



LAB TECHNIQUES

Assembled by:

Dr. AbdelMonem Soltan

Professor of Applied Mineralogy

**Applied Mineralogy and Building Materials Research Group
Ain Shams University**



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XRF

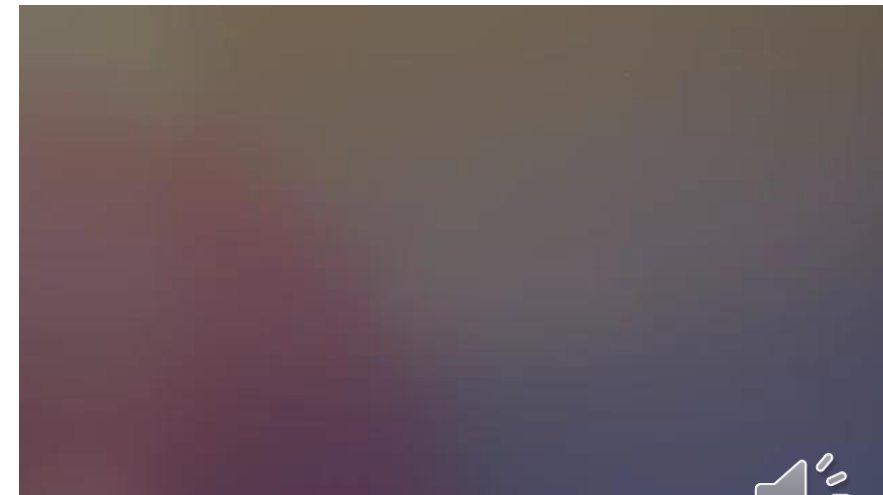
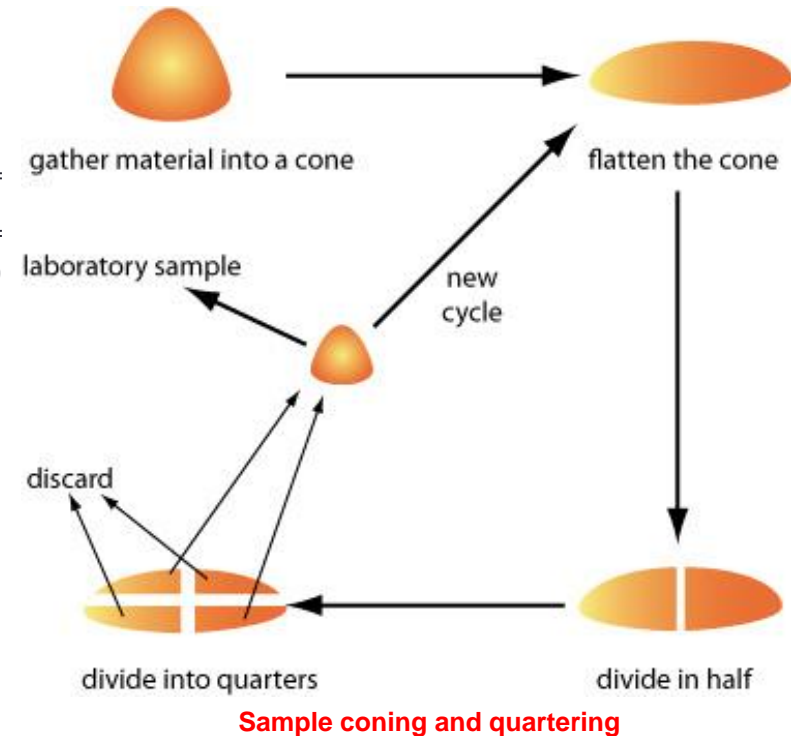


Mineral Analysis

The **sample analysis** is a continuous process achieved during all steps of mineral processing. After sample collection, the samples are reduced to quantities suitable for further analysis. **Analytical methods include particle size, chemical and mineralogical analyses.**

Before analysis, representative sample should be prepared by **coning and quartering**:

1. After thorough **mixing**, pile the sample into **cone**;
2. **Flatten** the cone;
3. **Quarter** the flattened cone into **four equal quarters**;
4. Two **diagonal sections** are discarded while the other two are **retained and mixed together**;
5. **Process is repeated until having suitable weight for all planned analyses.**



Sample coning and quartering

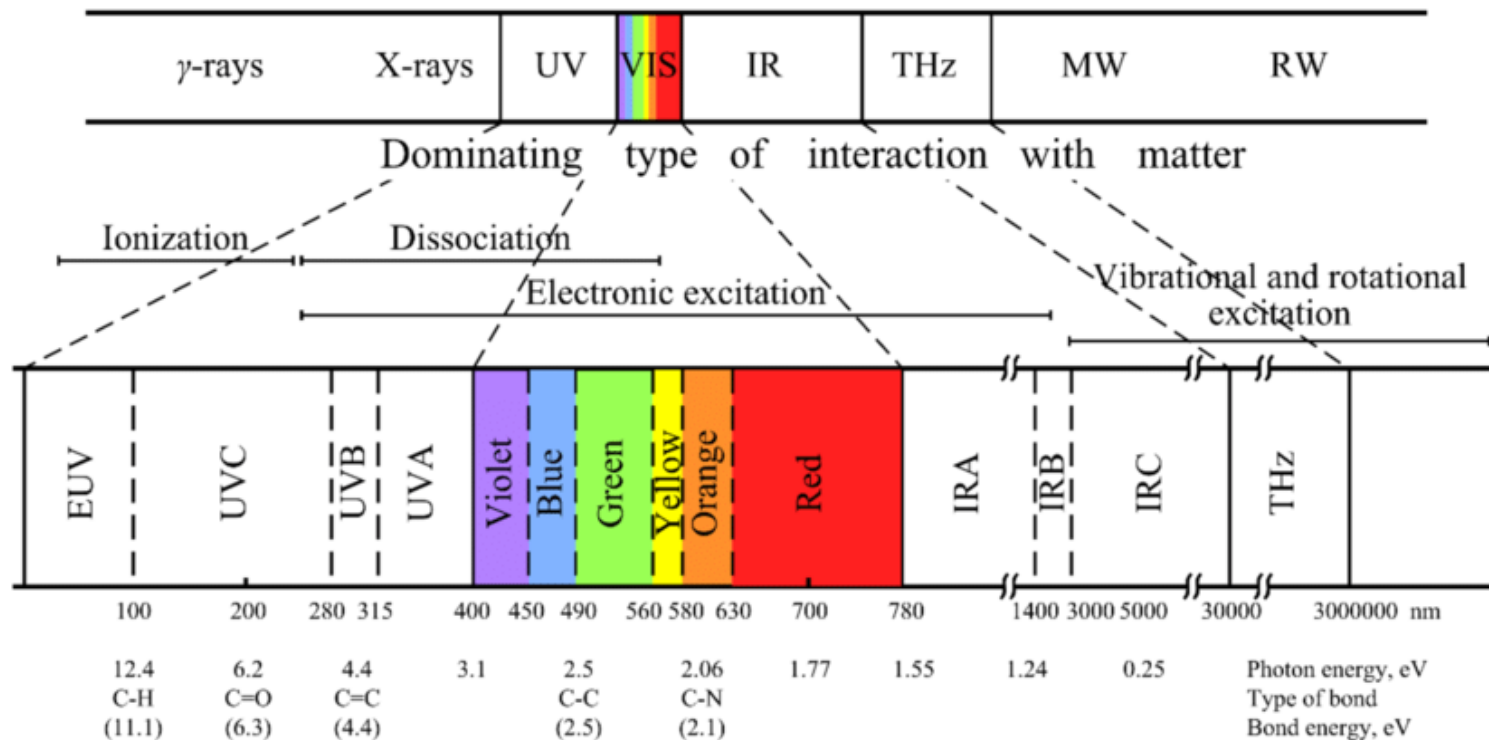
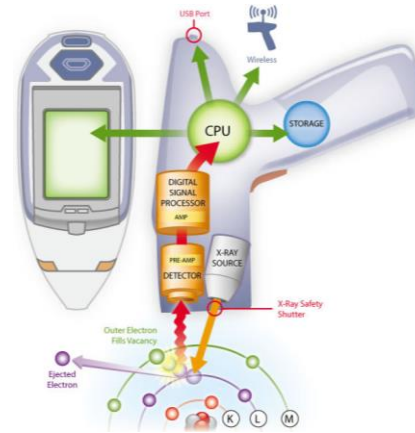


Sample coning and quartering



2. Basics of Spectroscopic Analysis

Comprehensive schemes are required to **assay (measuring the value of) ores**. Mineral and chemical compositions of the ores are dependent mainly on the spectroscopic techniques such as X-ray fluorescence (**XRF**), X-ray diffraction (**XRD**) and scanning electron microscope (**SEM**).

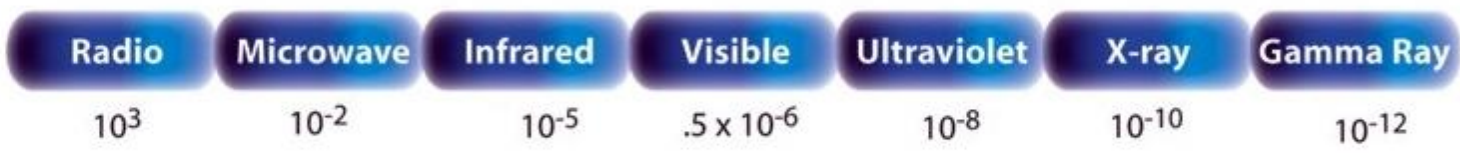


THE ELECTROMAGNETIC SPECTRUM

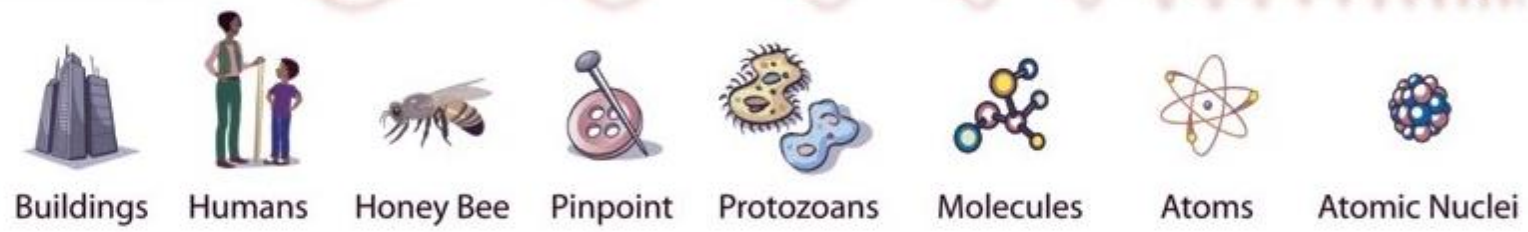
Penetrates Earth Atmosphere?



