal has high strength:weight, making it a desirable (but expensive) high-tech metal in jets, sports equipment, backpacking equipment, replacement for hip joints, new fad in jewelry, etc. Environmental ramifications to processing of titanium.

Spinel group: example of multiple oxide.

Based on CCP of oxygens; cations occupy both tetrahedral and octahedral sites. Twice as many tetr (12) as oct (6) sites.

⇒ **Halides.** Anions have high electronegativity, so tend to form ionic compounds. High symmetry; optical isotropy. **(Chapter 16)**

Halides are the “type” structures for several kinds of compounds

NaCl

halite
PbS, galena
MnS, alabandite
MgO, periclase

CsCl

CaF₂

fluorite
UO₂, uraninite
ThO₂, thorianite

NaCl = AB type (see figure)

Each cation and anion in octahedral (6-fold) coordination with each other.

CsCl: Each cation and anion in 8-fold coordination with each other. From radius-ratio considerations, 8-fold coordination occurs because Cs⁺ ion is so large.

CaF₂

Ca²⁺ in 8-fold coordination with F
F⁻ in 4-fold coordination with Ca

See figures that show unit cell based on either F or Ca.

Use of fluorite (fluoride): flux in steelmaking; making HF (use in smelting Al; industrial uses); fluoride in water supply and toothpaste (concerns about hyperfluoridation)

Fluorite-type structure is useful in materials engineered to contain/incorporate nuclear waste

⇒ **Carbonates:** examples of anionic complexes. **(Chapter 17)**

Bond strengths within complex > between the complex and other ions (anisodesmic).

Look at electrostatic valence distributions within the carbonate ion group vs. total charge on oxygen (i.e., what is left over for bonding of oxygen to other cations). Compare to situation with silicates (SiO₄ tetrahedral complexes). This is why silicate groups readily polymerize.

Calcite *Aragonite* *Dolomite* Groups: Based on structural similarities

Calcite, CaCO₃

Rhombohedral unit cell and space group. Derivative of NaCl structure, based on radius ratios. 6-fold coordination of Ca with O. Smaller cations: FeCO₃ (**siderite**), MgCO₃ (**magnesite**)

Aragonite, CaCO₃

Orthorhombic. 9-fold coordination of Ca with O. Structure adopted by larger cations (Ba, Sr, Pb). Aragonite is the higher-pressure polymorph cf. calcite, thus higher coordination number.

Dolomite, CaMg(CO₃)₂

Hexagonal (lower symmetry than calcite – why?). Considerable solid solution with MgCO₃

(magnesite) and CaCO_3 , but mostly at high temperature. See diagram: solvus; geothermometry.

Formation: sedimentary, low-T environment (ocean reaches saturation and ppts; shells of animals pile up); hydrothermal ppt. (heated waters have dissolved carbonate, cool and ppt.)

Uses of carbonates: vast usage (in diversity and volume), gravel, cement and concrete (make an artificial rock), neutralize acid (environmental, lawn, food processing, your tummy)

⇒ Other Anionic Groups: Sulfates, Phosphates, Arsenates, Molybdates, Nitrates (Ch. 17)

Sulfate examples: **Gypsum**, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ **Anhydrite**, CaSO_4
Precipitate from evaporating seawater, as does halite. Sedimentary, low-T environment.
Huge use in plaster and wallboard. Heat gypsum to partially de-water it:



When you pour water into Plaster of Paris, you cause re-hydration of the sulfate and form new gypsum. You also form interpenetrating crystals, which give the material its strength. You have made a “fake rock.”

Sulfates are also the natural weathering (oxidation) products of metal sulfide minerals. Found on top of deeply weathered ore deposits. Ex: **Antlerite**, $\text{Cu}_3\text{SO}_4(\text{OH})_4$

Environmentally significant: metal sulfates can precipitate from heavy-metal-laden acidic run-off from mine sites. Many of them are readily re-dissolved (re-release their heavy metals).

