Silicate Minerals

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Crustal Chemistry

- The earth's crust is composed of three common elements, on an atom percent basis
 Oxygen, 62.5%
 Silicon, 21.2%
 - ✤Aluminum, 6.47%
- Silicates are the most common minerals on the planet
- They are called "rock-forming" minerals for this reason

Other Common Cations

- Metal cations also contribute to minerals
- On an atom % basis:
 Sodium, 2.64
 Calcium, 1.94
 Iron, 1.92
 Magnesium, 1.84
 - ✤Potassium, 1.42

Types of Silicate Minerals in the Earth's Crust

- Silicates make up 92% of the crust
 - Plagioclase, 39%Alkali feldspar, 12%
 - ◆ Alkali feldspar
 ◆ Quartz, 12%
 - Qualtz, 12%Pyroxene, 11%
 - Amphiboles, 5%
 - Micas, 5%
 - Clays, 5%
 - ♦ Other silicates, 3%

Whole Earth

- When the mantle and core are included, the compositional picture changes
- Olivine is the main constituent of the upper mantle, and may be the most common mineral on earth
- The lower mantle is composed of other silicates
- The core is believed to be an Fe-Ni mix

Mineral Nomenclature

- Minerals are classified into classes, such as oxides, carbonates, and silicates
- · The silicates are divided into subclasses
- Within a class or subclass, we may have divisions into groups, such as the garnet group of the subclass nesosilicate or the spinel group of the oxides
- Minerals may also be classified as series, such as the olivine series of the nesosilicates

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Mineral Nomenclature 2

- Individual minerals are known as species, such as forsterite or fayalite of the olivine series
- A species may have varieties, such as Iceland Spar, tufa, or travertine of the mineral calcite

Silicate Nomenaclature

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Silicate Subclass	Alternative Name
Neso – (or Ortho) Silicates	Island
Sorosilicates	Couplet
Cyclosilicates	Ring
Inosilicates	Chain
Phyllosilicates	Layer
Tectosilicates (or Tekto-)	Framework

Silicate Anionic Group

- The silica tetrahedron is the basis for all the silicate structures
- The SiO₄ tetrahedron has a charge of ?









Nesosilicates

- Characterized by independent Si0₄ tetrahedra, which are not linked together directly
- They are bonded together by ionic bonds to interstitial cations
- The structures of the nesosilicates are therefore, very dependent on the size and charge of the interstitial cations
- Because the tetrahedral do not share oxygen, the Si:0 ratio is 1:4.

Interstitial Cations

- Since the SiO₄ tetrahedron has a charge of 4, two divalent cations, a trivalent and a monovalent, or a quadravalent cation are required to maintain electrical neutrality
- Several structure types are possible in the silicate structures the letter A = non-silicon cations with lower valency then Si^{4+} , B = Si or Al or other higher valent cations, O = oxygen

A_2SiO_4

- This group includes the olivine series
- Structure is based on an nearly HCP arrangement of the O²⁻ ions
- A ions are in octahedral voids
- B ion in a tetrahedral void
- ¹/₂ of the octahedral voids are occupied, 1/8 of the tetrahedral voids are occupied



• Fayalite – Fe_2SiO_4 Fa • Forsterite – Mg_2SiO_4 Fo

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Olivine Solid Solution Ranges

- Fosterite 0-10% Fe
- Chrysolite
- Hyalosiderite 30-50% Fe
- Mortonolite 50-70% Fe
- Ferrohortonolite 70-90% Fe
- Fayalite
- 90-100% Fe

10-30% Fe

Solid Solution Nomenclature

- As with some other important series an abbreviation is used for the end members compositions can be expressed using abbreviated symbols
- Example $Fe_{0.6}Mg_{1.4}SiO_4 = Fa_{30}Fo_{70}$

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Other Olivine Group Minerals

• CaMgSi0₄

• Mn_2SiO_4

- Monticellite Tephroite
- CaMnSi0₄
- Glaucochroite • CaFeSi0₄ Kirschsteinite

ASiO₄

- The most common mineral of this group is the mineral zircon, $ZrSi0_4$
- In zircon, the A ions are in distorted cubic coordination with 4 oxygens at one distance, 4 further away
- Zircon always contains some Hf and sometimes Th or U (may be metamict)
- Thorite, ThSi0₄, is isostructural but is often metamict because of radioactive decay

Garnets, $A_3B_2(SiO_4)_3$

• Larger A site is occupied by divalent cations which are relatively large, with a coordination number of VIII