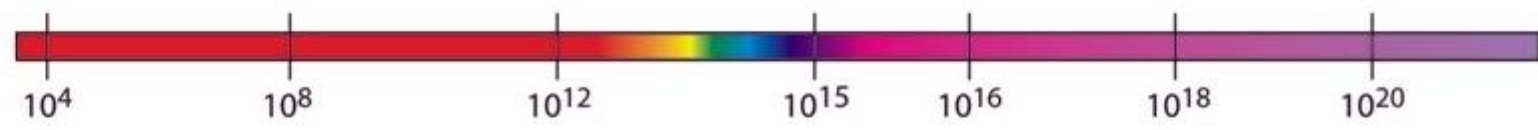
Wavelength (meters)



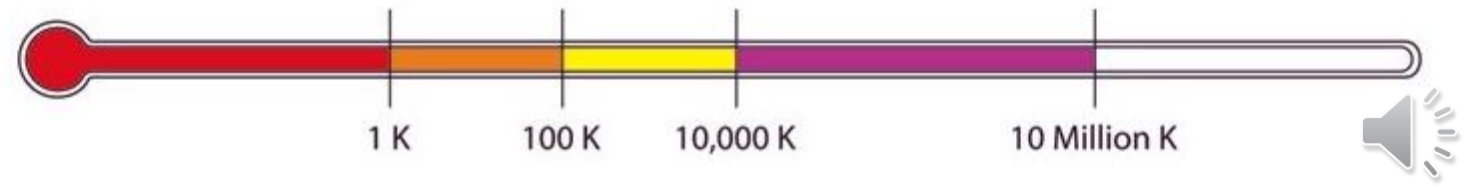
About the size of...



Frequency (Hz)

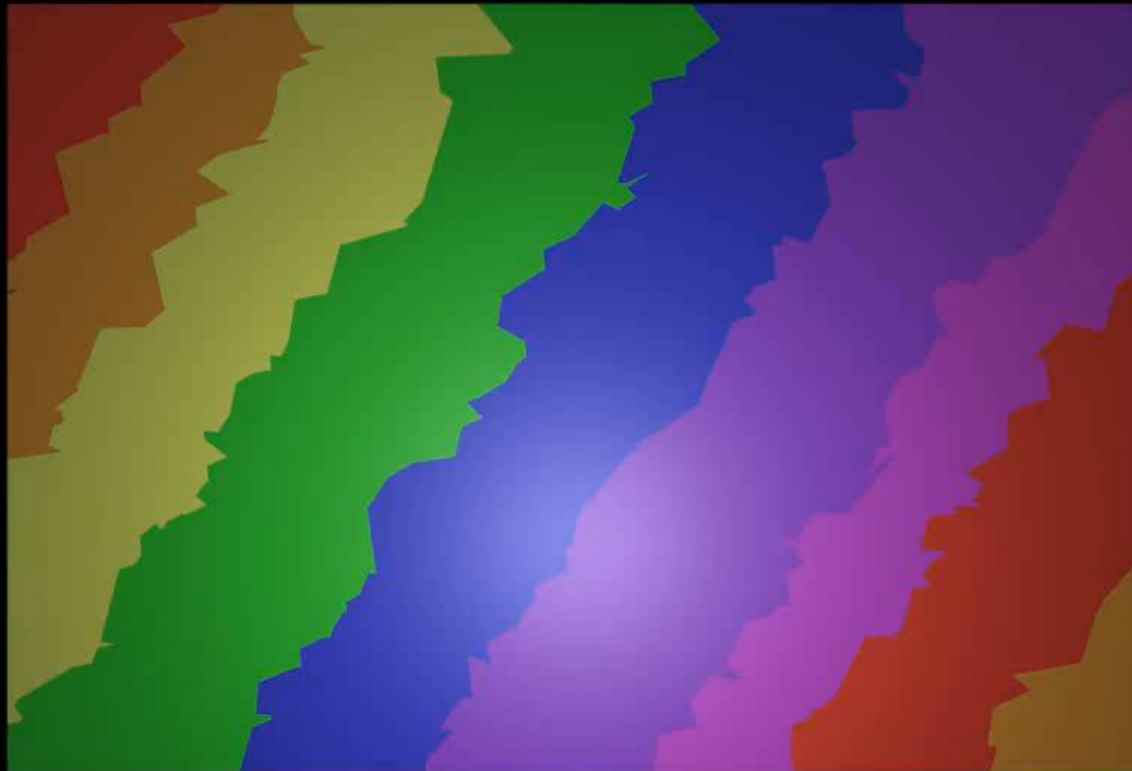


Temperature of bodies emitting the wavelength (K)



In the **emission spectroscopy**, **characteristic spectra are emitted from the sample in terms of energies and wavelengths then detected and measured by different devices.** In order to understand the different spectroscopic techniques, we should refresh our information about the **atomic structure.**





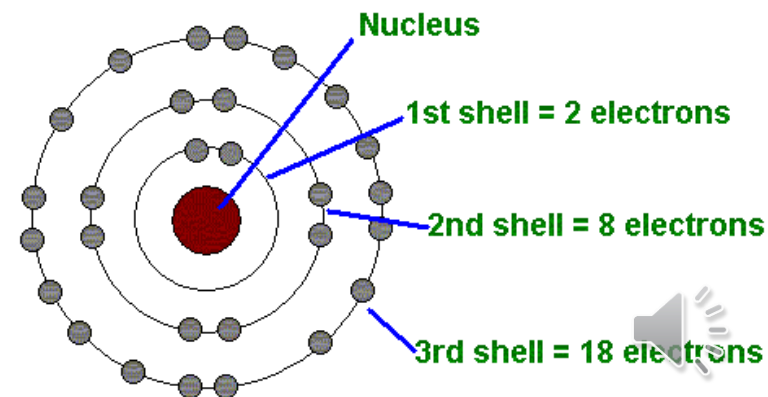
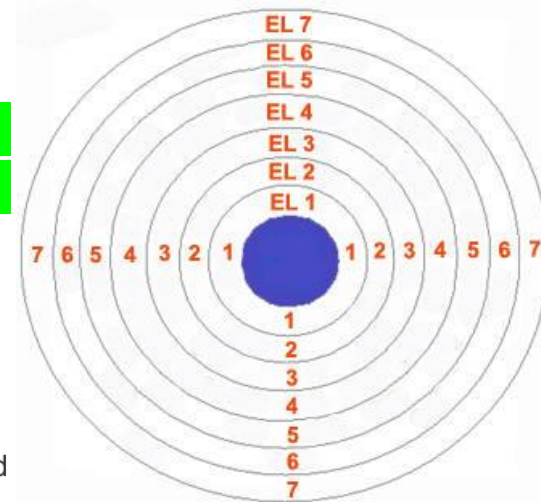
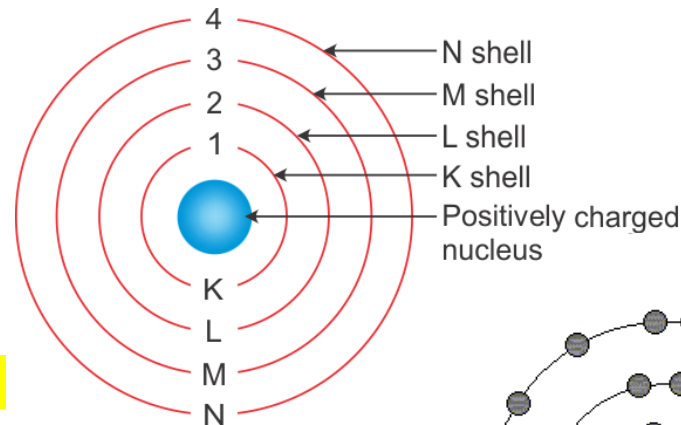
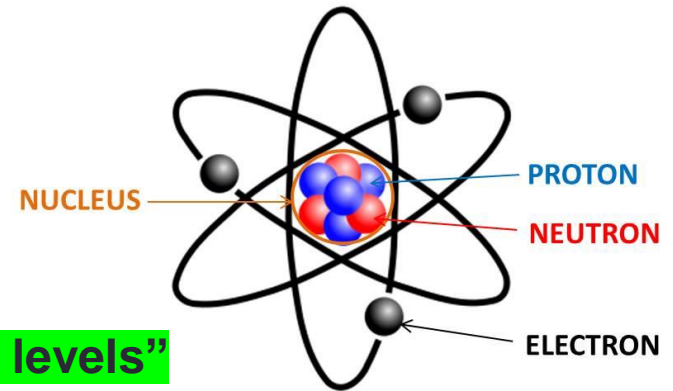
Atom structure

The atom is mainly composed of **nucleus** which contains protons, each carrying one positive charge, and uncharged particles called neutrons.

The nucleus is bounded by **"shells" or "energy levels"** occupied by **negative electrons**. Moving away from the nucleus, each new shell contains electrons at a **higher energy level than the previous shell**. **Electrons revolve around the nucleus in seven electronic shells/energy levels:- K, L, M, N, O, P & Q.**

Each **electronic shell** consists of some **sub-shells**:-

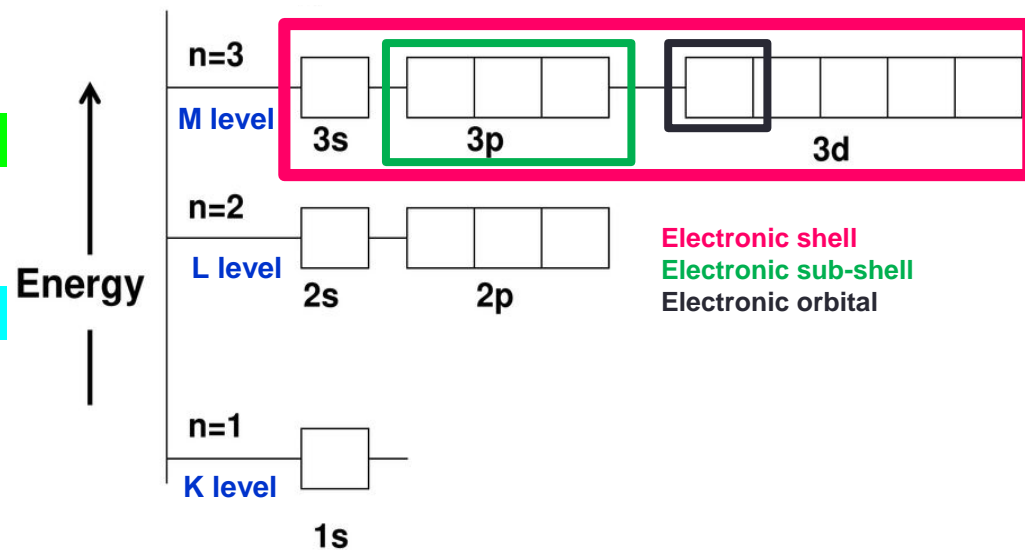
1. **K** contains only **1** sub-shell: **s**.
2. **L** contains **2** sub-shells: **s & p**.
3. **M** contains **3** sub-shells: **s, p & d**.
4. **N, O, P & Q** contain **4** sub-shells: **s, p, d & f**.



Each **sub-shell** consists of some **orbitals**. An orbital is basically the **region where the probability of finding the electron is maximum**. **Electrons** are constantly spinning in these atomic orbitals at **specific distances** from the nucleus.

