DAY 1 (Morning)

Introduction on Isotopes and Sample preparation

- **1- Isotopes:**
    - **Definitions:**
    - **Elemental and isotopic abundances**
    - **Nuclear Stability**
    - **Nuclear forces**
    - **Variations in isotopic abundances**
    - **Radiogenic isotopes - Nuclear processes**
    - **Stable isotopes - Chemical fractionation**
- **2- Definitions**
- **3- Sample preparation**
    - **Sampling**
    - **Crushing**
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1- Isotopes:

Definitions:

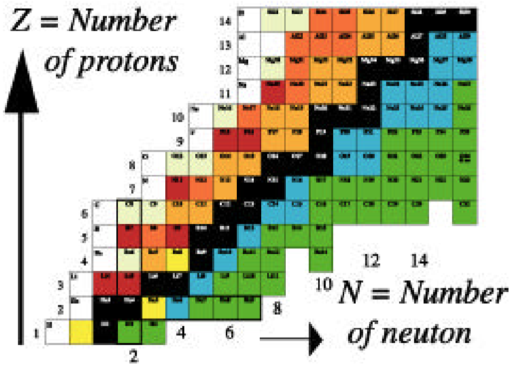
Atom: Identified and labeled according to the number of protons in its nucleus: atomic number: *Z*. The great importance of the atomic number derives from the observation that all atoms with the same atomic number have identical chemical properties. The periodic table of the elements assigns one place to every atomic number, and each of these places is labelled with the common name of the element.

Isotope: One of two or more species of atoms of a chemical element with the same atomic number (Z, figure 1.3, table 1.1) and position in the periodic table and nearly identical chemical behaviour but with different atomic masses and physical properties. Every chemical element has one or more isotopes. Many important properties of an isotope depend on its mass. The total number of neutrons and protons (mass number, symbol *A*), of the nucleus gives approximately the mass measured on the so-called atomic-mass-unit (amu) scale

The standard notation, $^{1}/_{1}H$ refers to the simplest isotope of hydrogen and $^{235}/_{92}U$ to an isotope of uranium widely used for nuclear power generation and nuclear weapons fabrication (Figure 1.1: isotope notation).

$$X_{Z=Atomic\_Number=Number\_of\_Pr oton}^{A=Mass\_Number=Mumber\_of\_Nucleons}$$

Figure1.1: Standard notation for isotopes. A-Z = numbers of neutrons = N

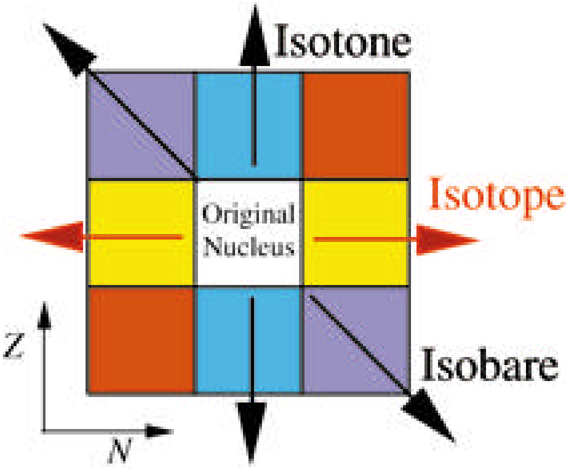


Elements are divided into nuclides and classified according to their atomic number (Z, vertical axe) and number of neutron (N, horizontal axe). See figure 1.2: the lower part of the chart of nuclide

Figure 1.2: The lower part of the chart of nuclides.

Isotone: Nuclide with the same N but different Z or A
Isobare: Nuclide with the same masse (A) but different
Isotope: Nuclide with the same Z but different N or A
Isomere: Same two nuclide but with different energy state (fundamental and excited state)

Figure 1.3: Classification of nuclide



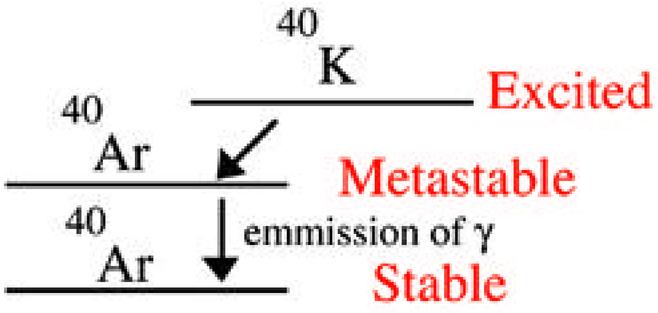


Figure 1.4: Example of isomere: ^{40}K - ^{40}Ar electron capture:

	N	Z	A	%
Isotopes Z = 20				
Calcium	20	20	40	96.97
Calcium	22	20	42	0.64
Calcium	23	20	43	0.145
Calcium	24	20	44	2.06
Calcium	26	20	46	0.0033
Calcium	28	20	48	0.185
Isotones N = 20				
Sulphur	20	16	36	0.0136
Chlorine	20	17	37	24.471
Argon	20	18	38	0.063
Potassium	20	19	39	93.1
Calcium	20	20	40	96.97
Isobars A = 40				
Argon	22	18	40	
Potassium	21	19	40	
Calcium	20	20	40	

Table 1.1: Examples of isotopes, isotones and isobars:

There are 264 stable isotopes in nature (with Z < 82). Other elements with Z> 82 are always radioactive (Bi, Th, U). The isotopic abundance depends on whether the A, Z or N number are odd or even.

A	Z	N	Number of Nuclide (stable isotope)
even	even	even	157
Odd	even	Odd	53
Odd	Odd	even	50
even	Odd	Odd	4
Total			264

Table 1.2: Stability of isotopes as a function of their A, Z and N numbers.

Elemental and isotopic abundances

*** Method**

To understand how the elements formed we need to understand a few astronomical observations and concepts. The universe began some 10 to 20 Ga ago with the Big Bang. Since then the universe has been expanding, cooling, and evolving. Our present understanding of nucleosynthesis comes mainly from two sorts of observations:

1- The abundance of isotopes and elements in:

- **Sun & Stars, gaseous nebula, interstellar fields** (observations of stars using spectroscopy),
- **Cosmic Ray**: much harder to measure. It is mainly made of protons, He and other elements such as Li, B etc…
- **Earth, moon, meteorites etc…:** The composition of the earth is only well known for the continental and oceanic crust but the mantle isn't still well characterized
- **Other planets, asteroids, comets etc… (in the solar system)**: Their composition isn't well characterized. For example we only know the composition of the atmosphere of Venus, rich in CO2.

2- Experiments on nuclear reactions that determine what reactions are possible (or probable) under given conditions.

*** Result**

The total mass of the earth is negligible in comparison with the total mass of the solar system. Ninety-height percent of the total mass of the solar system is located in the sun. The rest is shared between other planets, asteroids, comets, moon etc… Therefore, if we want to know the composition of the solar system, we need to look at the sun and other stars rather than the Earth (figure1.5, table 1.3). Figure 1.6 represent the different nucleosynthetic processes responsible for the formation of the different element in function of their atomic number.

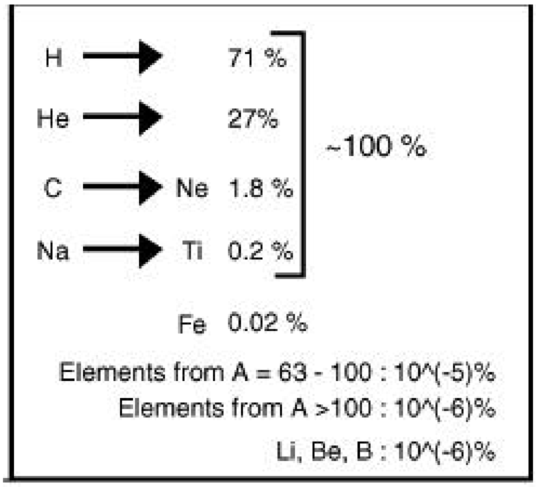


Figure 1.5: Cosmic abundances of the Elements. H, He and elements up to Ti represent nearly 100 % of the solar system composition

