

Chemistry of the Elements

The guidelines to understanding the characteristics of minerals from the nature of the elements and the rules that govern their interactions

In order to understand atomic structure, we must understand how electrons react with other charged particles

de Broglie: treat particles as waves using Planck's constant and momentum

Heisenberg Uncertainty Principle: impossible to determine the exact position and momentum of a particle

Schrödinger Equation: formula to describe the size, shape and orientation in space of orbitals around the nucleus

Rules for e⁻ occupying space around the nucleus

- 1) Orbitals s, p, d, f are predicted using the Schrödinger equation:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)\Psi_s$$

Orbital shapes become increasingly complex with increasing numbers of electrons

- 2) Size of orbitals increase as they get farther from the nucleus – the smallest lowest energy orbitals are closest to the nucleus (ground state)

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)\Psi_s$$

$R(r)$: distance of the electrons from the nucleus

Ψ_s : “spin function”, describes the direction of spin for the electrons

$\Theta(\theta)$: angle of rotation of the electrons relative to the z-axis

$\Phi(\phi)$: angle of rotation describing the direction that the electron is spinning

n: principle quantum number; describes the average distance of an electron from within the nucleus (ranging from 1 to infinity)

This value is associated with each of the shells around the nucleus (i.e. K, L, M, N, O which each have a number of s, p, d, f, or g orbitals filled)

l: azimuthal quantum number; defines the shape of the orbital by taking a measure of the angular momentum of each electron in the orbital

m_l : magnetic orbitals shows how the orbital of interest is related to others

m_s: spin quantum number; clockwise or counterclockwise spin direction of electrons in a specific orbital (+1/2 or -1/2)

3) With the different orbital shapes there are associated different numbers of orbitals – the result is a specific number of electrons per shaped orbital s, p, d, f

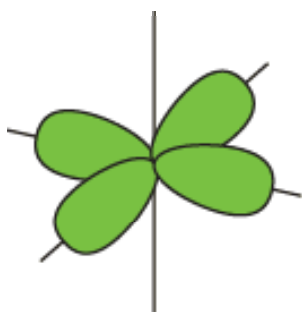
Type of orbital	# of orbitals	total # electrons
s	1	2
p	3	6
d	5	10
f	7	14

4) Each orbital can only accommodate 2 e⁻ spinning in opposite directions

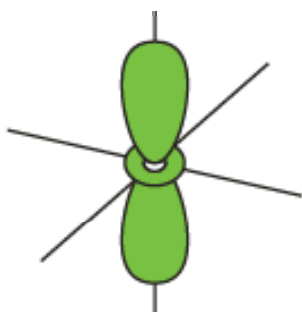
5) For most neutral atoms the filling order is:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 5s, 4d, 5p, 6s, 4f/5d, 6p, 7s, 5f/6d

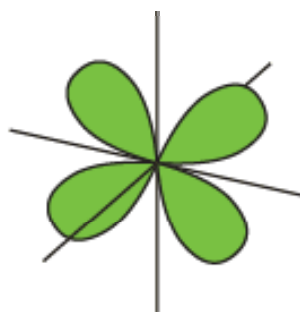
Electronic Configuration across the Periodic Table



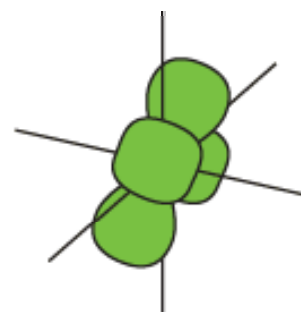
$d_{x^2 - y^2}$



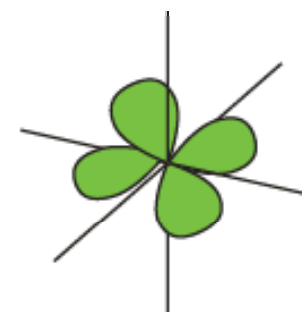
d_{z^2}



d_{xz}



d_{yz}



d_{xy}

Principle Quantum No. n	Subshell Designation	No. of orbital shell	Maximum No. of e ⁻	
1 (K)	1s	1	2	2
2 (L)	2s	1	2	8
	2p	3	6	
3 (M)	3s	1	2	18
	3p	3	6	
	3d	5	10	
4 (N)	4s	1	2	32
	4p	3	6	
	4d	5	10	
	4f	7	14	