The different orbitals are:

s = sharp, p = principal, d = diffuse, f = fundamental

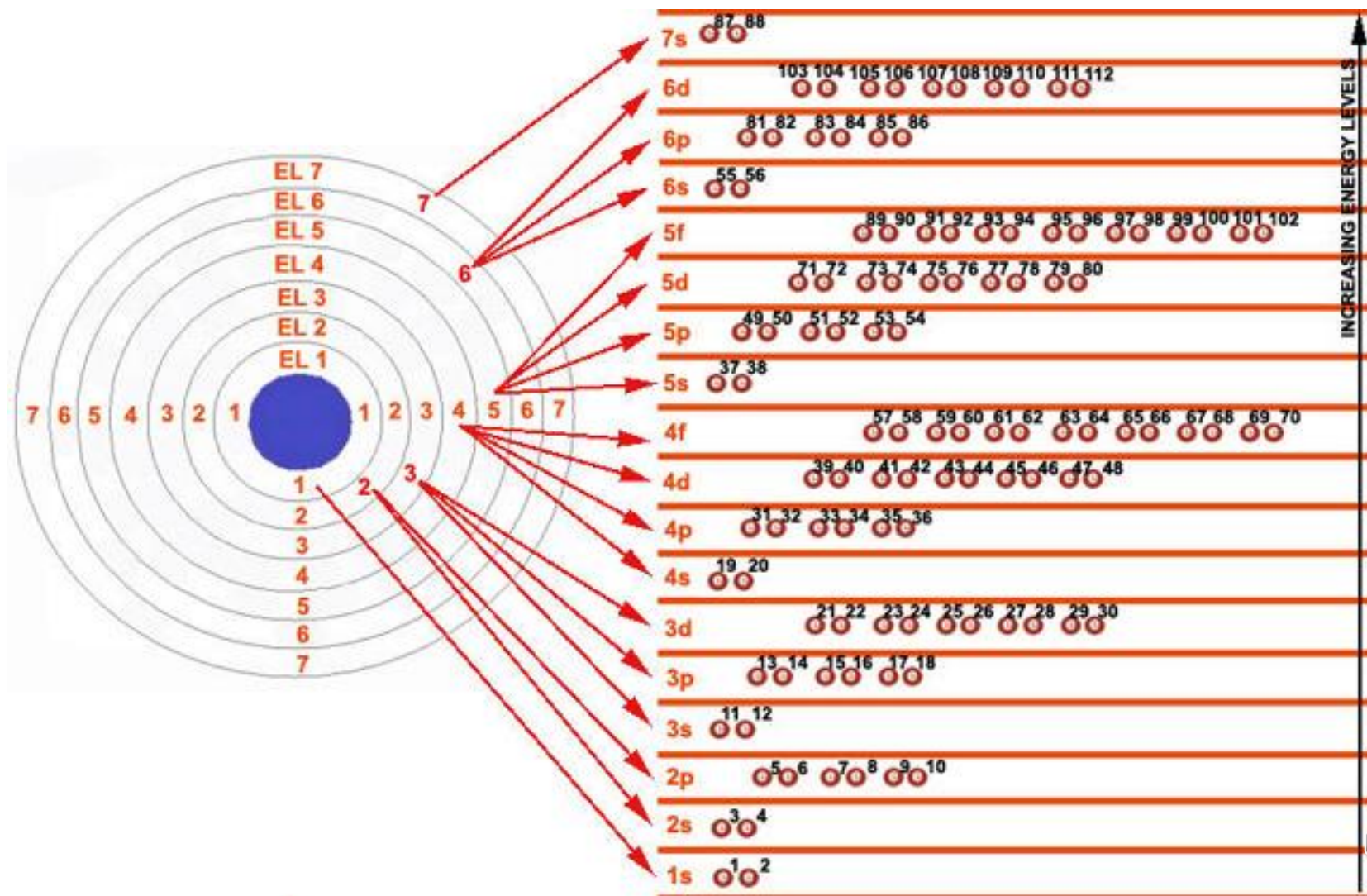


Each **orbital** can hold up to **2 electrons**.

1. **s sub-shell** contains **1 orbital** and can hold up to **2 electrons**.
2. **p sub-shell** contains **3 orbitals** and can hold up to **6 electrons**.
3. **d sub-shell** contains **5 orbitals** and can hold up to **10 electrons**.
4. **f sub-shell** contains **7 orbitals** and can hold up to **14 electrons**.

TYPE	SET	INDIVIDUAL ORBITALS					COLLECTIVE	
f	Cubic							
	General							
d	Common							
	"Tri-torus"							
p								
s								

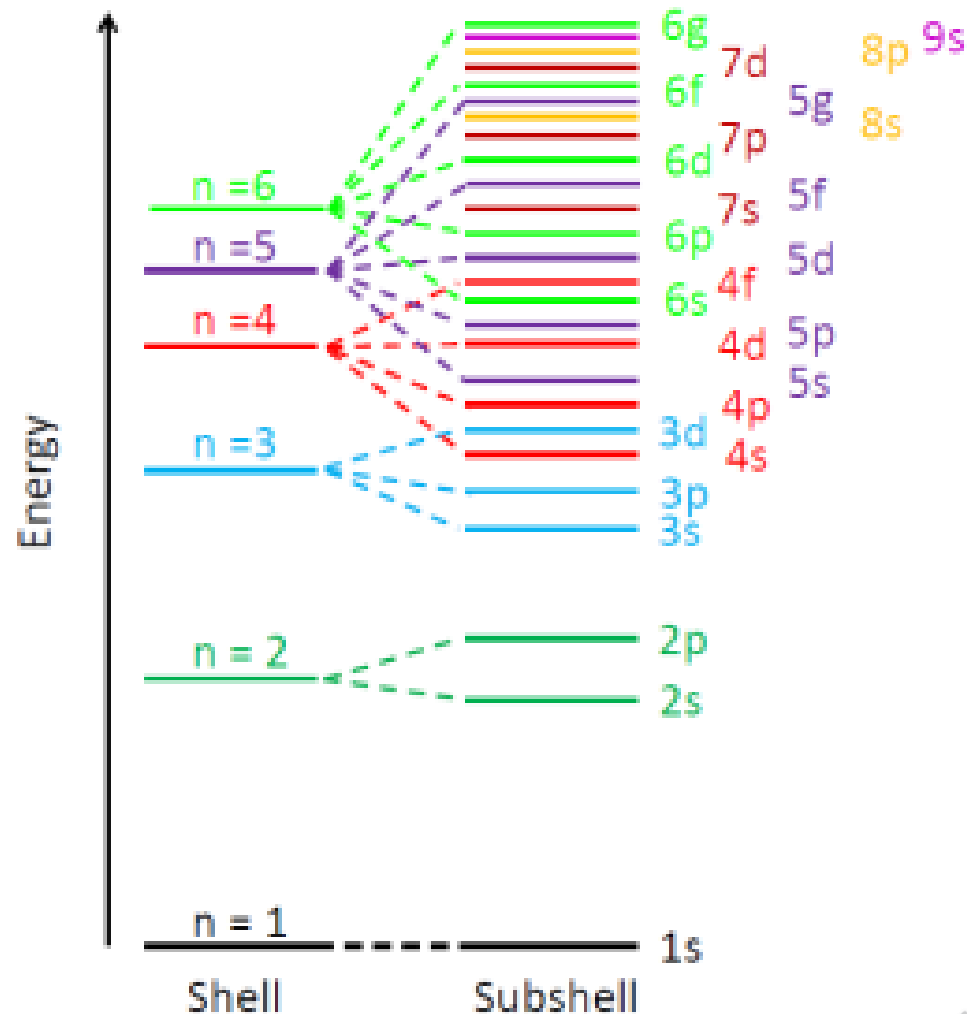
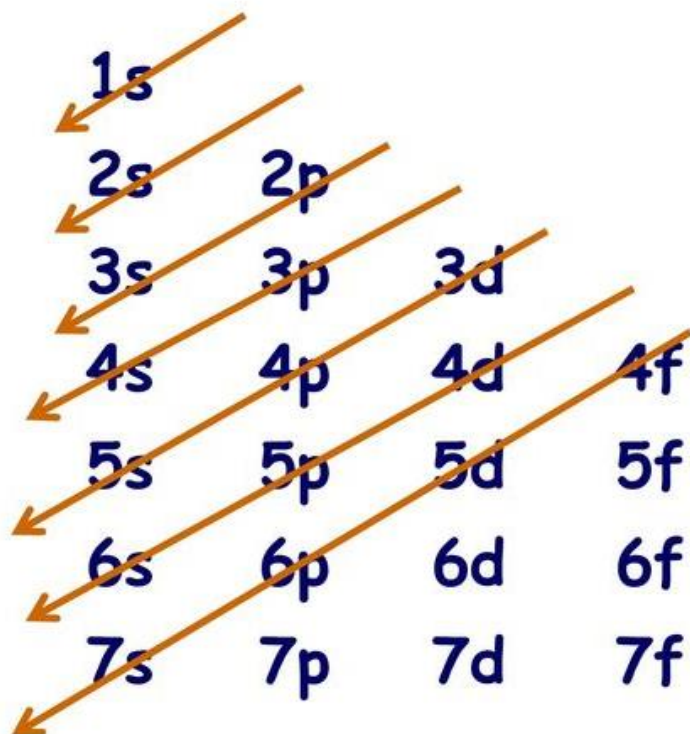
The diagram below indicates the total number of electrons to be found in each orbital. Strangely enough, with increasing atomic number, sometimes the additional electron does not automatically occupy the next energy level. In the diagram, the number shown near each of the electrons indicates the order in which they are added to the orbitals.



Electronic Configuration:-

The arrangement of electrons of each element in **their orbitals** is known as its **electronic configuration**. This arrangement is called the electronic configuration **at which the electrons fill the lower energy levels first.**

EL1	EL2	EL3	EL4	EL5	EL6	EL7
1s = 2	2s+2p=8	3s+3p+3d=18	4s+4p+4d+4f=32	5s+5p+5d+5f=32	6s+6p+6d=18	7s=2



Electron Configuration for Calcium



20
Ca
Calcium
40.08

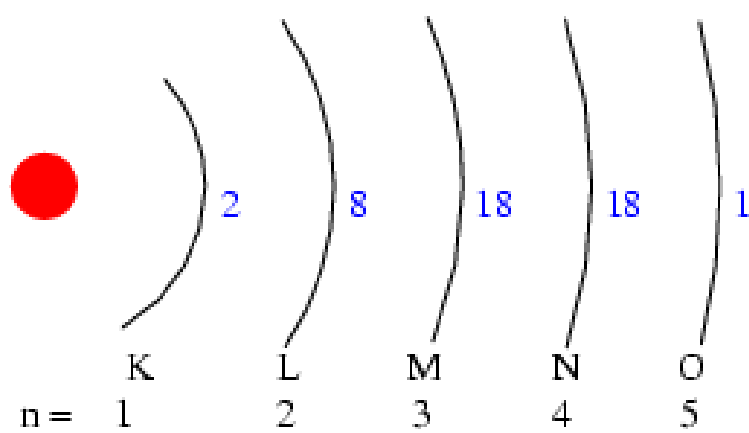
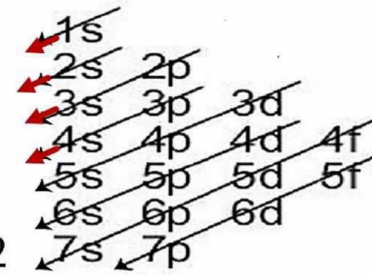
Atomic Number
Number of Protons
Number of Electrons

Find the number of electrons.

