ESS 312
Week 1 – Crystal Chemistry
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[overhead] Cross-section through the Earth

Observations about the planet – composition of the core, mantle and crust

What's the most abundant element in the Earth? [Oxygen]

What are the fundamental compositional features of the mantle? [Silicate, Mg, Fe, Ca-rich]

 ... the crust? [rich in silicon, aluminum, alkalies].

3. Differentiation of earth - core, mantle, crust, hydrosphere

[overhead]   Compositions of major earth reservoirs

    a) core *vs* silicate earth [Table 1.9 Brownlow (silicate-core)]
    b) silicate earth *vs* hydrosphere [Table 4.8 Faure (atmosphere)]
    c) differentiation of silicate earth – separation into mantle and continental crust [Table 21-2 K&B (earth—mantle—crust)]

    Contrast differences in major elements *vs* minor elements

Broadly: (i) think of the mantle as composed of olivine, orthopyroxene and a little Ca-bearing clinopyroxene, (ii) think of the crust as composed of feldspar and quartz, with a minor mafic component, similar overall to *andesite*, or *granodiorite* rock compositions.

How did this come about? We think the Earth formed as a fairly homogenous agglomeration of material similar in composition to certain types of meteorites. The transition from this state to the structured , tectonically active planet we know today is referred to as *differentiation*.

This is important to us. For example:

a) We have evolved to breathe oxygen – how do we come to have an atmosphere? Why is it O_2-rich? CO_2-poor? What role do geochemical *vs* biological reactions play in controlling the atmosphere's composition ?

b) We have populated the continetal crust. Why is there a distinct continental crust ? How and why is it different from oceanic crust? Has there always been a high and dry continental crust throughout Earth history?

c) The Earth's atmosphere and magnetic field protect us from cosmic radiation. Was there a thick atmosphere early in Earth's history? If not, how did early organisms cope ? When did the core form, and did it always support a magnetic field ?

Things turned out differently on the Moon and the other terrestrial planets ...

[overhead] Densities of the planets

The study of these processes and their history is *Geochemistry*

Goldschmidt's definition:

> *"The primary purpose of geochemistry is on the one hand to determine quantitatively the composition of the Earth and its parts, and on the other to discover the laws which control the distribution of the individual elements"*

Our aim is to teach you the priciples and familiarize you with the tools of geochemistry.

Differentiation is the chemical separation of the elements making up the Earth into compositionally distict *geochemical reservoirs*. The obvious questions are: (i) Why do the elements separate from one another into different reservoirs? (ii) Why do certain elements and groups of elements follow each other and concentrate together during differentiation?

What chemical properties control this behaviour ?

> valence
> ionic radius
> ionization potential – electron affinity
> electronegativity
> ionic potential (charge/radius ratio)

Periodic Table is organized according to the electron configuration of the elements. Electron configuration governs all the properties we've listed above.

Electrons surrounding the nucleus of the atom occupy different energy levels. These are described in terms of **shells** and **subshells**.

Shells denoted by quantum letter (K through Q) or number (1 through 7): These correspond to the **rows** on the periodic table - each new shell begins a new row.

Within each shell are subshell energy levels - given letter disignations s, p, d, f

subshell	number of e-	
s	2	(in 1 orbital)
p	6	(in 3 orbitals; first (2p) subshell in row 2)
d	10	(in 5 orbitals; first (3d) subshell in row 4)
f	14	(in 7 orbitals; first (4f) subshell in row 6)

[overhead]   filling sequence of shells and subshells

We build up the periodic table by filling the shells in succession:

H	$1s^1$	
He	$1s^2$	which results in a filled shell and a *noble gas* configuration
Li	$1s^2\ 2s^1$	
Be	$1s^2\ 2s^2$	
B	$1s^2\ 2s^2\ 2p^1$	

C	$1s^2\ 2s^2\ 2p^2$
N	$1s^2\ 2s^2\ 2p^3$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
Ne	$1s^2\ 2s^2\ 2p^6$ which brings us to the next filled shell and noble gas configuration

and so on ...

This leads to the concept of *valence* – the number of electrons in excess (for elements that form positive ions) or deficit (for those that form negative ions) of a noble gas electron configuration.

Evidently, the property of valence is connected to the outermost electrons.

A filled p shell, which brings the outermost shell up to a total of 8, 18 or 32 electrons is the most stable electon configuration — He, Ne, Ar, Kr, Xe, Rn — the noble gases

Elements with 1 'extra' electron beyond a noble gas configuration lose it easily, to form a *positive ion* of valence +1.
These behave as a geochemically coherent group, called the *alkali metals*.

Elements with 2 'extra' electrons can lose them, and are assigned a valence of +2.
These are the *alkaline earths*.