Phosphate example: **Apatite**, $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ fluorapatite, chlorapatite, hydroxylapatite
Occurs in igneous rocks (accessory phase), huge sedimentary phosphate deposits (Phosphoria Fm.). Marine phosphorites: upwelling of cool, phosphate-saturated sea water (algal blooms).
Biologically re-pptd. Form muds, nodules, crusts.

Apatite structure is very amenable to chemical substitution, as shown in composition of bones and teeth and in the rare-earth-element phosphors in our (color) TV screens.

Bones and teeth. $\text{F}^- \rightleftharpoons \text{OH}^-$ Arsenic story
Natural uranium concentration in phosphates/phosphorites, as in Florida

Use: huge industrial use in fertilizer; soda water; chemical and pharmaceutical industries; phosphors for lights and TV monitors.

Making of fertilizer has large environmental impacts (discuss in Environmental Mineralogy course): mining and quarrying, grinding, processing with sulfuric acid (largest consumption of this product), huge amount of “dirty” gypsum residue, release of uranium to the groundwater, spread of Cd onto fields. Phosphates get into surface and groundwaters.

☞ Structures of Silicate Minerals (Chapter 18)

☞ Introduction

Silicates comprise >25 % of known mineral species, including most igneous, rock-forming mins. Can view Earth's crust as packed oxygens, with interstitial metal ions – some structures with closest packing of oxygens, others less tight.

Coordination of metal ions determined mostly by radius ratio

Silicate bonds and packing: Si^{4+}

Ionic model: radius ratio of silicon:oxygen favors 4-fold coordination

Covalent model: Si forms hybrid sp^3 orbitals; Si-O bonds along these orbitals extend toward corners of a regular tetrahedron

So, Si-O bonds are effectively 50-50 in ionic-covalent character.

Aluminate bonds: Al^{3+} radius ratio with oxygen is slightly larger than Si's.

Al often in 4-fold coordination, replacing Si

Al also can be in 6-fold coordination with oxygen

$[\text{AlO}_4]^{5-}$ tetrahedron is larger than $[\text{SiO}_4]^{4-}$ tetrahedron

$[\text{AlO}_6]^{9-}$ for octahedron

*****Essential** ☞ Read indicated parts of textbook chapter 18.

☞ Silicate Polymerization

Classification

Mineral structure and chemistry

Evolution of igneous melts

As we just saw in contrasting discussion of carbonate anionic groups, in silicates, oxygen shares half of its charge with Si and half with metal cation. This dual sharing holds the mineral structure together; the equality of the sharing encourages polymerization.

Bridging oxygen = oxygen shared between two silica tetrahedra, thereby linking them.

Non-bridging oxygen = oxygen not shared between tetrahedra, but rather bonded between one tetrahedron and another metal cation.

Sharing of oxygens among silica tetrahedra leads to polymerization. Affects properties, such as melt viscosity.

How many of the 4 oxygens in a tetrahedron are shared? Depends on structural type.

0 to 4 oxygens shared by tetrahedron

Silica tetrahedra only every share corners, not edges, never faces

Sharing of oxygens gives rise to different Si:O ratios.

Different “cluster types” among tetrahedra have different shapes and valences.

Because different minerals form from/stabilized by specific Si:O, their individual formations are controlled by conditions in the melt, solution, etc.

Si:O ratio in igneous melt increases during differentiation (formation and removal of crystals from a melt, thereby changing the composition of the remaining melt), stabilizing a sequence of minerals. Begin with lowest Si:O (i.e., Si:O = 1:4, totally unshared tetrahedra) and work to highest Si:O (i.e., Si:O = 1:2, all corners of tetrahedra shared).

Olivine → Pyroxene → Quartz Bowen's Reaction Series (See hand-out)

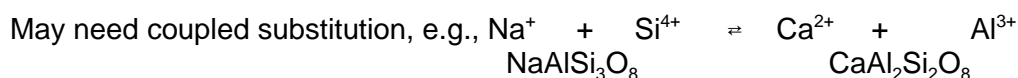
Other ions bonded within or between silicate groups

4-fold (tetrahedral): Si⁴⁺, Al³⁺

6-fold (octahedral): Mg, Fe²⁺, Fe³⁺, Mn²⁺, Al³⁺, Ti⁴⁺

Much solid solution among them. These elements develop ionic bonds with oxygen (weaker than Si-O bonds within tetrahedra), which link other cations to tetrahedra.