Z	Element	Concentration	Z	Element	Concentration
1	H	2.79E+10	44	Ru	1.86
2	He	2.72E+09	45	Rh	0.344
3	Li	57.1	46	Pd	1.39
4	Be	0.73	47	Ag	0.486
5	B	21.2	48	Cd	1.61
6	C	1.01E+07	49	In	0.184
7	N	3.13E+06	50	Sn	3.82
8	O	2.38E+07	51	Sb	0.309
9	F	843	52	Te	4.81
10	Ne	3.44E+06	53	I	0.9
11	Na	5.74E+04	54	Xe	4.7
12	Mg	1.07E+06	55	Cs	0.372
13	Al	8.49E+04	56	Ba	4.49
14	Si	1.00E+06	57	La	0.446
15	P	1.04E+04	58	Ce	1.136
16	S	5.15E+05	59	Pr	0.1669
17	Cl	5240	60	Nd	0.8279
18	Ar	1.01E+05	62	Sm	0.2582
19	K	3770	63	Eu	0.0973
20	Ca	6.11E+04	64	Gd	0.33
21	Sc	34.2	65	Tb	0.0603
22	Ti	2400	66	Dy	0.3942
23	V	293	67	Ho	0.0889
24	Cr	1.35E+04	68	Er	0.253
25	Mn	9550	69	Tm	0.0386
26	Fe	9.00E+05	70	Yb	0.243
27	Co	2250	71	Lu	0.0369
28	Ni	4.93E+04	72	Hf	0.176
29	Cu	522	73	Ta	0.0226
30	Zn	1260	74	W	0.137
31	Ga	37.8	75	Re	0.0507
32	Ge	119	76	Os	0.717
33	As	6.56	77	Ir	0.66
34	Se	62.1	78	Pt	1.37
35	Br	11.8	79	Au	0.186
36	Kr	45	80	Hg	0.52
37	Rb	7.09	81	Tl	0.184
38	Sr	23.5	82	Pb	3.15
39	Y	4.64	83	Bi	0.144
40	Zr	11.4	90	Th	0.0335
41	Nb	0.698	92	U	0.009
42	Mo	2.55			

Table 1.3: Cosmic abundances of the Elements in Atoms per 10^6 Atoms Si.

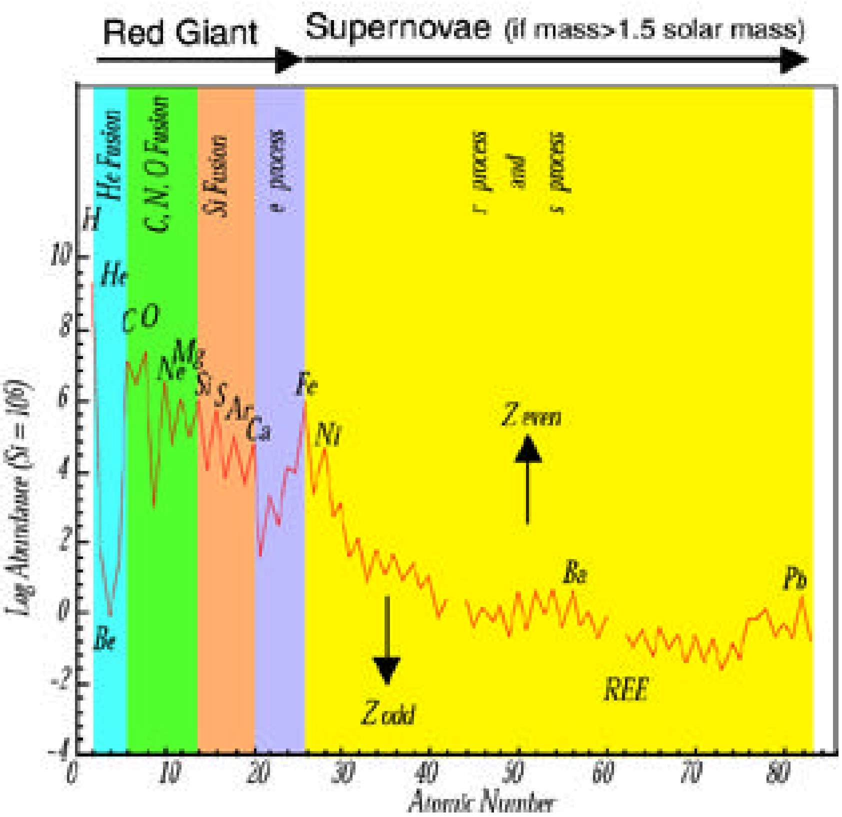


Figure 1.6: Nucleosynthetic processes as a function of the atomic number of the element.