At the other end of each row are the elements that are one electron short of a noble gas configuration. Although Cl, Br and I can lose 7 electrons to acquire a valence of +7, they more commonly acquire an additional electron to attain a noble gas electron configuration. In this case, they are assigned a valence of –1.
This group of elements is called the *halogens*.

Now, notice that when we get to filling the first 'd' subshell (3d), we have already begun to add electrons to shell 4 (the 4s electrons are lower in energy than the 3d electrons, hence the 4s shell is filled first). So we are filling an *inner shell*, and the valence behavior becomes more complicated (also the "Aufbau principle" which supposedly dictates the filling order of the subshells begins to break down – it does not accurately indicate the relative energies of the subshells as successive electrons are added – e.g. La -> Ce -> Pr –Nd fill in the sequence: $Xe6s^25d^1$ -> $Xe6s^24f^15d^1$ -> $Xe6s^24f^3$ -> $Xe6s^24f^4$; La, Pr and Nd are exclusively trivalent, and Ce can take both valence +3 and +4). So as we get into filling the inner subshells, (3d, 4f, 4d and so on) the connections between *outer* electron structure and valence become less obvious and intuitive.

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Atomic and ionic radii

Here we will consider ionic radii, because they are most useful in predicting the ability of

the elements to enter into crystal structures.

Start by making some predictions:

(i) How will radii vary as more electron shells are filled and we move from the top to the bottom of the periodic table? [intuitively ... radii increase down the columns. But note, we have to compare similar co-ordination states]

(ii) How will radii change as we move from left to right across each row? Remember that we are adding more protons to the nucleus as we add electrons to the atom. [less intuitively ... radii decrease, because the Coulomb attraction to the nucleus outweighs the mutual screening effects of the added electrons] .

[overhead: Ionic radii of trivalent REE, showing "lanthanide contraction". Note the radius of Eu^{2+} - opportunity to emphasize that the co-ordination state of the cation dictates its effective radius].

(iii) What about the radii of cations compared to anions ? [anions much larger – form by acquiring additional electrons].

To illustrate, compare O^{2-}, Mg^{2+}, Fe^{2+} and Si^{4+} as they substitute into a mineral like olivine or orthopyroxene.

Introduce the *ionic potential*, ratio of charge/radius. These two properties together have the greatest effect on geochemical behaviour, primarily by dictating which crystal structures they can enter into. Elements that can substitute for one another in mineral structures tend to behave *coherently*.

[overhead: Periodic table showing ionic radii].

Notice the similarity between elements like Fe^{II} – Co – Ni. Where is all the Co in the Earth? Crust? Mantle? Core? [The core — This prediction is based on the geochemical coherence of Co with Fe and Ni. However, we also notice that rocks from the crust and mantle are highly depleted in Co compared to the primitive meteoritic material from which we think the Earth formed].

Based on charge/radius ratio we can predict the strong coherence between element pairs such as Zr-Hf, Nb/Ta, and the overall coherence of the REE as a group.

What about Na and K? Will they be found predominantly in the crust or mantle? Likewise, what about Rb and Cs? Sr and Ca? This last one is beautifully illustrated by an example from *biomineralization*. Corals build their skeletons from the *aragonite* polymorph of $CaCO_3$, which has a large site capable of incorporating the Sr^{2+} ion. As a result, the Sr/Ca

ratio of coralline aragonite is very close to the ratio of seawater in which the corals grow – their metabolism cannot distinguish between the two ions.

From isolated atoms and ions, we move on to consider "bonding" the forces that bind atoms together in molecules and crystal structures.

Bonding concepts (this should be revision):

Ionic bonds - concept of electron donors (cations / metals) & electron acceptors (anions / nonmetals). Resulting ions attract one another via the Coulomb force – ionic bonds.

Covalent bonds - elements of similar metallic or non metallic character share electrons. Each atom affects the electron orbital of the other atom.

Tendency to donate or share electrons is governed by *Electronegativity* (or its converse, *Electropositivity*):
Elements with low electronegativity, such as the alkalis = electron donors
Elements with high electronegativity, such as the halogens = electron acceptors

Closely related to the *first ionization potential*.

[overhead] Electronegativities of the elements. Values are unitless. Notice the obvious periodicity (relation to electron shell and sub-shell filling).

[same overhead] First ionization potentials. Notice the similarity to electronegativity.

Bonding – it takes two to tango. The character of chemical bonds is largely dictated by *differences in the electronegativity of the participating atoms.* In the mineral world, bonds are neither strictly ionic or strictly covalent.

[overhead]   Example of oxygen bond character, from Faure's book: Difference in electronegativity suggests that Si–O bonds should be about 50% ionic, 50% covalent.