✤Typical cations are Ca²⁺, Mg²⁺, Fe²⁺, Mn²⁺, and some trivalent lanthanides

 The smaller B site is occupied by trivalent cations which are smaller, with a CN of VI
 Typical cations A1³⁺, Cr³⁺, Fe³⁺, and Ti⁴⁺

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Garnet Structure

- Silica tetrahedra are linked by the VI coordinated cations to form a three dimensional array
- VIII coordinated ions are distributed within this structure
- All garnets have isometric hexoctahedral symmetry

Calcium and Noncalcium Garnets

- Ca^{2+} is larger than Mg^{2+} , Fe^{2+} and Mn^{2+}
- Garnets can be split into two groups, the Ca and non-Ca garnets
- A similar division may be made for the B ions into A1, Fe³⁺ and Cr³⁺ garnets.

Ca Garnets				
Name	Formula	Color		
Uvarovite	Ca ₃ Cr ₂ (Si0 ₄) ₃	Emerald green		
Grossularite, also called cinnamon stone, essonite	Ca ₃ A1 ₂ (Si0 ₄) ₃	White green, yellow, cinnamon brown, pale red		
Andradite	Ca ₃ Fe ₂ (Si0 ₄) ₃	Yellow, green, brown, black		

Name	Formula	Color
Pyrope	Mg ₃ A1 ₂ (Si0 ₄) ₃	Deep red to black
Almandine	Fe ₃ A1 ₂ (Si0 ₄) ₃	Deep red to brown
Spessartite	$Mn_3A1_2(Si0_4)_3$	Brownish to red







Aluminosilicates

- Aluminosilicates have aluminum in addition to silicon in the structure
- They may belong to any silicate subclass



Kyanite, andalusite, and sillimaite have chemistry, but form under different P and T conditions







Staurolite

- Fe₂A1₉0₆(Si0₄)₄(O,OH)₂
- Crystals are prismatic
- Often twinned (penetration twins), with two varieties of cruciform twins



- CaTiO(Si0₄)
- Formerly known as
- An example of a titanosilicate
- N = 1.91 lusterresinous to adamantine

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Willimite



Willemite with Franklinite and Quartz New Jersey

• Zn₂SiO₄

- · Associated with other Zn ores
- Mn may replace Zn
- Often fluorescence



Sorosilicates

• Characterized by two Si04 tetrahedra joined through a single oxygen to give an Si:O ratio of 2:7



Epidote Group

- Contains both Si0₄ and Si₂0₇ groups
- General formula is $X_2^{VIII}Y_3^{VI}(Si0_4)O(OH)$
- $X = Ca^{2+}, Na^{+}$
- $Y = A1^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}$
- Epidote: $Ca_2(A1,Fe)A1_2O(Si_2O_7)(SiO_4)(OH)$
- Clinozoisite: Ca₂A1₃O (Si₂O₇)(SiO₄)(OH)

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Vesuvianite

- Formerly called Idocrase
- Ca₁₀(Mg, Fe)₂A1₄(Si0₄)₅(Si₂0₇)₂ (OH)₇
- Tetragonal $H = 6 \frac{1}{2}$
- Brown or green



Hemimorphite

- $Zn_4(Si_20_7)(OH)_2H_20$ is one mineral of the sorosilicate group with isolated Si₂0₇ groups, cross linked by Zn
- Formed as a secondary mineral in the oxidized portions of zinc deposits

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Cyclosilicates

- When three or more Si tetrahedral groups are linked, a cyclical structure is possible
- The Si:O ratio is 1:3
- Rings containing 3, 4, or 6 Si are possible, but only the rings with 6 Si are at all common













Gem Beryl

•Upper left, emerald •Lower left, morganiteUpper right, aquamarine •Lower right, golden beryl





• Elbaite, a gem variety of tourmaline

• Schorl crystal, with Striations, typical of tourmaline

Chrysocolla cyclosilicate

- Amorphous but similar to dioptase, a six-membered
- May contain Si_4O_{10} units, which would make it a phyllosilicate

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Inosilicates

- Inosilicates include two very important groups of silicates, the pyroxenes and the amphiboles
- Both have chain structures
- Si0₄ tetrahedra link together to form either a single chain or a double chain composed of two linked, parallel single chains