*** Model**

A polygenetic hypothesis with four phases of nucleosynthesis has been proposed to explain the abundances of the elements.

a- COSMOLOGICAL NUCLEOSYNTHESIS: Cosmological nucleosynthesis occurred shortly after the universe began and is responsible for the cosmic inventory of H and He, and some of the Li. Helium is the main product of nucleosynthesis in the interiors of normal, or “main sequence” stars (figure 1.7).

b- STELLAR NUCLEOSYNTHESIS: The lighter elements, up to and including Si, but excluding Li and Be, and a fraction of the heavier elements may be synthesized in the interiors of larger stars during the final stages of their evolution. Figure 1.7 the represent the sequence of light element production in an hypothetical star.

c- EXPLOSIVE NUCLEOSYNTHESIS: The synthesis of the remaining elements occurs as large stars exhaust the nuclear fuel in their interiors and explode during a supernova. Figure 1.8 illustrate the r and s process during supernova and their role in producing heavier isotopes.

d- NUCLEOSYNTHESIS IN INTERSTELLAR SPACE: Li and Be are continually produced in interstellar space by interaction of cosmic rays with matter.

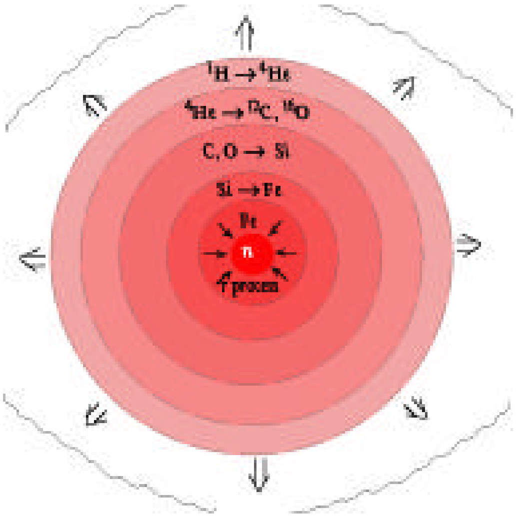


Figure 1.7: Schematic representation of the different stage of the evolution of star

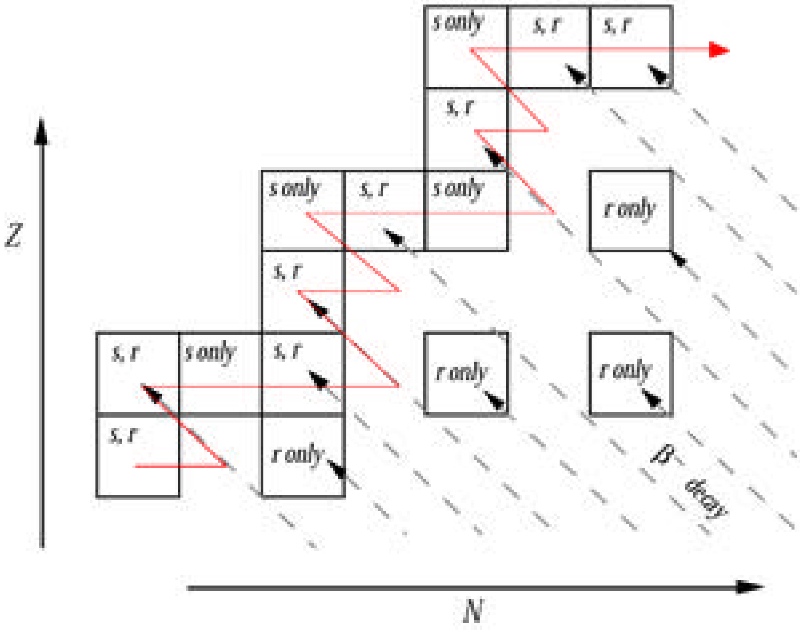


Figure 1.8: Role of rapid (r) and slow (s) neutron capture process in the formation of heavier isotopes. Note the competitive role of radioactivity _$^{-}$ decay to produce stable nuclides.

Nuclear stability

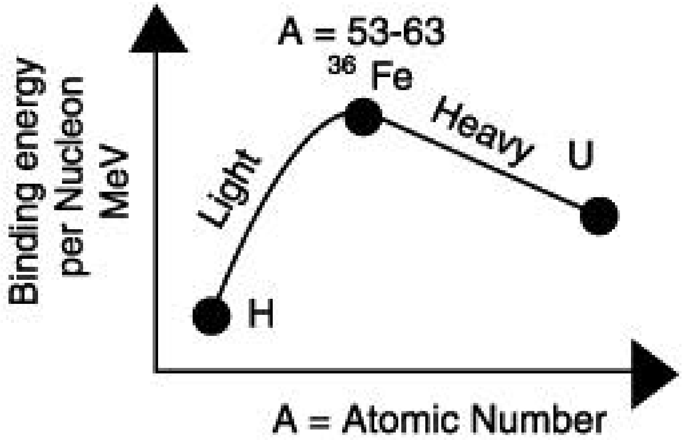


Figure 1.9: Variation in binding energy per nucleon versus the atomic number.