Must know the relative size each atom in its preferred valance state to begin building a mineral structure

- number of electrons and protons
- number of surrounding ions (coordination #)
- charge imbalance between the number of protons and electrons
- degree of covalency of the bonds
- amount of polarization (*how an atom responds to external electrical forces by reshaping itself or redistributing its charge*)
- P and T conditions

The result of polarization is commonly a distribution that favors concentrations of electrons at the poles

- *Fajan's Rules*:
 - 1) shortens bonds of small cations with high charge
 - 2) shortens bonds of large anions with high charge
 - 3) shortens bonds of non-inert gasses
- Spin state:
 - High spin: all e^- in the outermost shell spin the same way
 - Low spin: e^- in outer shell are spinning opposite directions
- These are all used in the calculation of ionic radii (most commonly after measurements using XRD or x-ray diffractometry)
 - Ionic radii values have been measured, standardized, and tabulated for most minerals based on whether the species is complexed with O^{2-} or F^- .

THE COLOR THAT WE SEE IN MINERALS

There are 5 major reasons that we see color in minerals in hand sample and in plane light microscopy

1) The presence of metal ions

The ions in the first row transition metals (Ti, V, Cr, Mn, Fe, Ce, Ni, Cu) have e⁻ in the five 3d orbitals that each split into different energies. When visible light reacts with these e⁻ it causes them to be excited to higher energy orbitals. The resulting wavelength transitions are subtracted from the incident light producing color.

2) Intervalance charge transfer

Transfers of e⁻ between 2 adjacent metal ions in adjacent cation sites. During this transfer, certain wavelengths are absorbed and removed from the incident spectrum.



tsavorite variety of grossular garnet (Kenya) due to V^{4+}

3) Natural ionizing radiation

This phenomenon can be related to 3 main effects of radiation damage that are commonly unique to particular species. A) alteration of the charge from Mn^{2+} to Mn^{3+} , B) e^- trapped in orbital shells where they are unstable, C) molecular clusters with unpaired e^-

4) Physical effects/ processes

The 3 main physical effects are A) films of foreign material covering a mineral face (oil on water – “Newtons colors”, B) diffraction gratings or regularly spaced mineral layers with unique indices of refraction, C) inclusions of foreign minerals, melt (glass) or fluids

5) Band gaps in semiconducting minerals

In this case e^- are promoted to higher energy states by interaction with visible light where e^- are more mobile