Orthopyroxenes

- Enstatite
- me MgSiO₃
- Hypersthene (Mg, Fe)SiO₃
- Orthoferrosilite Fe SiO₃



Enstatite

- Brownish orthopyroxene (opx)
- Lower photo is of Bronzite, an opx containing some Fe, and displaying an iridescence known as Schiller luster

		Clin	opyroxenes	
		х	Y	
ŀ	Diopside	Ca	Mg	Si ₂ O ₆
ŀ	Hedenbergite	Ca	Fe ²⁺	Si ₂ O ₆
ŀ	Augite	Ca	(Mg, Fe ²⁺) (Al, Fe ³⁺ , Ti)	Si ₂ O ₆
ŀ	Pigeonite	(Mg,Fe ²⁺ , Ca) (Mg, Fe ²⁺) (Al, Fe ³⁺)	Si ₂ O ₆
ŀ	Aegirine	Na	Fe ³⁺	Si ₂ O ₆
ŀ	Jadeite	Na	Al	Si ₂ O ₆
ŀ	Spodumene	Li	Al	Si ₂ O ₆
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Pyroxene Structure

- X: VIII coordination Na^+ or Ca^{2+}
- Y: VI coordination Mg, Fe²⁺, Fe³⁺, Al³⁺, Mn²⁺, Mn³⁺, Li⁺, Ti⁴⁺
- Si: IV coordination Si^{4+} or Al^{3+}



Spodumene Series

- The spodumene series of pyrxoenes involves X sites occupied by moderate to large size cations, Y by small trivalent cation
- Spodumene Li Al Si_2O_6
- Jadeite Na Al Si_2O_6
- Aegerine Na Fe^{3+} Si₂O₆

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Pyroxenoid Structure

- Large cations occupy both X and Y, producing the triclinic structure of the pyroxenoids
- Chains made of Si₂O₇ and SiO₄ groups linked together are present, and the chains are parallel to **b**
- Si:O = 1:3





Amphibole Chain



• Double chain of SiO₄ tetrahedra connected by corner sharing

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Amphibole Structure

- Amphiboles have a double chain structure formed by sharing three corners
- All have the basic Si₄O₁₁ double chains, with larger X ions are in VIII coordination, while smaller Y cations are in VI coordination
- Si:O = 1:2.75

Amphibole Formula

- The general formula is:
- $W_{0-1}X_{0-7}Y_{7-14}Z_{16}O_{44}(OH)_4$
- X: Na⁺, Ca²⁺, minor K⁺, Mn²⁺, Fe²⁺, Mg²⁺, Li⁺

- Y: Mg²⁺, Fe²⁺, Fe³⁺, Al³⁺, Mn²⁺, Mn³⁺, Ti⁴⁺
- Z: Si⁴⁺, Al³⁺













Orthoamphibole					
Orthoamphibole	e X,Y	Z			
Anthopyllite	(Mg, Fe2+) ₇	(Si ₈ O ₂₂)	(OH, F) ₂		
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- Phyllon is the Greek word for leaf phyllosilicates are thus "leaf-like", platy or flaky minerals which have a layered structure
- The basic silicate sheet structure is composed of a hexagonal grouping of tetrahedra





indefinitely in











Diphormic Phyllosilicates

- One t-layer, one o-layer
- 0.7nm repeat distance
- Kaolinite dioctahedral A1₄[Si₄O₁₀](OH)₈
- Serpentine trioctahedral $Mg_6[Si_4O_{10}](OH)_8$



Triphormic Phyllosilicates

- In this phyllosilicate the ratio of tetrahedral : octahedral layers is 2:1
- Basal spacing is generally around 0.9nm
- The structure is a t-o-t sandwoch, with apical oxygens pointing inward
- Pyrophyllite dioctahedral $Al_2{Si_4O_{10}}(OH)^2$
- Talc trioctahedral $Mg_3{Si_4O_{10}}(OH)_2$

Micas

- Another example of triphormic phyllosilicates
- The t-o-t layers are held together by layers of K⁺ cations, in the holes of the rings
- To balance the plus charge of the K ion, one quarter of the Si⁴⁺ are replaced by Al³⁺

Brittle Micas

- Half of the Si^{4+} ions are replaced by $A1^{3+}$
- This means the interlayer cations be divalent, like $Ca^{2\scriptscriptstyle +}$
- Ca²⁺ bonds are stronger and consequently the cages are not flexible
- Margite dioctahedral CaAl₂{Al₂Si₂O₁₀}(OH)₂
- Clintonite trioctahedral $CaMg_3{Al_2Si_2O_{10}}(OH)_2$