8-fold: larger cations (Ca²⁺) and lower-charge cations (Na⁺). Radius ratio shows 8-fold coord.



12-fold: largest cations, e.g., K, Rb, Ba. Don't substitute readily for ions in other groups.

NOTE: Frequently have sites of different coordination in same mineral. In same mineral, also may have recognizable distinction between sites of same coordination # (e.g., distorted and undistorted octahedron; # of shared electrons may control this)

Different ways of looking at silicate structures: Klein and Dutrow focus on silica tetrahedra; K&D begin with least polymerized and work toward most polymerized.

Cf. Bowen's Reaction Series in crystallization sequence of a fractionating silicate melt.

• **Read textbook chapter 18 and indicated parts of chapter 19.**

⇒ **Island Silicates, Isolated Tetrahedra, Nesosilicates** [SiO₄]⁴⁻

See Klein and Dutrow's table/list on p. 484

Si:O = 1:4 First silicates to crystallize from cooling basaltic melt, i.e., highest melting points

SiO₄ tetrahedra are linked by interstitial cations. Need to counterbalance -4 charge.

Examples: olivine group, garnet group, aluminosilicate polymorphs (Al₂SiO₅)

dating

Extra credit: explain this “odd” formula of X_2SiO_5 (not SiO_4)

⇒ **Double tetrahedra or Sorosilicates** [Si_2O_7]⁶⁻ See K&D’s list on page 498.

Si:O = 2:7 Isolated double tetrahedra, sharing one oxygen. Most group members are rare.

Most common members shown in table on page 506. NOTE how formulas are written.

Epidote group

Vesuvianite group

Some minerals have single, isolated tetrahedral groups, as well as double, shared tetrahedra.

Al’s in octahedral sites, coordinated to O and/or OH anions. Another octahedral site filled by Al^{3+} or Fe^{3+} .

Chains of octahedra are connected by SiO_4 and Si_2O_7 groups.

Epidote fairly common $Ca_2(Fe^{3+}, Al)Al_2O(SiO_4)(Si_2O_7)(OH)$
 low-grade metamorphic mineral
 hydration/alteration of plagioclase
 sometimes beautiful crystals; pistachio green

Vesuvianite - formed through contact metamorphism of limestone

⇒ **Ring Silicates = Cyclosilicates** [SiO_3]²⁻ See K&D’s list on page 502.

Si:O = 1:3 Rings of silica tetrahedra in which 2 oxygens shared per tetrahedron

Typically, 3-, 4-, or 6-fold rings. 6-fold is most common, as in **beryl** and **tourmaline**.

Beryl has channel along c-axis: OH^- , H_2O , F, He, large low-valence cations.

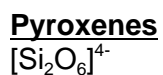
Granitic **pegmatites** (last material to crystallize from water-enriched melt; coarse).
 Emeralds and morganite are gem varieties.

Cordierite, $(Mg,Fe)_2Al_4Si_5O_{18} \cdot nH_2O$, forms from metamorphosed aluminous rocks. Holds CO_2 and H_2O in its channels.

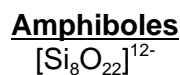
In **tourmaline**, get BO_3 triangularly coordinated groups. Huge amount of solid solution possible:
 $1^+ 2^+ \dots (BO_3)_3(Si_6O_{18})(OH)_4$. Often see mineral zoning.

⇒ **Chain Silicates = Inosilicates**

Si:O differs among sub-groups.



Pyroxenoids



Pyroxenes $[\text{Si}_2\text{O}_6]^{4-}$ See K&D's list on page 505.

Si:O = 1:3 as in the cyclosilicates. This is because each tetrahedron shares two oxygens.

Alternating layers of tetrahedral chains and octahedral bands, both parallel to (100) plane.

Bonds strongest along c-axis Si-O's. Thus, cleavages at (110) and (110); prismatic habit.