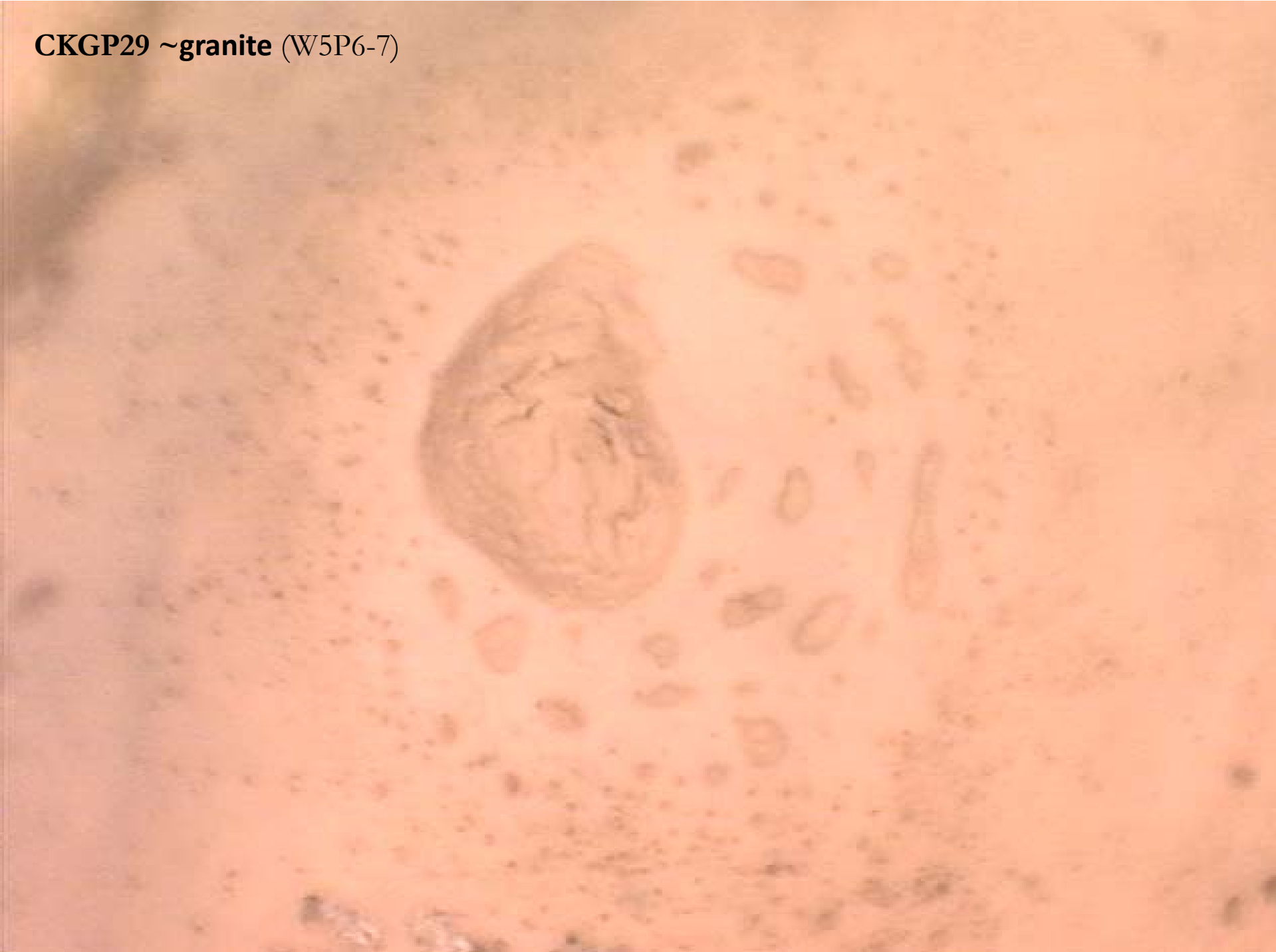
0.1 mm

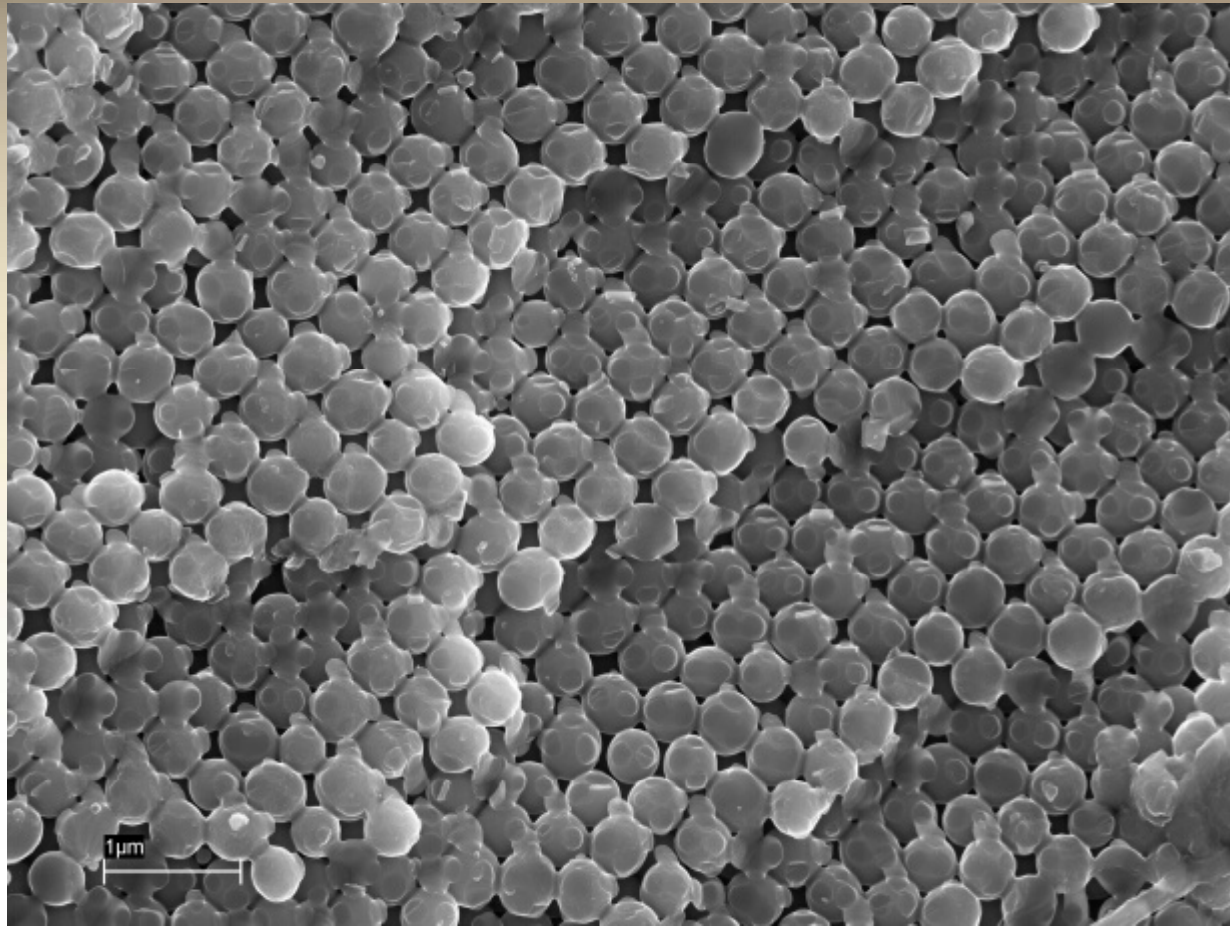


CKGP41 ~diorite-gabbro (W8P5)



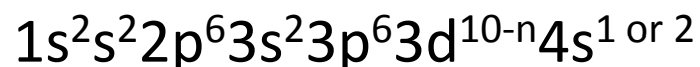