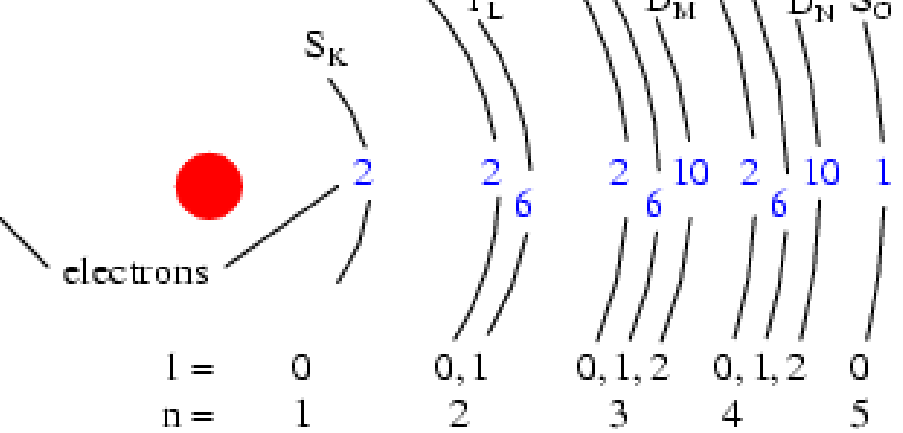
Electron Configuration Chart

s holds up to 2 p holds up to 6 d holds up to 10

20
Ca
Calcium
40.08



(a)



(b)

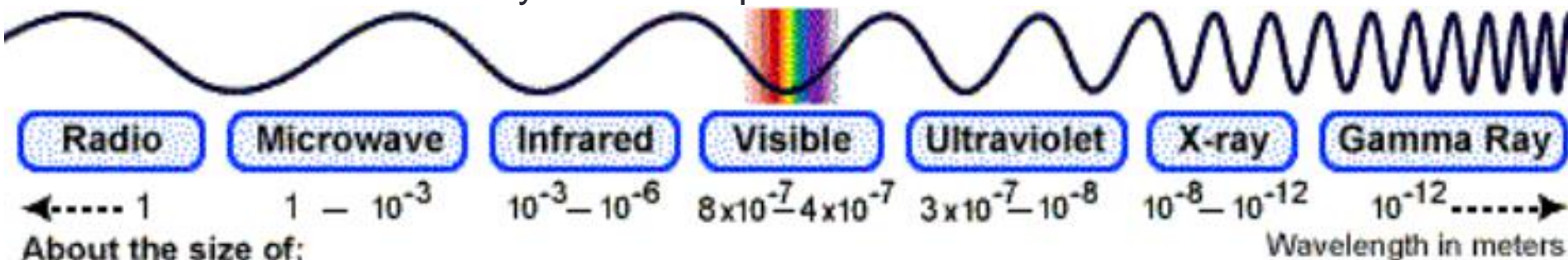


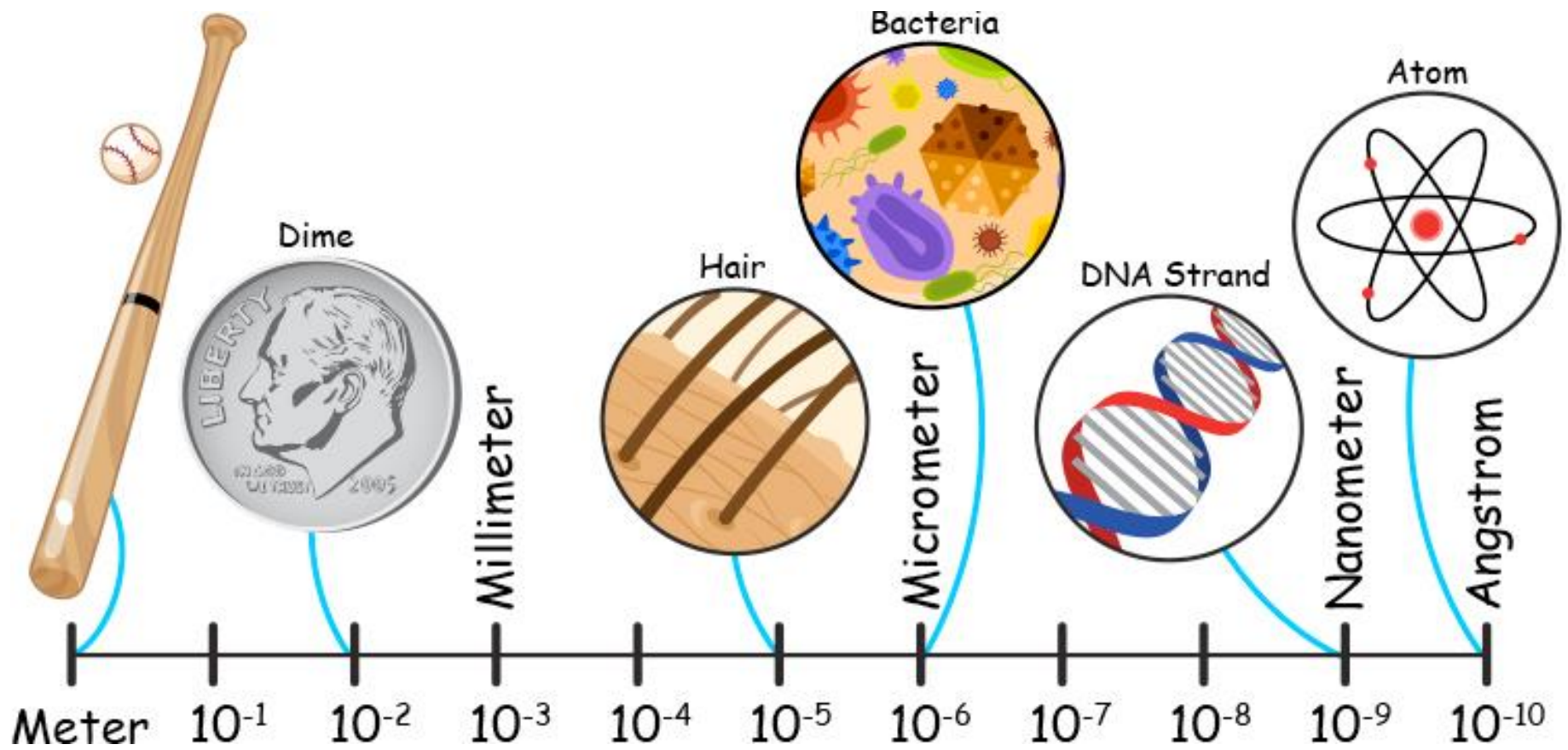
What is X-ray?

X-radiation (X-ray) is a form of **electromagnetic radiation (NOT-CHRGED)** and is characterized by energies lying between ultra-violet and gamma radiation. **X-rays** have a **wavelength** ranging from 0.01 to 10 **nanometers (0.1 – 100 angstrom)**, corresponding to **frequencies** in the range 30 **petahertz** to 30 **exahertz** (3×10^{16} Hz to 3×10^{19} Hz) and energies in the range 100 **eV** to 100 **keV**. **Wilhelm Röntgen** brought the **X-rays** properties to the attention of scientists. In many languages, **X-rays** are still named after him.



X-Rays are widely used in society for medical imaging in hospitals and baggage screening at airport security gates. Within science their properties are integral to many elemental and structural analytical techniques.





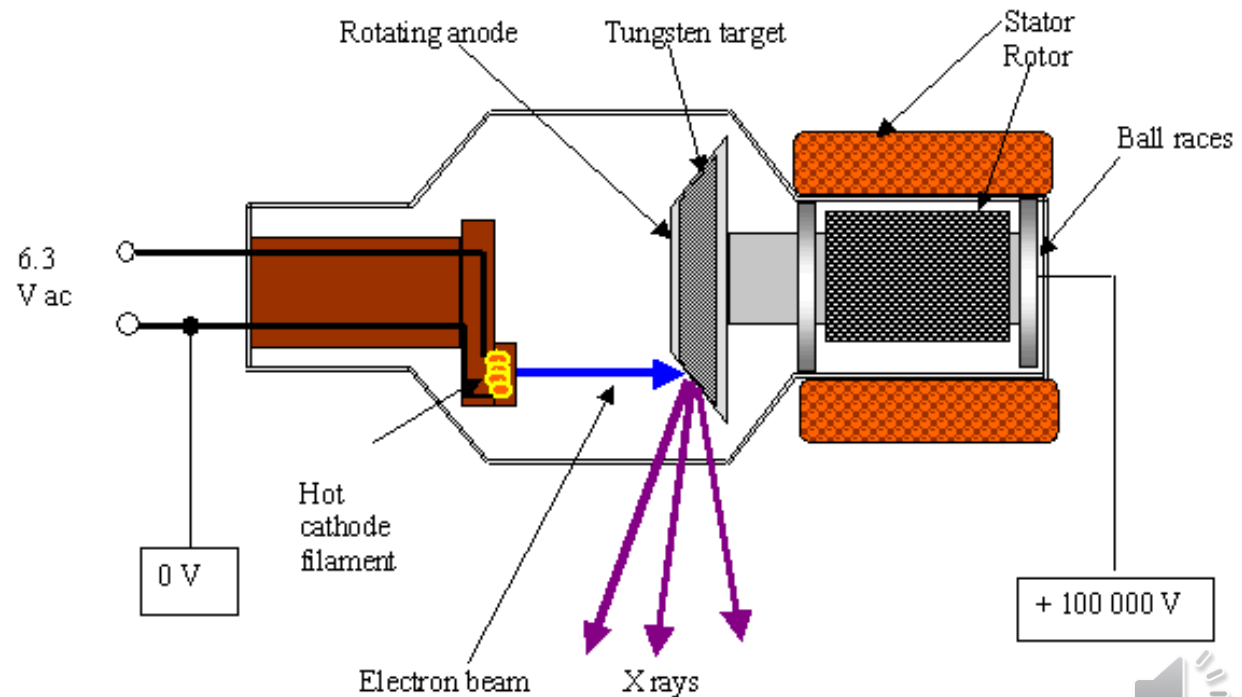
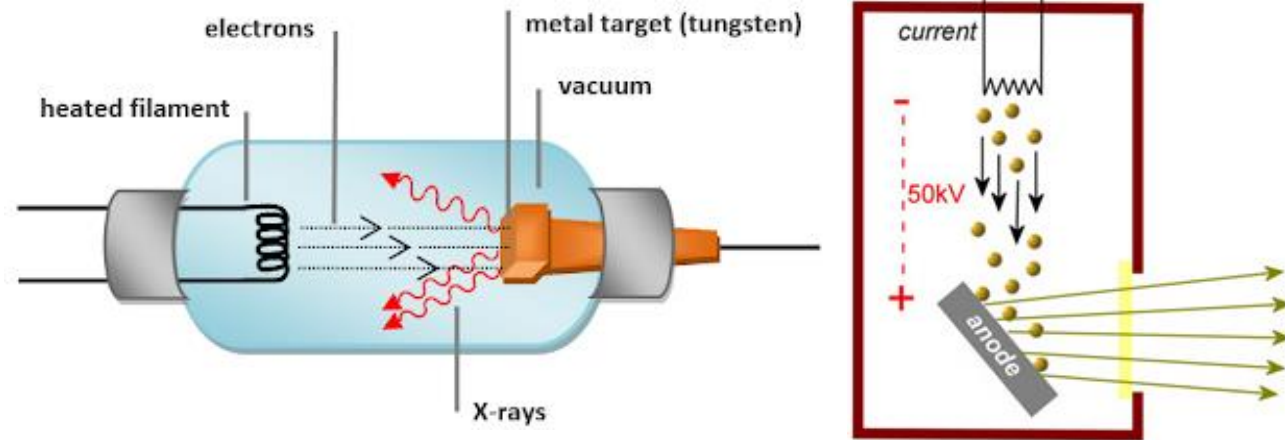
How to generate X-Ray?

A typical X-Ray generator passes **an electric current through a filament, which causes electrons to be emitted.**

These electrons are then accelerated by high voltage **towards an anode (target) (e.g., Mo, Rh, W).** The deceleration of the electrons when they hit the anode causes a broad **X-Ray**

continuum (primary/not-characteristic) to be emitted. This radiation is known as bremsstrahlung

(German: braking radiation).