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Tetraphormic Phyllosilicates

- t-o-t layers of either the pyrophyllite or talc type are joined by octahedral layers
- tot o tot o tot o tot Repeat distance is 1.4nm
- These minerals are chlorites
 Leptochlorites Fe²⁺ + Fe³⁺
 Orthochlorites Fe²⁺ only
- $[(Fe,Mg,Al)_{2-3}(OH)_6(Mg,Fe,Al)_{2-3}\{Al,Si)_4O_{10}\}(OH)_2]$

Tectosilicates

- The tectosilicates are three dimensional, or framework, silicates
- They involve linkage of SiO₄ tetrahedra through all four oxygen atoms
- The resulting structure is stable and strongly bonded

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• Si:O ratio is 1:2















- K-spar shows a variety of polymorphic forms
 - *Sanidine
 - *Orthoclase
 - * Misses alias
 - Microcline

Perthite and Antiperthite

- Albite in K-spar host = perthite
- K-spar in plagioclase host = antiperthite

Plagioclase Name

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- Plagioclases are triclinic
- Their a-b and b-c angles are a bit more oblique than microcline
- Hence the name: *plagio*-, oblique and *clase*, break

Plagioclase Feldspars

• Albite

An₀₋₁₀ - Found only in very sodic rocks, hence usually metamorphic or formed in marine conditions as a sedimentary cement, or by ion exchange with more calcic plagioclase.

- Oligoclase
- An_{10-30} The dominant plagioclase in granitic rocks
- Andesine
- ◆ An₃₀₋₅₀ Found in intermediate igneous rocks
- Labradorite
 - An₅₀₋₇₀ The dominant plagioclase in gabbro and basalt. Also, despite their name, most anorthosites are made up of labradorite.
- Bytownite
 - An_{70.90} The rarest. Requires both a lot of calcium and also significant sodium. Most igneous settings have too much sodium, most calc-silicate metamorphic settings have too little sodium.
- Anorthite
 - ♦ An₉₀₋₁₀₀ Generally a metamorphic mineral in calc-silicate rocks.
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Charge Balance

- Since Na and Ca differ in valence, Al has to substitute for Si to compensate
- The Al-Si orderings of albite and anorthite are different, and at low temperatures, plagioclases in the middle of the composition range also exsolve, but on a submicroscopic scale
- These submicroscopic textures are probably responsible for the iridescence of some plagioclases

Feldspathoids

- Alumino silicates but contain less SiO_2 than feldspars
- They are rich in alkalis
- The feldspathorids often include unusual anions such as Cl⁻, CO₃⁻, etc.

Important Feldspathoids

Nepheline (Na, K)AlSiO ₄			
Leucite K(AlSi ₂ O ₆)	Κ		
Sodalite Na ₈ (Al Si O ₄) ₆ Cl ₂	Cl		
Lazurite (Na,Ca) ₈ (AlSiO ₄) ₆ (SO ₄ , S, Cl) ₂	SO4, S, Cl		
Petalite Li (Al Si ₄ O ₁₀)			

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Scapolites

- Metamorphic rock minerals probably derived from feldspars
- The alumino-silicate framework forms chains in the c-direction and has large open spaces which can accommodate large anions such a Cl, CO₃, SO₄

Scapolite Minerals

- Marialite $Na_4(AlSi_3O_8)_3(Cl_2,CO_3,SO_4)$
- Meionite $Ca_4(Al_2Si_2O_8)_3(Cl_2,CO_3,SO_4)$

Zeolites

- Hydrous alumino-silicates with very open structures.
- Rings of A1O₄ and SiO₄ tetrahedra are penetrated by open channels in the structure
- Non-silicon cations hold the structure together.

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Cation Exchange

- Water can easily pass though these channels and dissolve and replace the cations present in the structure
- This process in known as cation exchange and is reversible
- Thus, the zeolites can serve as catalysts and watersoftening agents
- Petroleum companies have been particularly interested in zeolites for this reason

Important Natural Zeolites

- $\bullet \ Chabazite \qquad Ca_2(Al_2Si_4O_{12}){\cdot}6H_2O$
- Heulandite $Ca(Al_2Si_70_{18}) \cdot 6H_2O$
- Stibnite $Ca_2Na(Al_5Si_{13}O_{36})\cdot 14H_2O$
- Natrolite $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$
- Analcime $Na(AlSi_2O_6) \cdot H_2O$

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