CKGP29 ~granite (W5P6-7)





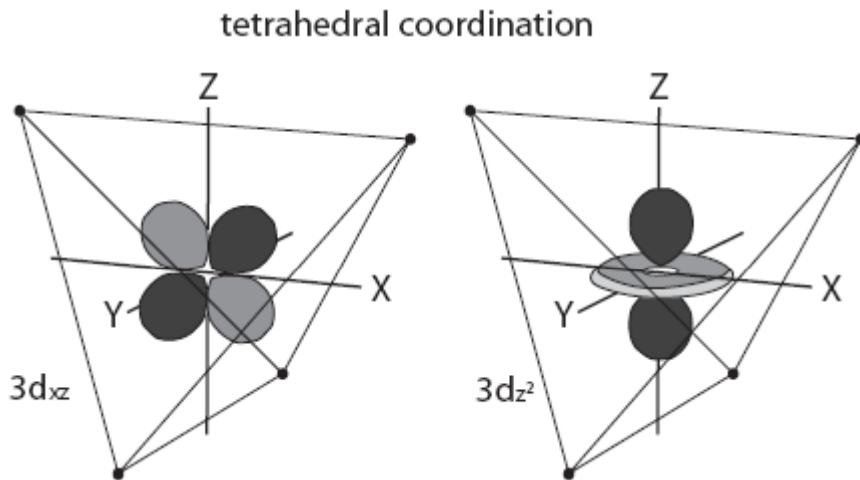
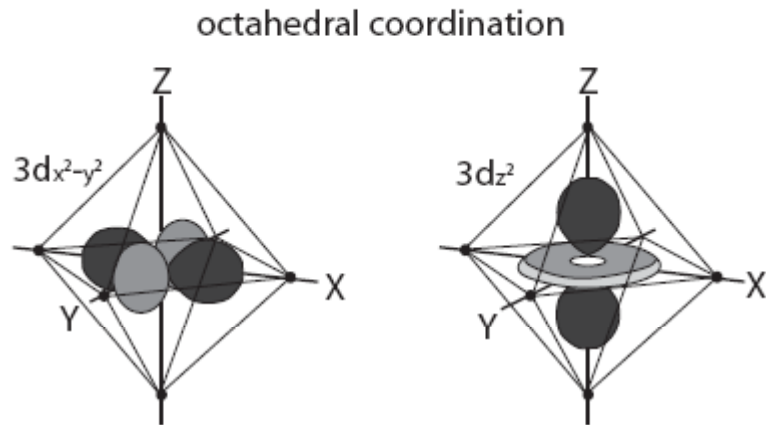
Focusing back on the transition metals (Z = 21-30)