See 2 structural diagrams. Use your CD ROM.

Chemically represented as XYZ_2O_6 **X** = M2 site (irreg. 6-fold): $\text{Na}^+, \text{Ca}^{2+}, \text{Fe}^{2+}, \text{Mg}$

Y = M1 site (regular oct.): $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mg}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Cr}^{3+}$

Z = $\text{Si}^{4+}, \text{Al}^{3+}$ (tetrahedral)

X cations often bigger than Y (thus, occupy the distorted octahedral site).

In tetrahedral chains, tetrahedra alternate in pointing up or down.

The two free apices per tetrahedron link with the double octahedral bands.

Called **I-beam construction** or **"t-o-t"** See how they control cleavage (and angle).

Pyroxene chemistry summarized by the pyroxene quadrilateral (hand-out; K&D, p. 448, Fig. 18.15). Note how symmetry changes with chemistry.

Base: $\text{Mg}^{2+} \rightleftharpoons \text{Fe}^{2+}$; no Ca. **Orthopyroxene**.

Add Ca: **diopside-hedenbergite** complete solid solution. Clinopyroxene.

Apex is **wollastonite**, which is a **pyroxenoid**.

Augite (solid solution) and **sub-calcic augite**

Pigeonite: only stable at high temperature. If quickly quenched, remains pigeonite. If slowly cooled, exsolves into oriented intergrowth of clinopyroxene and orthopyroxene.

Other pyroxene compositions:

acmite $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$

jadeite $\text{NaAlSi}_2\text{O}_6$

Geologic occurrence: pyroxenes are common in mafic (Mg-Fe-rich) igneous rocks and in metamorphosed limestones (i.e., marbles).

Amphiboles $[\text{Si}_8\text{O}_{22}]^{12-}$ See K&D list on text page 514.

**Analogy with pyroxene (chemistry, structure)

**Asbestos issue

Si:O = 4:11 Si_8O_{22}

Structural analogy with pyroxene:

Double chains of tetra., cross-linked so 3 out of 4 apices shared on cross-linked tetr.; other tetr. share only 2 oxygens

As for pyroxene, adjacent double chains alternate apex up and apex down for tetr., and chains are parallel to c-axis

In amphiboles, octahedral chains are alternately 3 and 4 polyhedra wide. Have 4 distinct types of octahedral sites: M1, M2, M3, M4 (cf. 2 types of octa. sites in pyroxene)

Tetr. double chains oriented in back-to-back pairs with oct. chains between

OH groups reside along each side of connecting octa. chains; OH's coordinated to apices of octa. that are not shared with tetra., in center of large holes in rings formed by chains. Also can have F or Cl in this position: (OH, F, Cl).

A-sites arise because of extra width of double tetrahedral chain; 10- to 12-fold coordinated. Thus, accommodate Na^+ and K^+ , needed for charge balance; so, usually not completely full. Can be empty.

Double tetrahedral chains and wide bands of octahedra account for wider t-o-t l-beams and thus different cleavage angles from pyroxene (120° and 60° cleavages in amph.)

General formula: $\text{W}_{0-1}\text{X}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH},\text{F},\text{Cl})_2$

W = Na^+ , K^+

A-site: X - XII

X = Ca^{2+} , Mn^{2+} , Fe^{2+} , Mg^{2+} , Na^+ , Li^+

M4-site: VI - VIII

Y = Mn^{2+} , Fe^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Ti^{4+}

M1, M2, M3 sites: VI

Z = Si^{4+} , Al^{3+}

Tetrahedral site: IV

Can view chemistry, as well as structure, in analogy with pyroxenes

Brucite-type: $Mg^{VI}(OH)_2$

Types of bonding between sheets:

Different sandwiches (T-O, T-O-T) and different glues (H-bond, van der Waals, M^+)

T-O: bound by weak hydrogen bonds. **Kaolinite, serpentines**

T-O-T: bound by van der Waals forces, also weak. **Pyrophyllite and talc**

Most phyllosilicates have hydroxyl (OH) groups in center of 6-fold rings of tetrahedra, on level with the unshared apical oxygens of the tetrahedra.