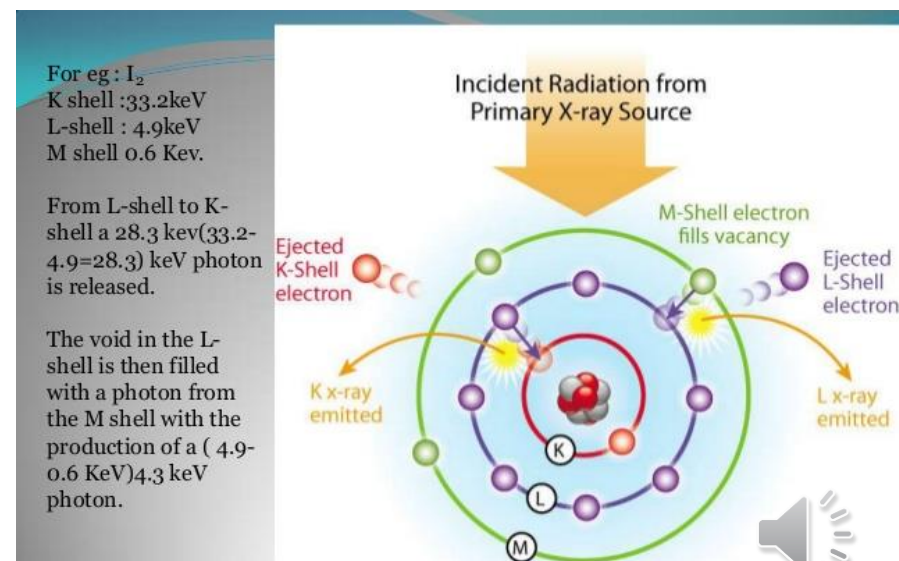
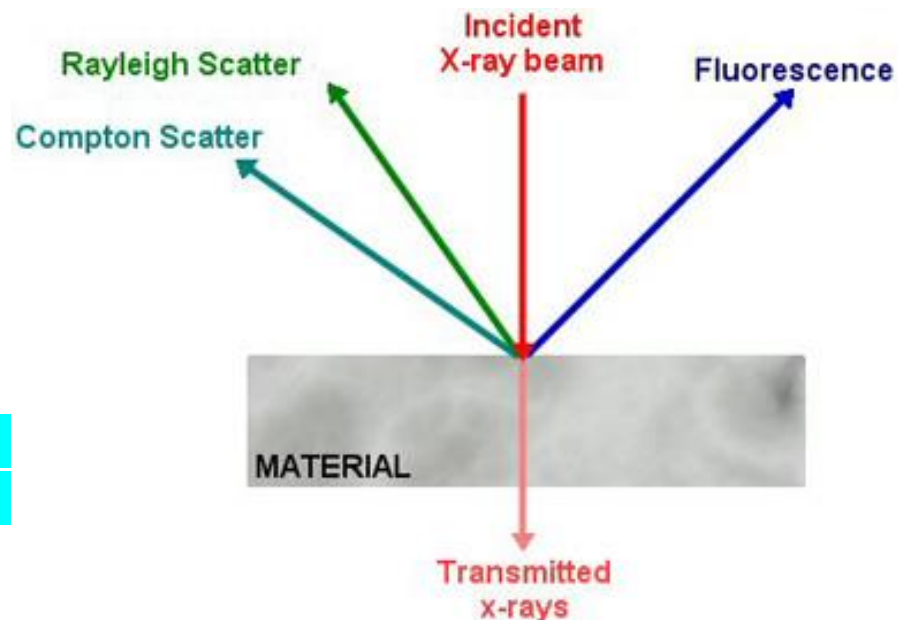
Interaction of X-rays with matter

On reaching a material, some of the X-rays will be **absorbed**, **scattered** – if neither process occurs, the X-Rays will be **transmitted** through the material.

When **absorption** occurs, the X-Rays interact with the material at the atomic level, causing subsequent fluorescence – it is the **X-Ray Fluorescence (characteristic)** which forms the basis of **XRF spectroscopy**.

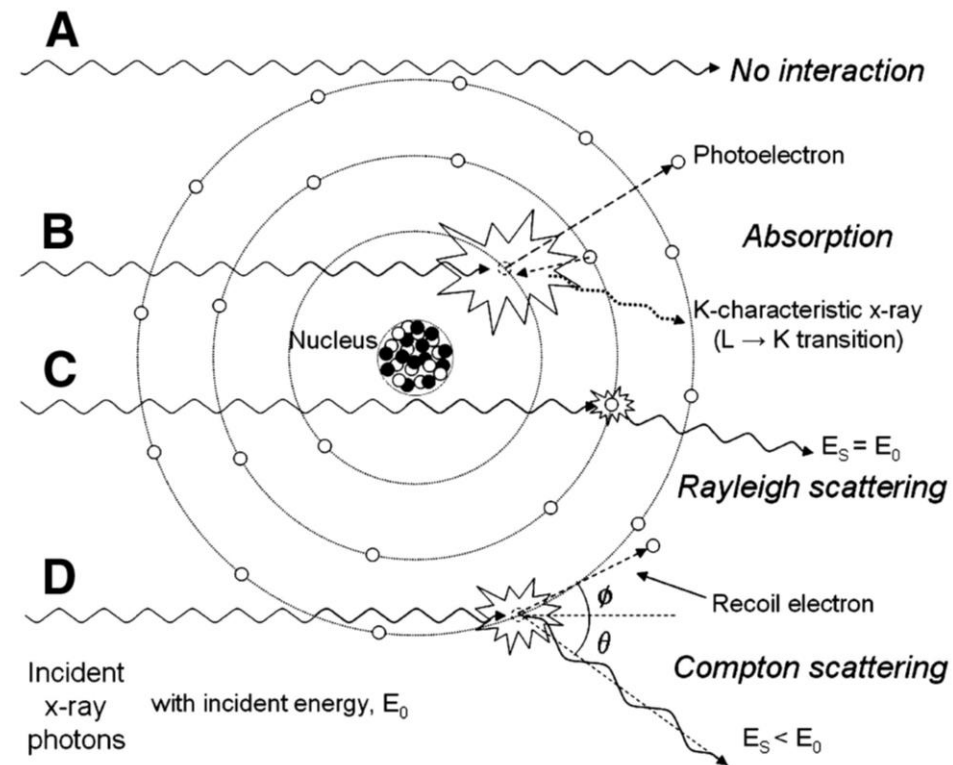
The X-Rays can also be **scattered** from the material. This scattering can occur both **without** and **with** loss of energy, called **Rayleigh** and **Compton** scattering respectively.

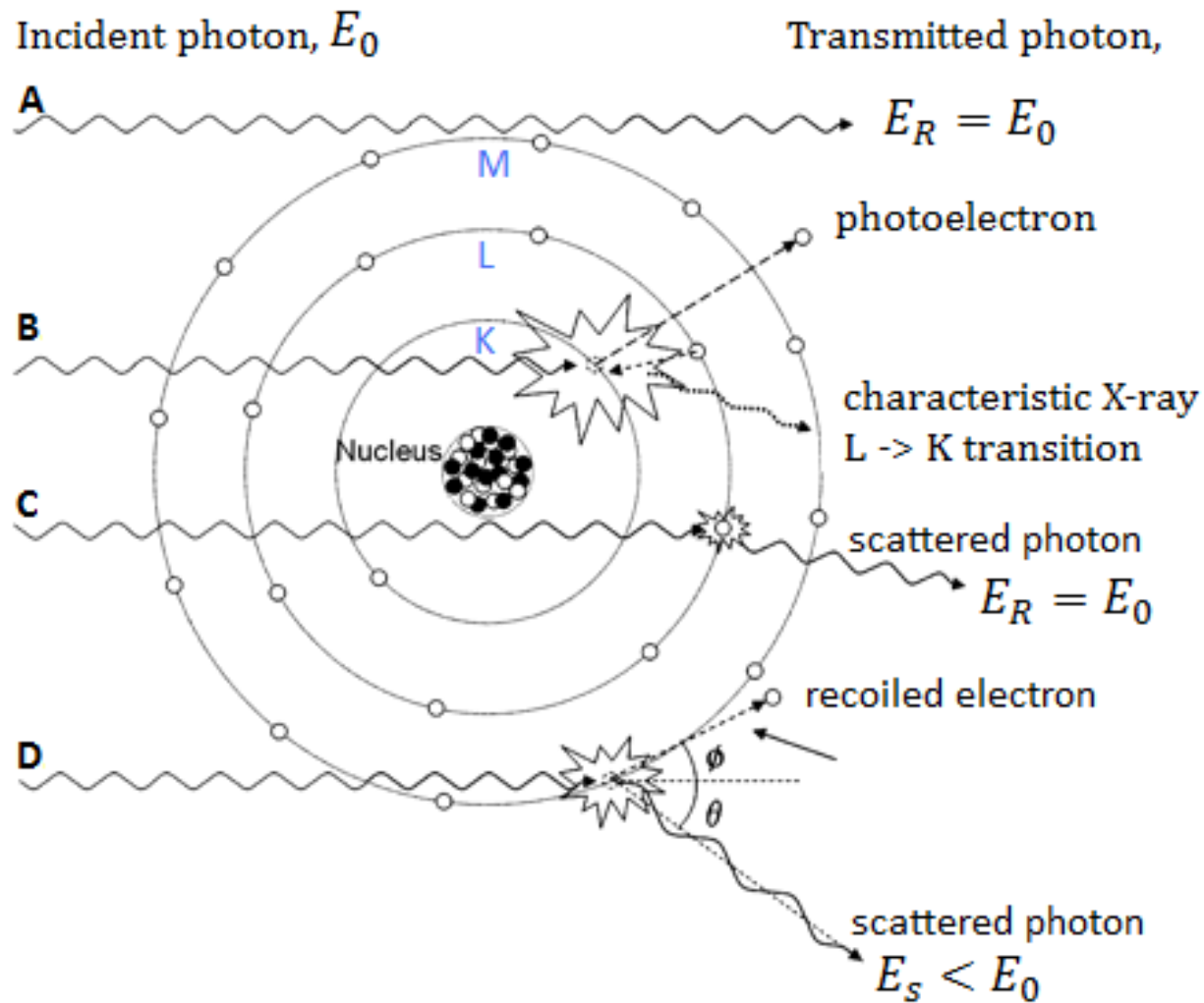
The ratio of absorption/fluorescence, Compton and Rayleigh scatter and transmission depends on the sample thickness, density and composition, and the X-Ray energy.



The **X-ray** interactions with matter are:

- 1) Primary **X-ray** unattenuated beam does not interact with material.
- 2) Photoelectric **absorption** results in **total absorption of the incident X-ray energy by the electrons**. Here the electron leaves its shell to a higher energy one.
- 3) **Rayleigh scattering** is the interaction between the element electron (or whole atom) in which **no energy is exchanged, and the incident X-ray energy equals scattered X-ray energy with small angular change in direction**.
- 4) **Compton scattering** interactions occur with **loosely bound electrons** (outer-shell electrons) causing the ionization effect.