- These have shells below 3p completely filled and incompletely filled 3d orbitals; therefore,



- Whenever an ion is isolated, all 3d orbitals are perfectly shaped and have the same energy – these are called **degenerate**
Another way to think of this is that e- in this instance have an equal probability of being located in any of the 5 orbitals
- According to **Hund's first rule**, there is no pairing of e-'s until each of the available orbitals contains one e-

This rule becomes slightly more complex when ions are not isolated, i.e. when we have 4, 6, 8, or 12 coordinated polyhedra with O as the nearest neighbor to all cations



- If charge is unevenly distributed such that e^- closest to O in the polyhedra corners are repelled most strongly
- In the octahedral case, repulsion raises the energy of the orbitals usually oriented along the axes to create [3d_{xy}](#), [3d_{xz}](#), and [3d_{yz}](#) with orbitals between the axes
- In the tetrahedral case, the opposite happens with each 3d_{xz}, 3d_{xy}, and 3d_{yz} (with orbital between the axes) reverting to a lower energy state because of the proximity of O

This is the concept of *crystal field splitting*

FIELD TRIP to the ADIRONDACKS

Expected return ~5:00 pm Sunday evening

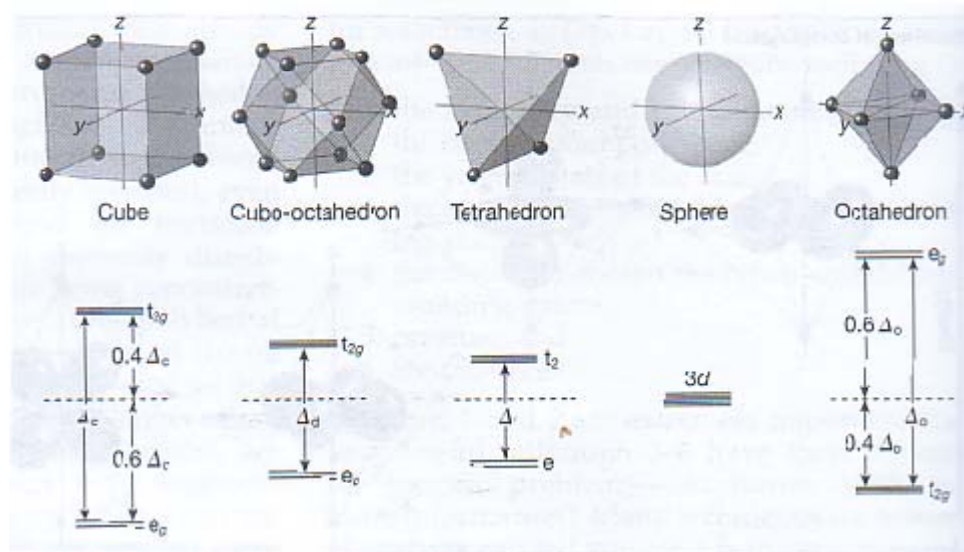
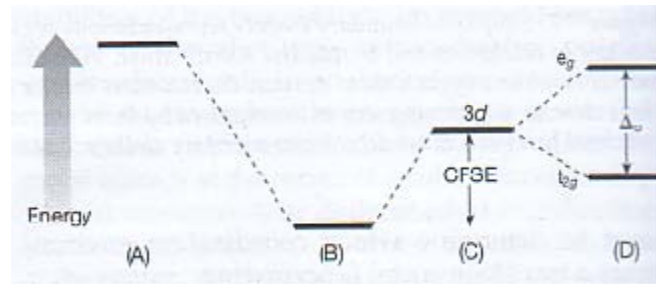
Trip cost will be \$20.00 per person. *This does not include dinner 10/4 so please plan accordingly.*

We will meet at the loading dock behind Morrill 3 (right behind our classroom) at **7:30am SHARP!!!**

PLEASE REMEMBER to bring good sturdy shoes/ boots for hiking to outcrops and in mines we will be visiting.

