

EPSc 352: Lecture Overview for Part 1, Mineral Chemistry

Fill out questionnaires: please print

Hand-outs: syllabus, homework set #1; first lab to come by e-mail

Goals of the Course

Walk through syllabus: schedule, expectations

☺☺ **Assignment: Begin reading chapters 1 and 3 in your text.** NOTE: The designation "K&D" refers to your textbook, Klein and Dutrow (2008) *Mineral Science*.

Page 9, Fig. 1.9: 5 major aspects of "mineral science"

Definition of a mineral: properties and examples of their implications

Ways of classifying minerals: according to one's use of minerals; by analogy with chemical compounds

Mineral definition "challenged" by the notion of biominerals

Each mineral is defined as a combination of a **structure and a **composition**: examples

Begin the course by investigating compositional/chemical aspects of minerals

Bulk composition (**define**) of the earth (especially the crust) is our starting (and ending) point

Fundamental observations:

Earth is not homogeneous in composition or structure

Many types of minerals (not infinite #); distributed differently throughout earth

Layered structure of the earth, each layer with a different average composition and bulk geophysical properties, e.g., transmission of seismic waves

Compositions of existing minerals reflect the bulk chemical reservoir and the ways in which elements distribute themselves among various (competing) species.

Chemical affinities: chalcophile, lithophile, siderophile

Average abundance vs. local concentration

Walk through the geochemical hand-outs #1-4 on crustal averages.

Hand-outs #5-7: 98.5 wt.% of earth's crust from only 8 elements, O, Si, Al, K, Na, Fe, Mg, Ca

Hand-out #3 describes major, minor, trace, and dispersed elements

Element distribution is governed by (geo)chemical laws

How do we get a whole ore deposit of a geochemically minor/trace element like Au?

Element partitioning (choice): crystal chemistry

Efficiency in separating and concentrating elements

Minerals as repositories for and reservoirs of the elements

Mineral must reach saturation in order to form, i.e., create a compound rather than remain as dispersed elements.

How much concentration over crustal average concentration is required for saturation?
Elements that form own mineral vs. those that “hop a ride” in solid solution

Crystal chemistry: relation between mineral's composition, structure, and chemical & physical properties, including optical properties under the microscope.

☞ Review (romp through!) atomic structure and electronic configuration.

Importance of atomic/ionic size and charge (electronic structure) in stabilization of minerals.

Atomic radii: actual radii (0.46 - 2.62 Å) vs. effective radii (# and type of neighbors, ion charge)

Impetus for chemical reactions (including mineral formation):

attain lowest possible energy state

Hand-outs 8-10: orbital structure, aufbau principle, electronic configurations.

Valence electrons are those in the highest-energy orbitals; gained or lost in reaction

Principles of lowest energy

Transition elements: oxidation states, color in minerals

Valence electrons (in the highest-energy orbitals): those that participate in reactions

Structure of the periodic table

Elements in same column have same # electrons in valence shell, so chemically similar

Regular pattern to atomic/ionic radii down same column and across same row

☞ **Nature of Chemical Bonds**

5 types of bonds (3 of them involving valence electrons):

Type of bond:

1) is determined by electronic properties of participating atoms,

2) controls chemical and physical properties of compound (see K&D Table 3.10 on p.

56),

3) is “gradational” (% ionic character, etc.); see K&D Fig. 3.19 on p. 60

Driving force for bonding: **achieve stable electronic configuration** (mimic noble gases); Table 3.6 on pp. 44-45 shows electron configurations of the neutral elements

Can predict compound formation/stabilization and bond strength through knowledge of specific energetic and electronic tendencies of the atoms:

electronegativity – see K&D Fig. 3.22 on p. 60

ionization potential (Table 3.5 on p. 43)

electron affinity (inverse of ionization potential)

In ionically bonded compounds, those with greatest Δ electronegativities have strongest bonds.

Second important factor in atomic interactions is atomic/ionic radii.