If Al substituted for some Si in tetrahedral sheets, then no longer have electrical neutrality. Generate means by which T-O-T sheets can be linked via cations:

(1) T-O-T + cations OR (2) T-O-T + H_2O + cations

If one Al substitutes for every fourth Si, need univalent interlayer cations, as in true micas. Increases hardness. Cations in 12-fold coordination. **Muscovite, phlogopite, biotite.**

$[AlSi_3]O_{10}$ groups require either something like KAl_2 (dioctahedral) or KMg_3 (trioctahedral).

Trioctahedral $KMg_3(AlSi_3O_{10})(OH)_2$ **phlogopite**

Diocahedral $KAl_2(AlSi_3O_{10})(OH)_2$ **muscovite**

If half of Si's replaced by Al, then need divalent cation for charge balance, such as Ca. Thus, layers bound more strongly; produces "brittle micas" such as margarite: $CaAl_2(Al_2Si_2O_{10})(OH)_2$

Chlorite = talc layer + brucite layer

Chemistry of micas and clays: little solid solution between dioctahedral and trioctahedral types.

Much $Fe^{2+} \rightleftharpoons Mg^{2+}$, $Al^{3+} \rightleftharpoons Fe^{3+}$, $Ca^{2+} \rightleftharpoons Na^+$ (need further charge balance here)

Serpentines

$Mg_3Si_2O_5(OH)_4$ trioctahedral. Mismatch of T and O layers. Three "almost" polymorphs.

Antigorite lizardite chrysotile (sheets roll into fibers → asbestos)

>90% of asbestos used commercially is/was chrysotile; not so harmful to lungs as amphibole.

Under microscope, can distinguish amphibole (crocidolite) from serpentine (chrysotile) asbestos

Clays

Types: **kaolinite**, **illite**, **smectite**, **vermiculite**, **chlorite**, **mixed-layer clays**
 Simple T-O Exchange, Swells
 Flocculate

T-O and T-O-T type units, analogous to micas

Substitutions in one or both T and O sites/layers cause charge deficiencies that are accommodated by adding cations to interlayer volume. Can make use of cation exchange properties of smectites, as we did in lab.

Importance of clays:

Weathering products of, e.g., feldspars. Form soils.
 Clay liners, clay filters (with properties we explored in lab).

Uses of other sheet silicates:

Serpentinites: beautiful when polished; facings on buildings
 Serpentine asbestos
 Micas are very good electrical and thermal insulators; isinglass.

Geologic Occurrences of Sheet Silicates:

Clays are typically secondary minerals, derived from Al-rich precursors such as feldspars.

Serpentines and chlorites are derived from moderate-temperature alteration (hydration) or mafic minerals (esp. olivine); thus, also secondary.

Where those Al-rich, clay-rich sediments get metamorphosed, you can get kyanite, andalusite, and sillimanite, as well as mica schists.

Some igneous micas. Since dioctahedral and trioctahedral micas are so different, you can get both muscovite and biotite in the same rock.

⇒ **Framework Silicates = Tectosilicates** See K&D list on page 534.

Si:O = 1:2 [SiO₂]⁰ **SiO₂ phases, Feldspars, Feldspathoids, Zeolites**

This group comprises 70% of earth's crustal rocks.

All 4 oxygens in silica tetrahedron are shared; complete connectivity, fully polymerized. Last minerals to crystallize from a cooling silicate melt.

SiO₂ Group

SiO₂ is electrically neutral. Don't need charge-balancing cations. In fact, quartz is compositionally very pure except for a little substitution by Al³⁺ (counterbalanced by X⁺).

At least 9 ways to link the silica tetrahedra into a framework – thus, 9 polymorphs of SiO₂, including: 1 artificial, 1 (stishovite) in which Si is in octahedral coordination with oxygen.

Different polymorphs stable at different P and T conditions

high-X → low-X: displacive transition of α → β type

X → Y → Z: reconstructive transitions. Major density changes.