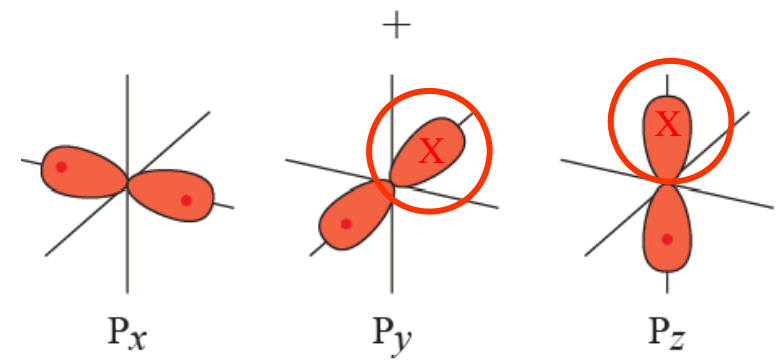
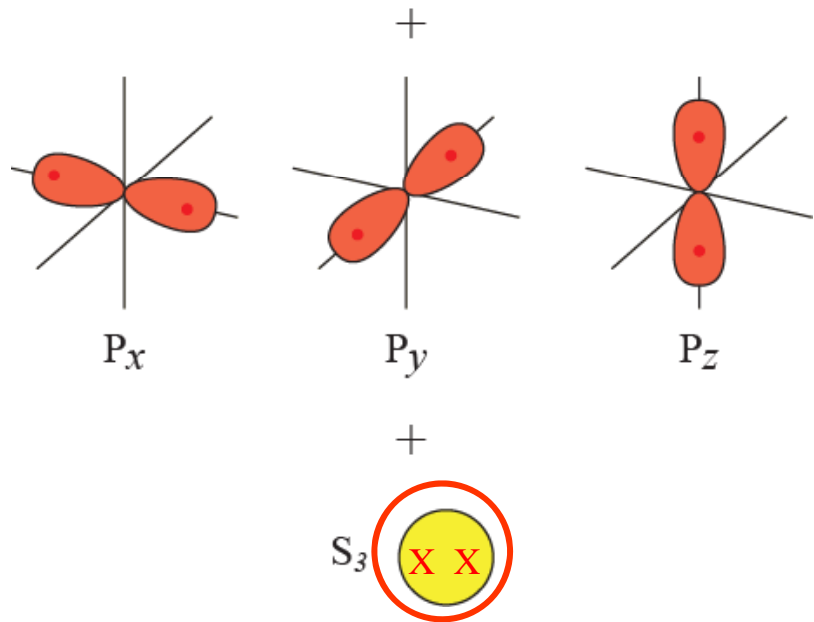
Please also bring a field book, handlens, writing implements, raingear and extra warm clothes.

Optional equipment: rock hammer, colored pencils, clipboard, sleeping bag



Ionisation

In the case of oxygen, the 2p orbital **accepts** 2 e⁻ and the orbital is filled, creating an oxygen **anion** with a 2-negative charge (O²⁻)



While in magnesium, the outermost 3s orbital **gives up** 2 e⁻ and the orbital is empty, creating an oxygen **cation** with a 2-positive charge (Mg²⁺)

The energy required to remove the most weakly held electron from a neutral atom is the **first ionisation potential**. The energy requires to remove the next electron is the **second ionisation potential** and so

on.
 An ion forms by gaining or losing its **valence** electrons and taking on the orbital electron configuration of a noble-gas.

Radiogenic Isotopes

There are some elements, with perhaps the geologically important being Th and U ($Z = 90$ and 92), which have isotopes that are unstable.

^{232}Th , has 142 neutrons and 90 protons. ^{238}U has 146 neutrons and 92 protons.

The electronic configuration of unstable atoms changes by radioactive decay.

This involves the rejection of either as *alpha* particle (^4He), or a *beta* particle (e^-).