Effective radius (1/2 distance between 2 nuclei) depends on (distortions of) electron clouds of atoms/ions; radius changes as function of # of nearest neighbors, their electronegativities, and their charges.

5 types of bonds: simply are models for characteristics of bonding

Remember: Driving force for bonding is to achieve stable electronic configuration (mimic noble gases)

Basic models of bonding are

ionic: geometric, fitting together of spheres of different sizes (next week's lab)

covalent: nature & shape of atomic orbitals with unpaired electrons; orbitals overlap

Together with metallic bonding, these 3 types involve valence electrons.

Ionic bonding model: ions are simple spheres (with a size/radius and a charge)

"Lose" or "gain" electrons to mimic noble-gas configuration

Non-directional bonding: high symmetry

Shorter the bond length, stronger the bond (imparts properties; K&D pp. 54-55)

Higher the charges on the ions, stronger the bond (shorter the length)

If Δ electroneg. ≥ 2.0 (from Pauling's data), bonding is ionic (see K&D, p. 61, Fig. 3.21)

Covalent bonding model: electron sharing

Occurs among atoms with high but similar electronegativities

Polarized electron cloud produces highly directional bonds

Lower symmetry than ionic bonds. (Many ionic compounds are cubic, e.g., NaCl)

Elements in columns IIIa, IVa, Va, VIa have several valence electrons, permitting multiple bonds & atomic clusters, e.g., CO_3^{2-} , SO_4^{2-} , SiO_4^{4-} : Trigonal planar, tetrahedral atomic arrangements.

% of bonding type: greater the Δ electroneg., more ionic in character. Silicate minerals have strong covalent and ionic character (**K&D, p. 60, Fig. 3.19 and p. 61, Fig. 3.21**).

Metallic bond: electrons de-localized. Luster, electrical conductivity. Low but similar electroneg.

Bonds that do not involve valence electrons:

van der Waals bonds: weakest type, but still significant.

Force develops between electrically neutral clusters (molecules) due to slight imbalances in electron distribution ("residual charges")

Observed in organic compounds, graphite (between planes)


Hydrogen bonds: second weakest type. Develop if H is bonded to a strongly electronegative

element (which “strips” hydrogen of its electron and leaves it with a local positive charge).
 Molecule becomes polar; electrostatic attraction to negative ion in adjacent molecule.
 Dipole-dipole interactions
 Examples: ice, layer silicate minerals such as clays

Types of bonds determine physical and chemical properties of minerals (K&D, p. 56, Table 3.10)

**Formation of a mineral involves chemical (electronic) parameters [bonding discussions] and geometric constraints.

Next, look at the physical configuration (geometry) of atoms in crystals (**lecture, Lab 2**).

 **Ionic Packing and Ionic Model of Bonding:** physical “fit”
Coordination polyhedron: geometry of arrangement (#, shape) of “shell” of nearest neighbors

Ramification of coordination polyhedra: maintain overall electrical neutrality; consider coordination number of each type of ion

Example of fluorite, CaF_2 . Ca^{2+} surrounded by 8 ions (fluorides): $+2/8 = +1/4$
 F^- surrounded by 4 ions (calciums): $-1/4$ Cancel

Geometric constraints on ion packing dominantly due to relative sizes (radii) of ions

Closest packing: metals; some planes within oxide and silicate minerals; 12-fold coordination

Begin with 2-D layer of spheres: 1 in the middle and 6 around it

Two ways to build the 2-D closest-packed layers into a 3-D closest-packed array: consider positions of spheres and interstices

ABAB... stacking for hexagonal closest packing (HCP)

ABCABC... stacking for cubic closest packing (CCP), whose arrangement is also known as face-centered cubic (FCC)

****Both HCP & CCP are equally closely packed, i.e., closest-packed, with 12-fold coordination**

Alternative packing, which is NOT closest packing is body-centered cubic (BCC)

Have considered closest-packing (HCP, CCP) and “pretty-close-packing” (BCC) models.

Consider framework of packed anions, which provide interstices as sites for cations.