**A. TRANSMITTED
UNAFFECTED**
No interaction

**B. PHOTOELECTRIC
ABSORPTION**
Collision with a tightly
bound inner-shell electron

**C. RAYLEIGH
SCATTERING**
Elastic collision with a
bound outer-shell electron

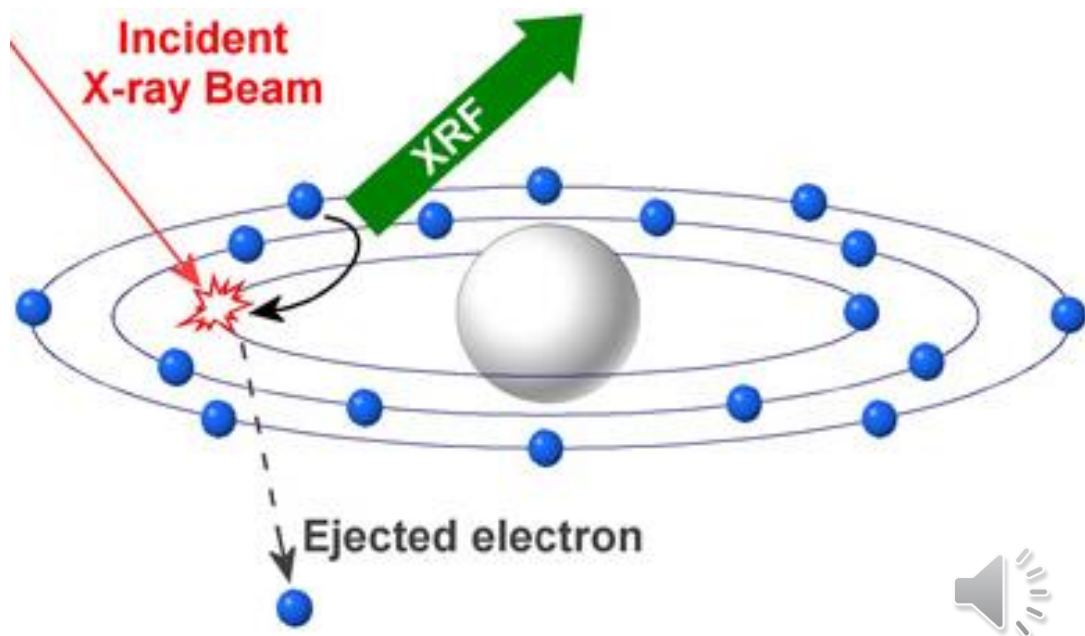
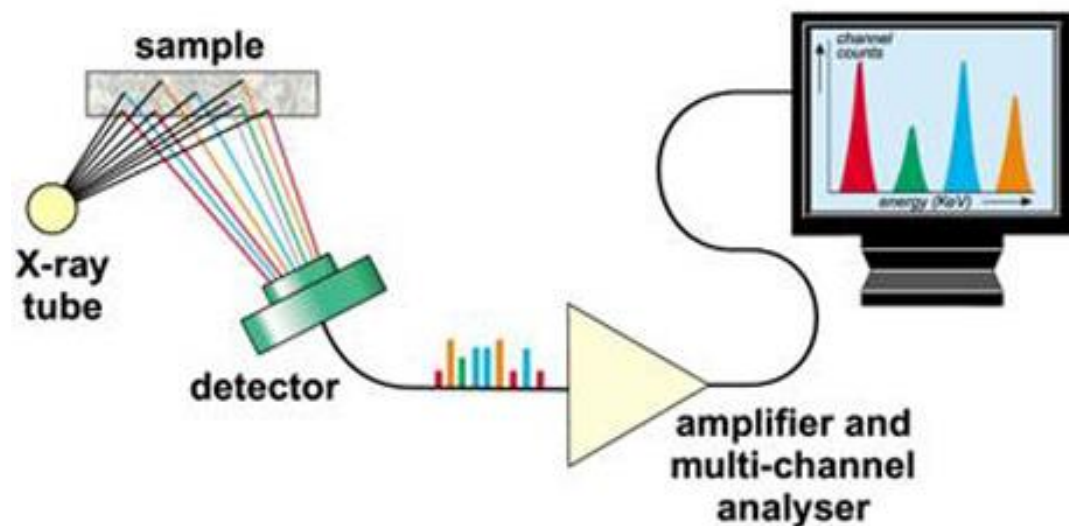
**D. COMPTON
SCATTERING**
Inelastic collision with
weakly bound outer-shell
electron



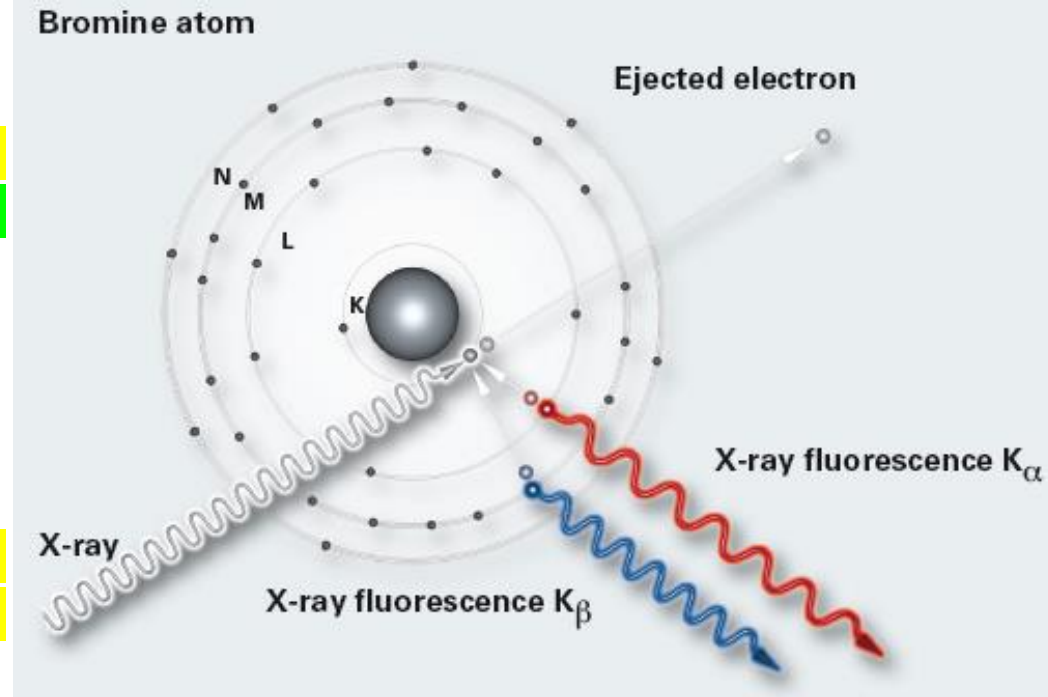
3. X-ray fluorescence analysis (XRF)

XRF is an acronym for **X-ray fluorescence (characteristic)**, a process whereby electrons are displaced from their atomic orbital positions, releasing a burst of energy that is characteristic of a specific element. This release of energy (spectra) is then detected by the **detector** in XRF instrument, which in turn categorizes the **energies and/or wavelength of the element**.

An **X-ray beam** with enough energy to affect the **electrons in the inner shells** of the atoms in a sample is created by an **X-ray tube**. The **X-ray beam** is then emitted from the front end of the handheld XRF analyzer.

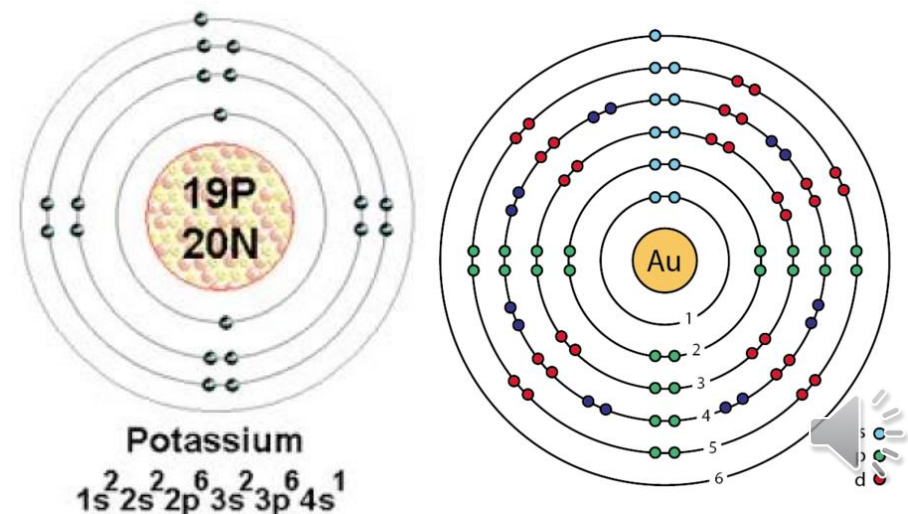


The incident X-ray beam (primary) interacts with the atoms in the sample by displacing electrons from the inner orbital shells of the atom (out of the inner atomic shells K and L). This displacement happens when the primary X-ray beam energy is higher than the binding energy of the electrons with which it interacts. That the primary X-ray energy is absorbed by the electron to be ejected.

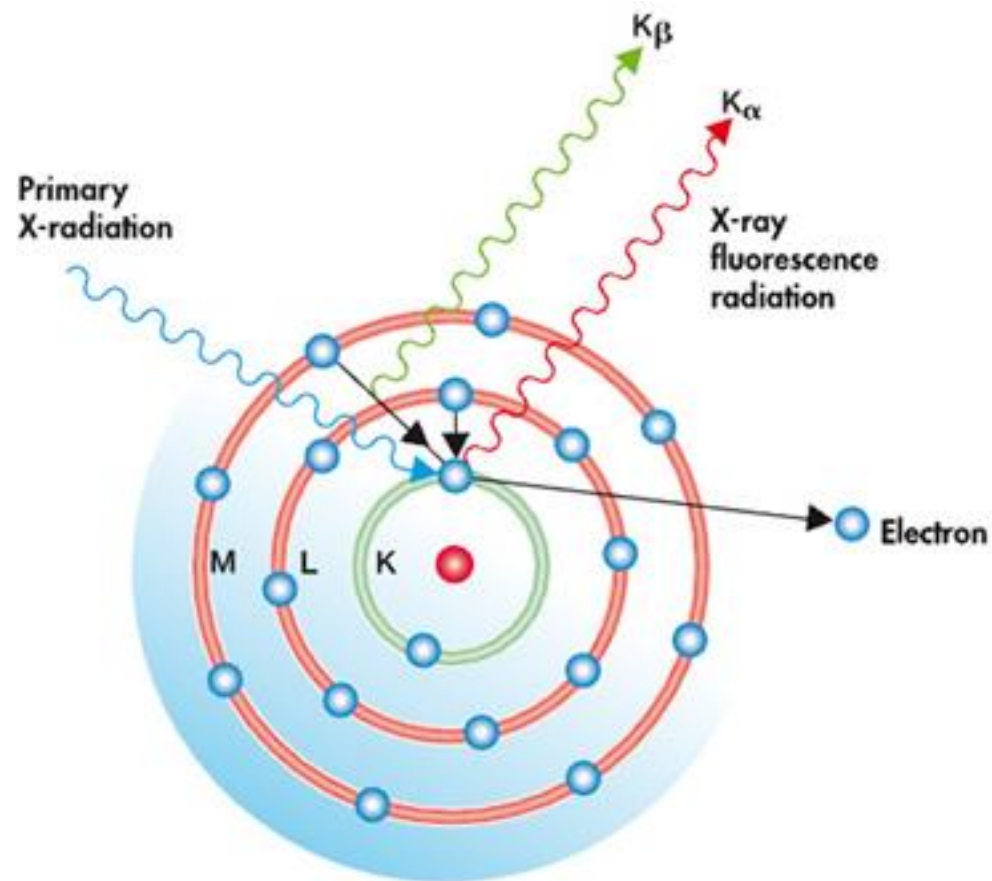


An L to K transition is traditionally called K_{α} , an M to K transition is called K_{β} .