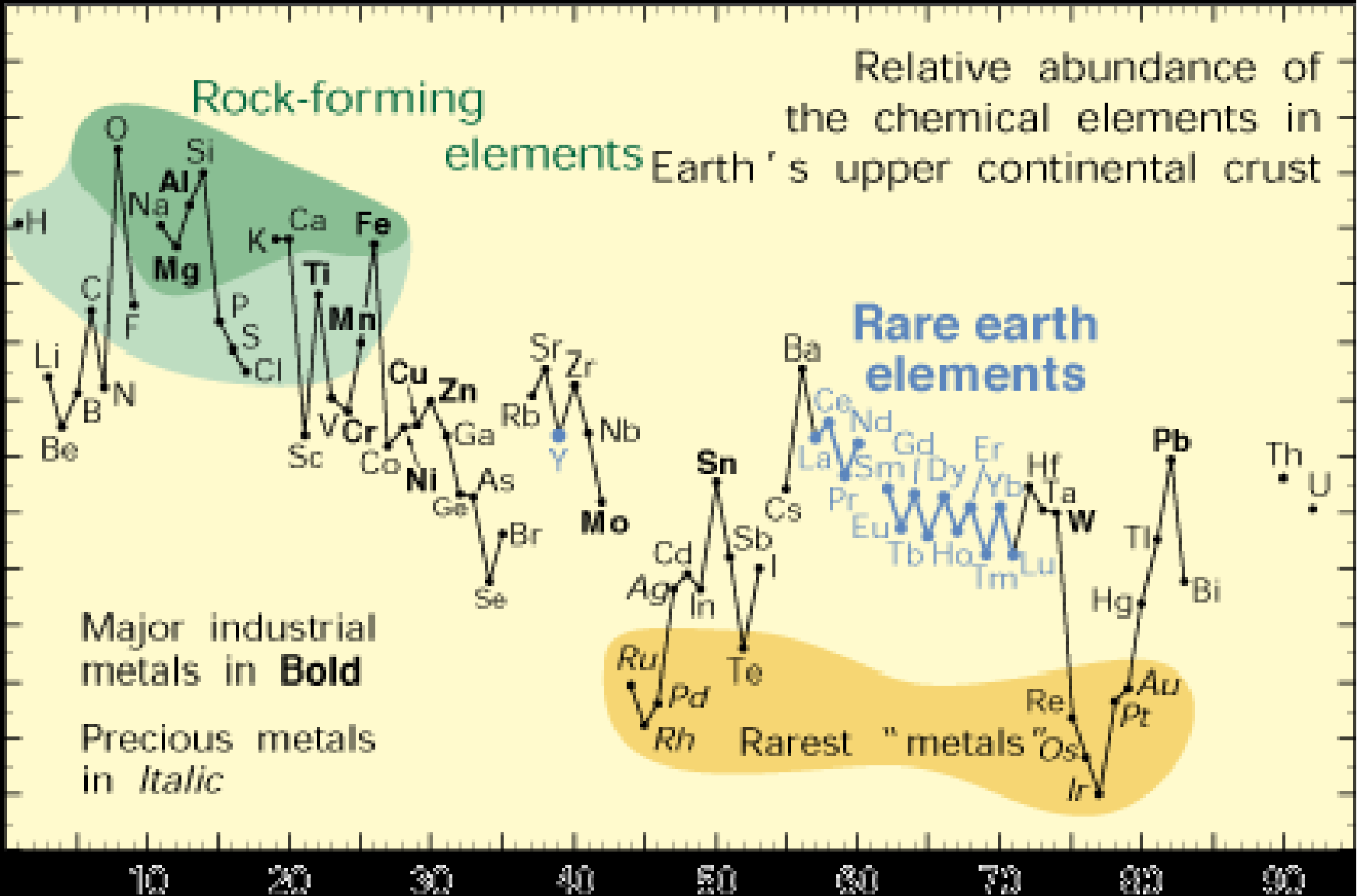
Each new atomic arrangement created by decay is a new element, and is a daughter product of the original parent element.

The rate of radiogenic decay is called the half-life.

The end product of ^{232}Th and ^{238}U radioactive decay are ^{208}Pb and ^{206}Pb .

Abundance, atoms of element per 10⁶ atoms of Si

10⁶
10⁵
10⁴
10³
10²
10¹



Major industrial metals in **Bold**

Precious metals in *Italic*

Rarest "metals"