“No-rattle limit”: look at radius ratios of cation:anion to see which cations “fit” the interstitial sites
 Hand-outs #15 and 16: geometry of coordination polyhedra, tables of radius ratios

Pauling's Rules: principles guiding ways in which ions cluster into coordination groups and in which those groups are organized into larger (stable) structures. Hand-out #18, K&D p. 69.

1. Coordination polyhedra are determined by ionic radius ratios
2. For structure to be stable, total strength of all valence bonds reaching the anion from all neighboring cations must equal the charge on the anion. Electrostatic valency principle.
3. Coordination polyhedra in same structure tend not to share edges or, esp., faces.
4. Cations with high valence and small coordination # really avoid sharing.
5. Number of different types of coordination polyhedra (sites) in one structure is small.

If all bonds in ionic compound have ~equal strength, compound is isodesmic; for different bond strengths, it is anisodesmic. Relative strengths of its bonds affect behavior of a mineral.

Isodesmic example is fluorite, CaF_2 (K&D, p. 74). Note how geometric consideration of radius ratio is in accord with electrostatic consideration of charge balance.

Anisodesmic example is calcite, CaCO_3

Further comments on coordination polyhedra:

- mineral can have multiple types of coordination polyhedra
- frequently, different ions in the structure have different coordination numbers
- mineral may show closest packing only along certain planes in crystal
- not all polyhedra are occupied – “sites” are present, but need not be filled
- polyhedra may be distorted (not regular)
- changes may occur in polyhedron due to pressure
- CaCO₃ example
 - Ca in 6-fold coordination with oxygen in calcite
 - Ca in 9-fold coordination with oxygen in aragonite

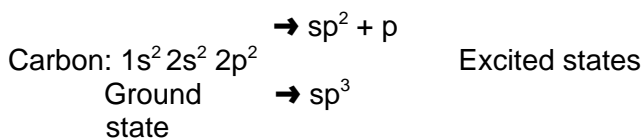
Ionic model: geometric considerations (packing), ion sizes, ion charges, electrostatic nature.

Covalent Model of Bonding

Angular relations are important: orbital shapes, bond angle distribution in atoms vs. molecules
Orbitals of molecules may differ from simple “sum” of atomic orbitals: hybridization, HO #19

Hand-out Table 5.3: Note # of electrons involved; create one kind of hybrid orbital with symmetric disposition of electrons that typically might be in different orbitals

Create a new geometry for hybrid orbital. Carbon as an example of hybridization of orbitals.



Graphite:

$sp^2 + p$
 $3\sigma + 1\pi$ bonds
 trigonal planar C
 very strong within plane
 weak bonds between planes

Diamond:

sp^3
 4σ bonds
 tetrahedral C
 same bond strength in all directions
 cf. SiO_4^{4-} groups

Hand-outs #20, 21

**Can use ionic model, covalent model, or demands of charge balance to derive CH_4 structure.

Composition of Minerals

Mineral analyses: Bulk vs. point analysis; chemistry vs. oxidation state vs. isotopic analysis

Total chemical analysis: list of components in wt. % (typically of oxides)

Definition of mineral: fixed proportions of elements. Group names for minerals with same rules.

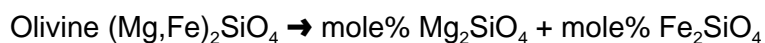
Olivine: X_2SiO_4	Alkali Feldspar: $XAlSi_3O_8$	Plagioclase Felspar
Mg_2SiO_4 Fe_2SiO_4	$KAlSi_3O_8$ $NaAlSi_3O_8$	$CaAl_2Si_2O_8$ $NaAlSi_3O_8$
forsterite fayalite	K-feldspar albite	anorthite albite
Fo Fa	Or (Ksp) Ab	An Ab

Consider the variability of mineral composition; what is it about its composition that defines a mineral? Compositional guidelines for minerals. Here are some types of formulas:

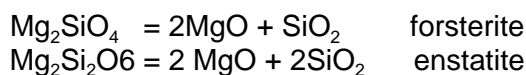
$(Mg,Fe)_2SiO_4$ olivine	Maintains ratio of $\Sigma 2$ cations/1 SiO_4
$Ca_5(PO_4)_3(F,Cl,OH)$ apatite	Parentheses indicate <u>ion sites</u>
$CaSO_4 \cdot 2H_2O$ gypsum	Two water molecules associated with each $CaSO_4$ molecule
$(Ca,Mg)CO_3$ $(Mg,Ca)CO_3$	Calcite with some magnesium (Mg) Magnesite with some calcium (Ca)
$CaMg(CO_3)_2$ dolomite	Stoichiometric mineral whose structure demands a) Ca:Mg = 1, b) 1Ca + 1Mg for every $2CO_3$
$Fe_{1-x}S$ pyrrhotite, e.g., $Fe_{0.97}S$	Two unusual aspects: a) non-stoichiometric, b) <u>variable</u> cation:anion ratio. Defect structure.

► Converting a bulk chemical analysis in wt. % oxides into the mineral(s) it represents.

Overall/bulk mineral = Σ compositional end members



End-member mineral = Σ oxides



Create your own flowchart; see Tables 5.6 & 5.7 and accompanying text on K&D pages 101-104

convert wt. % oxides to moles of oxides
partition available oxides/cations among the "rules" for each end member
which are the limiting oxides (what runs out first)?
See my "helpful hints" hand-out

Normalization:

to a specific # of oxygens, i.e., according to the stoichiometry of a specific mineral
to a subset of the cations to describe mineral in terms of % of end members

► Compositional Variation in Minerals

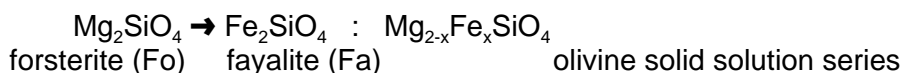
A_xB_y is a daltonide compound, i.e., typical kind of stoichiometry in which **x** and **y** are both positive integers. Many minerals have range of #'s for x and y, as well as variety of atomic/ionic species for A and B: **solid solution**.

3 types of solid solution: substitutional, interstitial, omissionsal (defect).

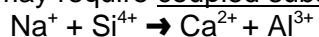
****Be sure to read the sections of your text on solid solution (pp. 97-99)**

Substitutional solid solution, as in olivine and plagioclase series.

same ionic charge similar (within 15%) ionic radius



may require coupled substitution to maintain charge balance



albite (Ab) anorthite (An) plagioclase solid solution series of the feldspars

Some "rules" about solid solution:

extent of substitution possible is controlled by structure
can get solid solution even if minerals are not isostructural (i.e., same geometric structure)
greater extent of solid solution at elevated temperature; exsolution at lower temperature

Major factors that control the amount of solid solution (i.e., % substitution) in a mineral are:

relative sizes of ions, atoms, or ionic groups ($\pm 15\%$)
charges on ions involved in substitution; need electrical neutrality in the structure
temperature and pressure of formation
availability of ions: geology, processes, other competing minerals

Consider atomic substitution in interpreting mineral analysis; one element may occupy more

than one structural site, e.g., Al

Interstitial solid solution: fill voids between ions. Small ions: C, B, H, N. Channels, voids. Sequestration issues.

Omissional (defect) solid solution: typically filled site is left empty
example: pyrrhotite, Fe_{1-x}S (cf. troilite) Some Fe sites left vacant.
See **K&D, p. 97, Table 5.7**



Representing Compositions: see your CD, unit I, "Graphical Representation"

Binary: notation and graphing with 2 end members (K&D, pp. 104-105)

Ternary: 3 end members (K&D, pp. 105-107)

☺☺ **Begin reading chapters 1 and 2 in Ehlers' *Interpretation of Geological Phase Diagrams*, which is on reserve (book itself on reserve in the EPSc library; chapters also sent to you by e-mail).**