Isotopes are said to be stable if, when left alone, they show no perceptible tendency to change spontaneously

Scale of nuclear stability is based on a comparison of measured masses with the masses of their constituent electrons, protons, and neutrons.

The actual masses of all the stable isotopes differ appreciably from the sums of their individual particle masses. For example, the isotope $^{12}/_{6}$ C, which has a particularly stable nucleus, has an atomic mass defined to be exactly 12 amu. The total separate masses of 6 electrons and 6 protons, treated as 6 hydrogen atoms and 6 neutrons, add up to 12.09894 amu. The difference, _m, between the actual mass of the assembled isotope and the masses of the particles gives a measure of the stability of the isotope: the larger and more negative the value of _m, the greater the stability of the isotope.

The quantity of energy calculated is called the nuclear binding energy (EB).

Division of the binding energy EB by A, the mass number, yields the binding energy per nucleon. This important quantity reaches a maximum value for nuclei in the vicinity of 56Fe.

Nuclear forces

All nuclides are stable. For some combinations of N and Z, a nucleus forms, but is unstable, with half-lives from $>10^{15}$ yrs to $<10^{-12}$ sec. N » Z for stable nuclei. Thus a significant portion of the nucleus consists of protons, which obviously tend to repel each other by electrostatic force.

From the observation that nuclei exist at all, it is apparent that another force must exist which is stronger than coulomb repulsion at short distances. It must be negligible at larger distances, otherwise all matter would collapse into a single nucleus. This force, called the nuclear force, is a manifestation of one of the fundamental forces of nature, called the strong force. If this force is assigned a strength of 1, then the strengths of other forces are: electromagnetic 10^{-2} ; weak force 10^{-5} ; gravity 10^{-39}. Just as electromagnetic forces are mediated by a particle, the photon, the nuclear force is mediated by the pion.

A comparison of the relative strengths of the nuclear and electromagnetic forces as a function of distance is shown in figure 1.10.

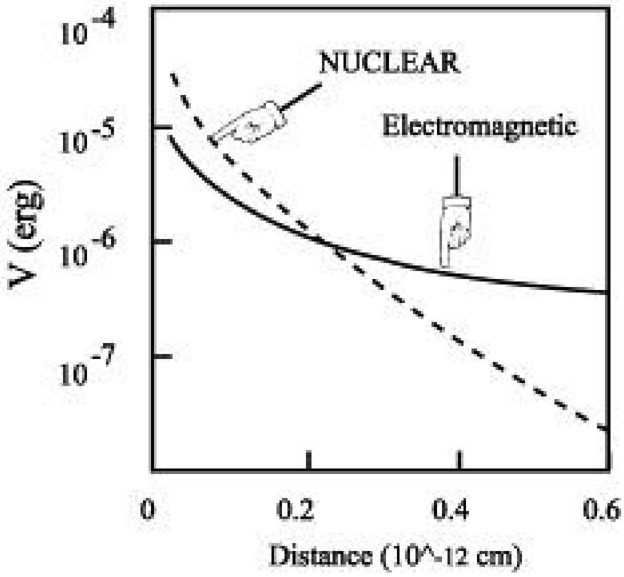


Figure 1.10: The nuclear and electromagnetic potential of a proton as a function of distance from the proton.