(Note: Electrons are fixed at specific energies in their positions in an atom, and this determines their orbits. Additionally, the spacing between the orbital shells of an atom is unique to the atoms of each element, so an atom of potassium (K) has different spacing between its electron shells than an atom of gold (Au), or silver (Ag), etc).

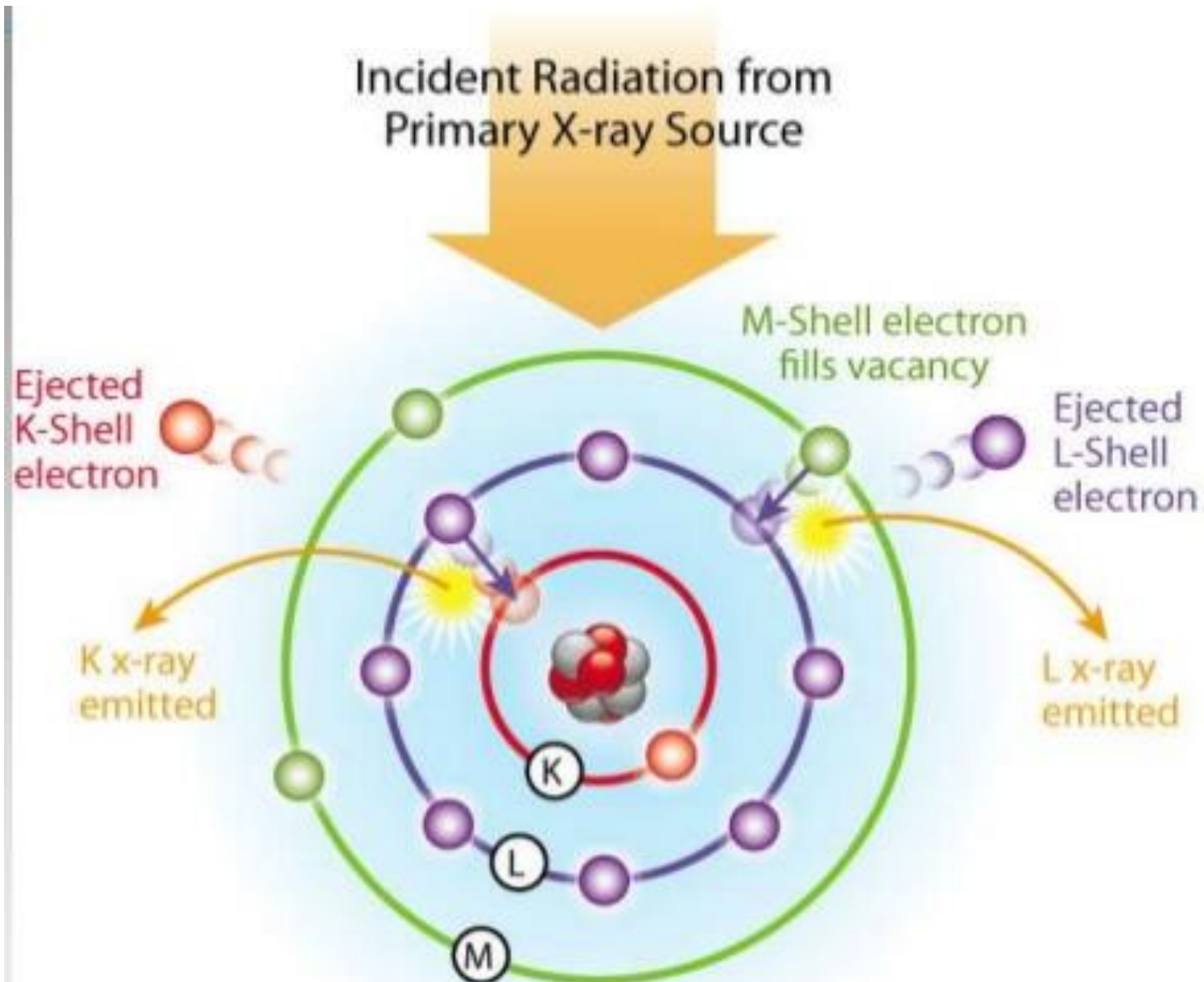


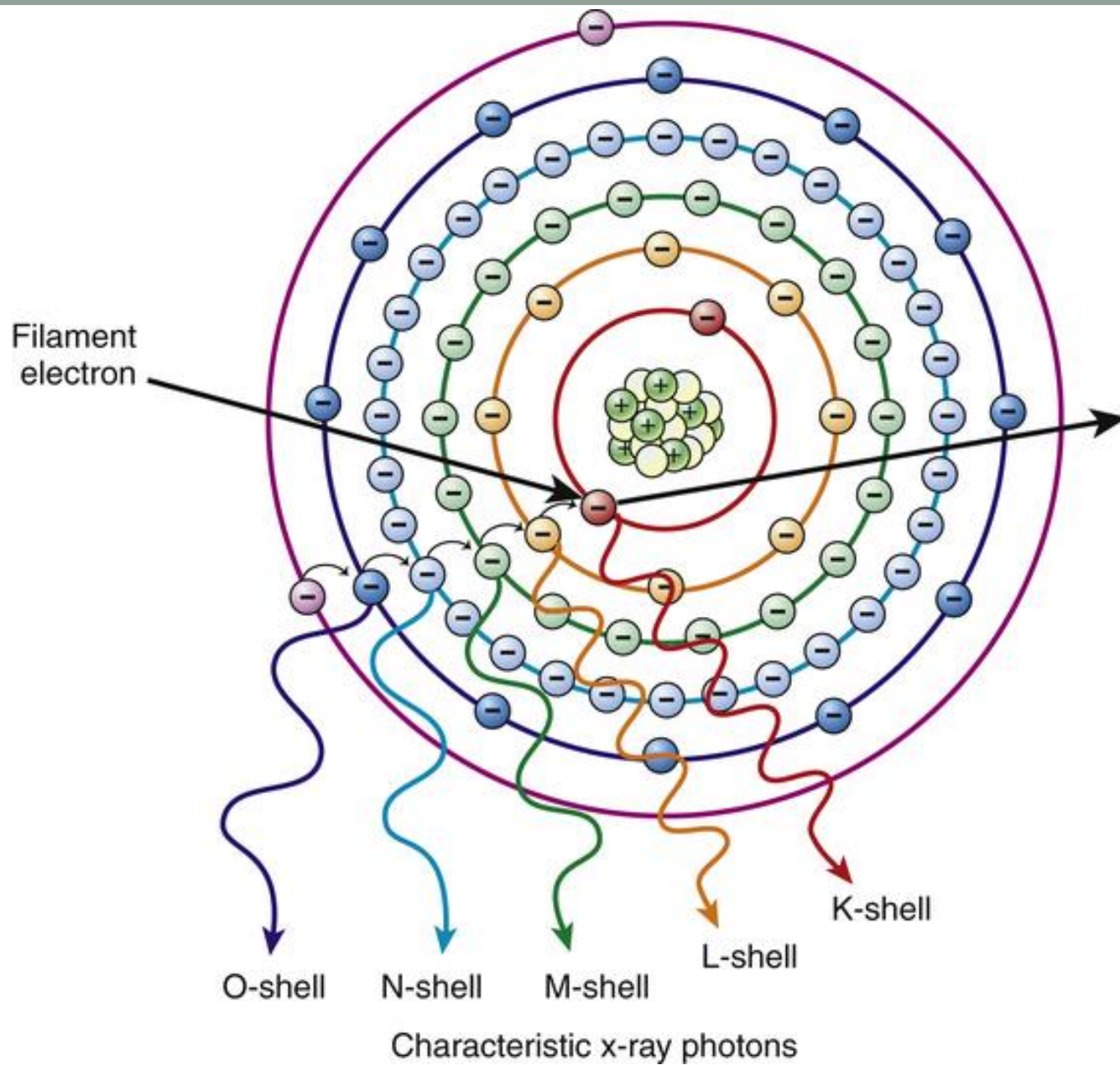
When electrons are knocked out of their orbits, they leave behind **vacancies**, making the atom unstable. The atom must immediately correct the instability by **filling the vacancies** that the displaced electrons left behind. **Those vacancies** can be **filled by electrons from higher orbits (of higher energy) that move down to a lower orbit (of lower energy) where a vacancy exist.** For example, if an electron is displaced from the innermost shell of the atom (the one closest to the nucleus, mainly K and L), an electron from the next shell up can move down to fill the vacancy.



An L to K transition is traditionally called K_{α} , an M to K transition is called K_{β} .

Therefore, an electron loses some energy **[This is fluorescence (secondary "characteristic" X-ray)]** when it drops from a higher electron shell (L) to an **electron shell closer to the nucleus (of lower energy) (K).** The amount of energy lost (**fluorescence**) is equivalent to the difference in energy between the two electron shells, which is determined by the distance between them. **The distance between the two orbital shells is unique to each element (finger print).**





A characteristic interaction event. Note that as outer-shell electrons fill inner-shell vacancies, their excess energy is released as characteristic x-ray photons.

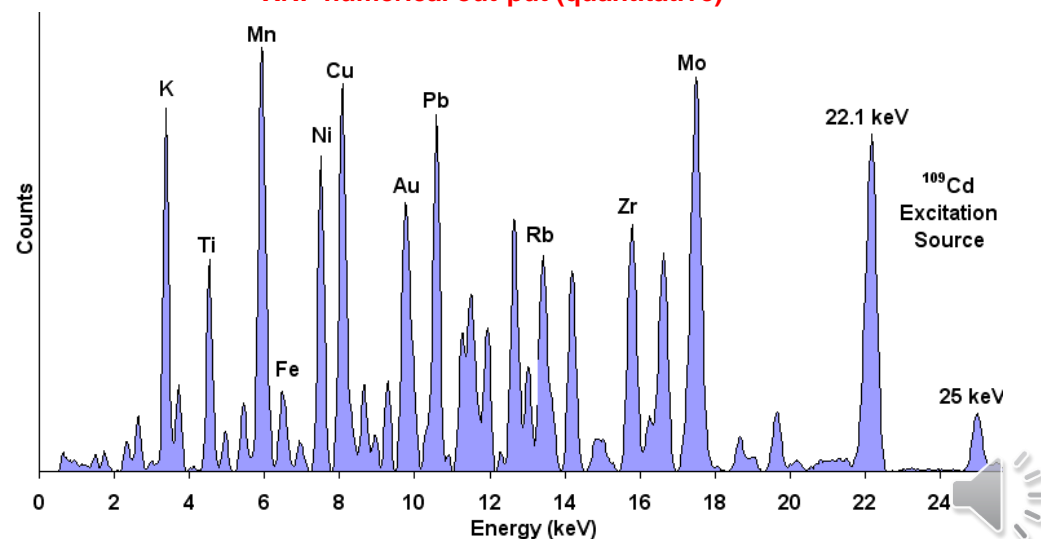


The energy lost (**fluoresced**) (**this is X-ray fluorescence of characteristic energy and wavelength (secondary "X-ray")**) can be used to identify the element from which it emanates, **because the amount of energy lost in the fluorescence process (secondary "characteristic" X-ray) is unique to each element (like finger print and independent of the atom's chemical bond).**

The individual **fluorescent energies detected** are specific to the elements that are present in the sample. In order to determine the **quantity** of each element present, the proportion in which the individual energies appear can be calculated by the instrument or by other software.