Coesite is much more compact in structure than other polymorphs

Stishovite has a rutile-type structure: edge-sharing chains of octahedra

Other morphologic types of SiO₂, e.g., fibrous (e.g., **chalcedony**), microgranular (e.g., **flint**, **chert**, **novaculite**), **opal** (SiO₂•nH₂O; amorphous spherules of silicate in CCP or HCP, with water and/or air in voids).

Geologic occurrence: can be very abundant in igneous (e.g., granite) and metamorphic rocks. Due to high resistance during weathering, quartz becomes concentrated in sediments.

Uses of SiO₂: mortar and concrete (sand), abrasive (sandpaper, scouring cleansers, honing stone), building stone (sandstone, granite), piezoelectric (watches, radio oscillator), lenses and other optics, quartz is optically active (rotates plane of polarization of light), source of Si for solar cells and silicon wafers in computers.

Silicosis issues. Lung scarring.

Quartz is compositionally **incompatible with nepheline, corundum, and forsterite** because the addition of SiO₂ to each of those minerals produces a different stable mineral (albite, kyanite/andalusite/sillimanite, and enstatite, respectively).

Some SiO₂ polymorphs have structures from which feldspars and other tectosilicates can be derived.

Feldspar Group: Plagioclase (Ca, Na) and alkali feldspars (K, Na)

Also framework of silica tetrahedra: SiO₄ and AlO₄ tetrahedra. Substitution of Al³⁺ for Si⁴⁺ creates need for charge-balance, i.e., counterbalancing cations.

Feldspars are structurally based on coesite structure; derivative structures.

Alkali feldspars: K^+ (microcline, orthoclase, sanidine) is 9-fold coordinated with oxygen. Na^+ (albite) is only 6- or 7-fold coordinated. Explains limits to solid solution.

Ordering of Al in the tetrahedral sites has important structural implications.

Twinning is symmetrically different in the compositionally different feldspars. See polysynthetic twinning in the surface of many plagioclase grains (only seen on certain planes).

Solid solution is more limited at low temperature, especially in alkali feldspars. Get exsolution, producing oriented intergrowths. **Perthite** (if K-spar dominates) and **antiperthite** (if plagioclase dominates).

Plagioclase feldspars: Almost complete solid solution at high temperature between Ca^{2+} member (anorthite) and Na^+ member (albite). See K&D, page 476, Fig. 18.56 for extent of solid solution among all three feldspar members as a function of temperature. Plagioclase feldspars of various Ca^{2+}/Na^+ ratios are major components of mafic rocks; also in felsic rocks.

Geologic occurrence: abundant in igneous rocks except for ultramafic rocks; very abundant in granites (both compositional types).

Uses of feldspar: mild abrasive, porcelain, pottery, semi-precious gem.

Feldspathoid Group

$Si^{4+} : Al^{3+}$ is between 1:1 and 4:1. Thus, feldspathoids are less siliceous than feldspars. They crystallize from low- SiO_2 melts, usually high in alkalis.

Leucite $KAlSi_2O_6$ (= Kspar - SiO_2)

Nepheline $(Na,K)AlSiO_4$ (albite - $2SiO_2$)

Zeolite Group

Framework of SiO_4 and AlO_4 tetrahedra, sharing corners, charge-balanced by cations.

Like feldspars in many ways, but has large, interconnecting channels and H_2O .

Unlike most hydrated minerals, zeolites can be heated until all H_2O is driven off, yet still maintain structural integrity. Can re-hydrate.

Environmental usefulness:

cation-exchange capacity (as in water softeners/exchangers for hard water)

can be dehydrated to leave large channels open; use as molecular sieves; use to absorb unwanted components such as ammonia, mercury vapor.

Huge industry in synthesizing zeolite-analog phases that have specific channel

dimensions, for use as molecular sieves for specific purposes. Something like 2000 types of synthetic zeolites have been created.

Geologic occurrence: authigenic sedimentary mineral (large, stratified deposits); product of alteration of volcanic tuffs that reacted with seawater. Often associated with basalts, e.g., in Paterson, NJ and Poonah, India. Vug-filling phases in the latter cases.