What does it mean for a bond to be 50% ionic? – the electron cloud is deformed (but not completely removed) from the anion; the electron cloud of the anion is **polarized**

Other types of bonds (less common/important in geochemistry)

Metallic bonds – electrons are not bound or confined to the neighbourhood of specific atoms. Atoms share electrons with all neighbors – immersed in a "sea" of electrons. Substances with metallic bonds are electrically and thermally conductive.

Van der Waals bonds – compartively weak bonds between induced dipoles. Electric field of one molecule induces polarity in the electron orbits of another; resulting attraction forms a bond. Bonding force decreases by distance^{-6} (double the distance, bond strength decreases to 1/64)

Relate bond type to physical properties of minerals

[overhead - TABLE 1-2 from Frye]

Ionic bonds	Atoms differ in electronegativity	High MP	Non directional. Coulomb attraction is shared between co-ordinated atoms	Strong, hard minerals (with exceptions)	Insulating. Melt to weakly conductive ionic liquids
Covalent bonds	Atoms closer in electronegativity	Usually lower MP	Inter-atomic forces spatially directed. Similar atoms	Strong, hard minerals (with exceptions)	Insulating. Melt to molecular liquids that remain insulators
Metallic bonds	Similar (or identical) atoms	Lower MP	Non-directional bonds	Variable	Conductive
Van der Waals bonds		Very low MP	Non-directional bonds	Weak, soft	Insulating

Given these controls on bonding between atoms, what controls the arrangement of atoms to form crystals?

Pauling's rules describe the arrangement of atoms to form ionically-bonded crystals, but can be generalized quite well to silicate minerals:

Anions surround cations (i.e., are coordinated); distance between them is the sum of the two radii; the coordination number determined by ratio of radii.

Bonds are equally shared between cation and surrounding anion, the charge on the cation (valence) is equal to the negative of the total of electrostatic bonds.

Polyhedra tend not to share edges or faces; cations tend to be as far apart from each other of physically possible – like charge repels. E.g., joining Si tetrahedra at only one apex maximizes distance between cations.

In crystals with different types of cations (e.g., both high and low charge) the polyhedra containing cations with high charge and small radii tend not to share faces, edges *or corners* with each other Another way of stating distance between cations is maximized.

Pauling's rules govern the formation of crystalline solids. In the Earth, 10-12 "major elements" make up the majority of the mineral composition. In almost all cases, the remaining "trace elements" substitute for geochemically similar major elements. Substitution is governed by **Goldschmidt's rules.**

[overhead] Goldschmidt's rules

Ions of one element can extensively replace those of another if they have the same charge and their radii differ by less than about 15% (how much substitution? Depends on availability and *Temperature* – relate to how sites and ions behave more and more similarly at higher temperatures)

Ions whose charges differ by one unit substitute readily for one another provided electrical neutrality of the crystal is maintained. For more than one unit charge difference, substitution is quite limited.

When two different ions can occupy a particular position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with surrounding anions; (ionic potential = charge/radius). Thus concentrated in early formed minerals.

Even if size and charge are same, substitution may be limited if two ions have different electronegativities, and thus form bonds of different ionic character

(The last rule was added by Ringwood to explain discrepancies such as lack of Na^+ and Cu^+ inter-substitution)

Summary: (i) Understanding some very simple chemical properties allows us to make useful and interesting predictions about the composition of the Earth's crust, mantle and core. (ii) These properties allow us to group the elements by their geochemical behaviour, as pioneered by Goldschmidt:

[Illustrate this with a Periodic Table. A good web link is: http://en.wikipedia.org/wiki/Goldschmidt_classification]

Lithophile elements – rock forming elements found primarily in silicate and oxide minerals. The alkali and alkaline earth elements, transition metals at the left-hand side of the table (V, Ti, Cr, Y, Zr, Nb, the REE, Hf, Ta and W), as well as Al and Si, B, P and O.
Siderophile ("iron-loving") elements – those that segregate with Fe into the metallic phase in meteorites and the Fe-rich metallic core. The middle-group transition elements, including the noble metals.
Chalcophile elements – those that bond primarily with sulfur. Transition elements and semi-metals that sit to the right of the siderophiles.
Atmophile elements – those that do not readily form minerals at all, and are found primarily in the atmosphere and oceans.

Goldschmidt's classification has been distilled a bit further by modern geochemists, who recognize various sub-divisions:

Large Ion Lithophile Elements (LILE) – as the name suggests
Platinum Group Elements (PGE) – the noble metals – a sub-division of the siderophiles
High Field Strength Elements (HFSE) – high ionic potentials: Ti-V to Hf-Ta