Elemental component	Concentration w/ normalization	Measuring unit	Detection limit	Elemental line measured	Intensity (kcps)
Al ₂ O ₃	0.14	mass%	0.02	Al-Kα	0.10
SiO ₂	0.12	mass%	0.02	Si-Kα	0.08
P ₂ O ₅	0.05	mass%	0.01	P-Kα	0.05
SO ₃	0.06	mass%	0.01	S-Kα	0.08
K ₂ O	0.11	mass%	0.01	K-Kα	0.33
TiO ₂	0.05	mass%	0.02	Ti-Kα	0.04
Cr ₂ O ₃	0.04	mass%	0.01	Cr-Kα	0.08
Fe ₂ O ₃	0.05	mass%	0.01	Fe-Kα	0.29
NiO	0.06	mass%	0.01	Ni-Kα	0.38
CuO	97.60	mass%	0.03	Cu-Kα	629.19
ZnO	1.73	mass%	0.02	Zn-Kα	15.69

XRF numerical out-put (quantitative)

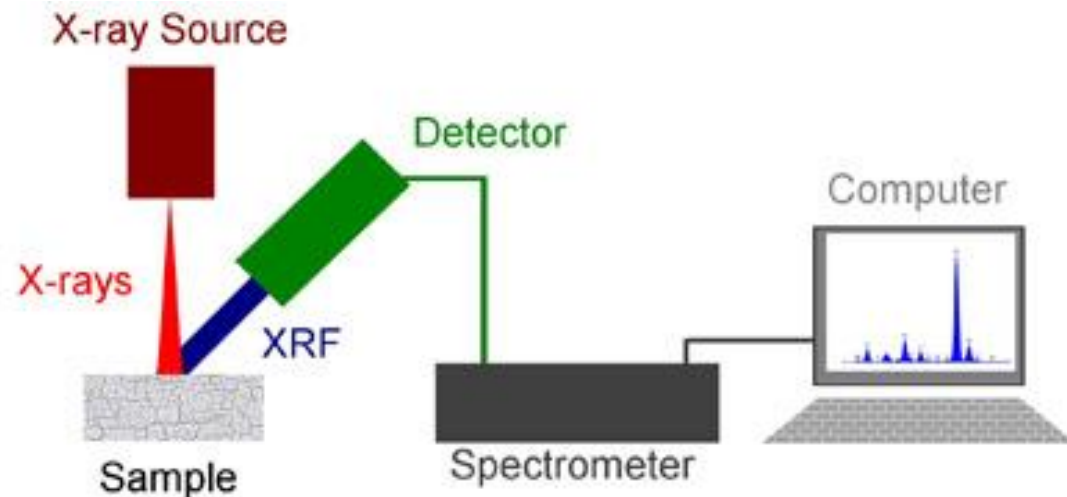


XRF graphical out-put (qualitative)

The **fluorescent radiation** can be analyzed by one of two systems: either by sorting the **energies** of the photons (**energy-dispersive analysis**) (**EDXRF**) or by separating the **wavelengths** of the radiation (**wavelength-dispersive analysis**) (**WDXRF**). Once sorted, the intensity of **each characteristic radiation** is directly related to the **amount of each element** in the material.

Energy Dispersive XRF (**EDXRF**)

An energy dispersive detection system directly measures the different **energies of the emitted X-Rays** from the sample. By counting and plotting the relative numbers of X-Rays at each energy an XRF spectrum is generated.



Wavelength Dispersive (**WDXRF**)

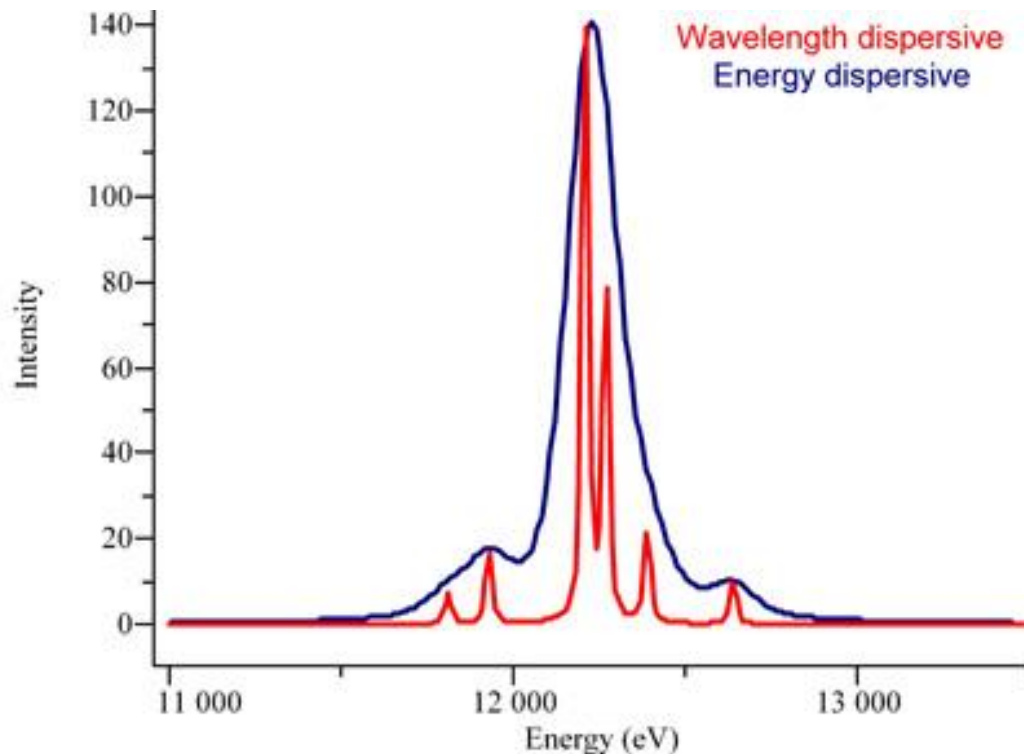
A wavelength dispersive detection system physically separates the **fluorescent X-Rays** according to their **wavelengths**.

The **fluorescent X-rays** are directed to a crystal, which diffracts the X-Rays in different directions according to their wavelengths (energies).

On a sequential system a detector is placed at a fixed position, and the crystal is rotated so that different wavelengths are picked up by the detector.

Comparison between EDXRF and WDXRF

The principal difference between EDXRF (EDX) and WDXRF (WDX) techniques lies in the achievable energy (spectral) resolution. WDX systems can routinely provide working resolutions between 5 eV and 20 eV, depending on their set up, whereas EDX systems typically provide resolutions ranging from 150 eV to 300 eV or more, depending on the type of detector used.



The higher resolution of WDX provides advantages in the spectral overlaps, so that complex samples can be more accurately characterized. However, the additional optical components of a WDXRF system are expensive.

In EDX, the characteristic spectrum of all the sample elements can be acquired simultaneously so the elemental concentration can be detected within seconds. However, WDX spectrum acquisition is either made in a point by point which is time consuming otherwise a number of simultaneous detectors should be positioned (which is an expensive option).

Examples of the XRF analyses of some minerals and rocks

XRF of quartz

Name	SaMp4	SaMp5	SaMp13	Eo98-8
SiO ₂	98.51	97.09	98.56	98.43
TiO ₂	0.01	0.01	0.01	0.01
Al ₂ O ₃	0.27	1.04	0.88	0.79
Fe ₂ O _{3tot}	0.39	0.22	0.11	0.05
MnO	0.04	0.04	0.04	0.04
MgO	0.04	0.06	0.01	0.02
CaO	0.11	0.10	0.21	0.11
Na ₂ O	0.49	0.44	0.06	0.07
K ₂ O	0.04	0.05	0.06	0.07
P ₂ O ₅	0.01	0.01	0.01	0.01
LOI	0.09	0.94	0.00	0.38
Total	100.00	100.00	100.00	99.98
Ba	7	37	bdl	4.8
Ce	1.2	0.7	1.1	1.1
Cr	6	7	2	2
Cu	50.5	11	5.2	9.2
Ga	0.3	0.4	0.3	0.3
Ge	1.6	0.9	2.1	0.5
Hf	bdl	0.1	bdl	0.1
La	0.6	0.5	0.5	0.5
Nb	bdl	0.3	0.2	0.2
Nd	0.5	0.5	0.3	0.4
Ni	3	1	bdl	bdl
Pb	13	1	15	17
Rb	1.2	0.9	3.4	2.0
Sm	0.09	0.1	0.1	bdl
Sr	bdl	5	bdl	6
Ta	bdl	0.05	0.05	bdl
Th	0.1	0.2	1.1	bdl
U	bdl	0.1	0.4	0.3
V	10.9	2.2	bdl	2.0
Y	0.37	0.35	0.11	0.25
Zr	1	2	1	1

XRF of sandstone

Chemical Formula	Quantity [%wt]
SiO ₂	89.454
Al ₂ O ₃	4.354
Fe ₂ O ₃	1.41
K ₂ O	1.101
TiO ₂	0.347
Na ₂ O	0.341
MgO	0.318
CaO	0.311
SO ₃	0.3
Mn ₃ O ₄	0.037
ZrO ₂	0.036
P ₂ O ₅	0.018
SrO	0.004
ZnO ₂	0.002
PbO	0.002



XRF of calcite

Chemical species	CAM	CCI	CCJ	CRO	CRT	CSQ
Na ₂ O	<0.1	0.1	<0.1	0.1	<0.1	<0.1
MgO	<0.1	3.2	1.3	0.1	<0.1	<0.1
Al ₂ O ₃	<0.1	<0.1	0.1	<0.1	0.8	<0.1
SiO ₂	<0.1	3.9	0.3	0.1	0.5	4.5
P ₂ O ₅	<0.1	0.2	<0.1	<0.1	<0.1	0.3
SO ₃	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
K ₂ O	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CaO	55.7	51.2	53.8	55.8	55.8	54.0
TiO ₂	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MnO	<0.1	<0.1	0.1	<0.1	<0.1	0.1
Fe ₂ O ₃	<0.1	<0.1	0.1	<0.1	<0.1	0.2
SrO	<0.1	<0.1	0.7	<0.1	<0.1	0.2
WL(*)	43.6	41.6	43.0	43.6	42.8	39.6

(*) WL = Weight loss

XRF of limestone

component	HL	KR	KW	PB
SiO ₂	1.36	2.95	0.85	4.32
Al ₂ O ₃	0.57	0.74	0.24	0.56
Fe ₂ O ₃	0.19	0.32	0.09	0.25
CaO	54.04	52.43	54.10	52.17
MgO	1.27	0.47	0.89	1.47
Na ₂ O	n/a	< 0.096	< 0.2	n/a
K ₂ O	0.09	0.21	0.06	0.13

XRF of basalt

Stapafell Mountain, Iceland ^a

Weight%

SiO ₂	48.25
Al ₂ O ₃	14.95
CaO	11.85
Fe ₂ O ₃	12.25
FeO	
K ₂ O	0.309
MgO	9.50
MnO	0.187
Na ₂ O	2.01
P ₂ O ₅	0.207
TiO ₂	1.63
Total	101.14

XRF of granite

Oxide Composition	Weight Percentage (%)
SiO ₂	70
Al ₂ O ₃	16
K ₂ O	6.1
Fe ₂ O ₃	2.3
CaO	2.2
Na ₂ O	1.9
MgO	0.88
TiO ₂	0.30
P ₂ O ₅	0.18
MnO	0.18
SO ₃	0.12
Rb ₂ O	0.058
BaO	0.049



<https://www.youtube.com/watch?v=pcPaRXSMFW8>