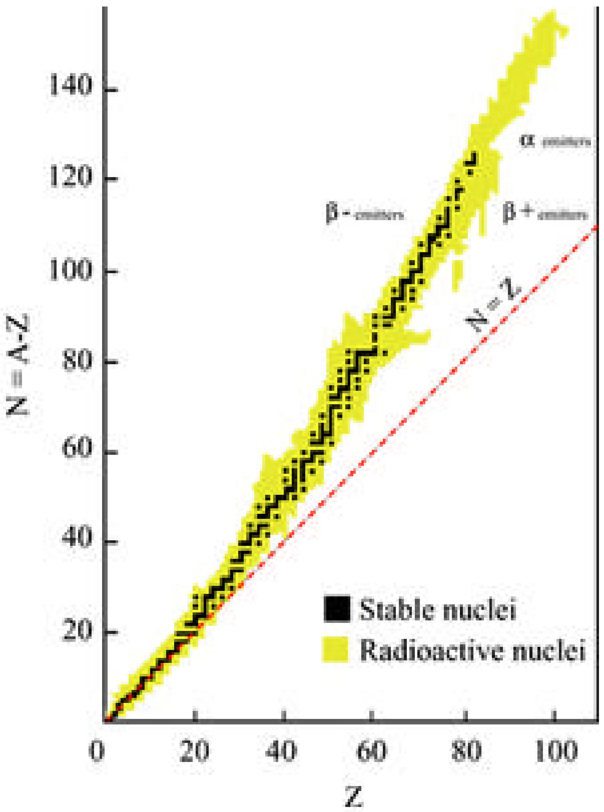


Figure 1.11: N vs. Z showing which nuclides are stable or radioactive.

Why are some combinations of N and Z more stables than others ? The answer has to do with the forces between nucleons and how nucleons are organized within the nucleus. The structure and organization of the nucleus are questions still being actively researched in physics, and full treatment is certainly beyond the scope of this course.

Variations in isotopic abundance

Although isotopic abundance are fairly constant throughout the solar system, variations do occur. Variations in stable isotopic abundance provide geologists and astronomers with valuable clues to the histories of the objects under study. Several different processes can cause abundance to vary, among them radioactive decay and mass fractionation.

* Radiogenic isotopes - Nuclear processes

Only a small fraction of the isotopes are known to be stable indefinitely. All the others disintegrate spontaneously with the release of energy by processes broadly designated as radioactive decay. Each “parent” radioactive isotope eventually decays into one or at most a few stable isotope “daughters” specific to that parent. The basic equation of radioactive decay is:

$$\frac{dN}{dt} = -\lambda N \qquad \int_{N_0}^{N} \frac{dN}{N} = \int_0^t -\lambda dt \qquad \ln\frac{N}{N_0} = -\lambda t$$

$$\frac{N}{N_0} = e^{-\lambda t} \Leftrightarrow N = N_0 e^{-\lambda t}$$

$$\ln\frac{1}{2} = -\lambda t_{1/2} \Leftrightarrow \ln 2 = \lambda t_{1/2}$$

This is the definition of a half-life: $t_{1/2}$

$$D = N_0 - N$$

$$D = Ne^{\lambda t} - N = N(e^{\lambda t} - 1)$$

$$D = D_0 + N(e^{\lambda t} - 1)$$

Example: Rb-Sr isotopic system

$$^{87}Sr = {}^{87}Sr_0 + {}^{87}Rb(e^{\lambda t} - 1)$$

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right) + \frac{^{87}Rb}{^{86}Sr}(e^{\lambda t} - 1)$$

Under ordinary conditions, the disintegration of each radioactive isotope proceeds at a well-defined and characteristic rate. Thus, without replenishment, any radioactive isotope will ultimately vanish. Some isotopes, however, decay so slowly that they persist on Earth today even after the passage of more than 4.5 Ga years since the last significant injection of freshly synthesised atoms from some nearby star.

Isotope	Natural Abundance (%)	Half-life (Year)	Mode of decay	Stable product
40 K	0.011	1.25*10(9)	EC	40 Ar
87 Rb	27.83	4.88*10(10)	β–	87 Sr
147Sm	15.0	1.06*10(11)	α	143 Nd
176 Lu	2.6	3.53*10(10)	β–	176 Hf
187 Re	62.602	4.56*10(10)	β–	187 Os
232 Th	100	14.00*10(9)	α, β–	208 Pb
235 U	0.7204	0.7038*10(9)	α, β–	207 Pb
238 U	99.2739	4.468*10(9)	α, β–	206 Pb

Table 1.3: list of classic naturally-occurring radioactive isotopes. β^- = beta decay, EC = electron capture, α = alpha decay.

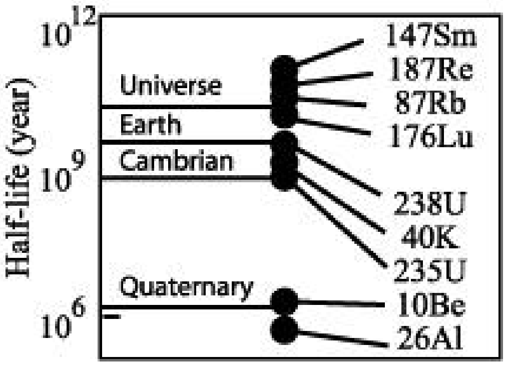


Figure 1.12: Unstable nuclides with half-lives over 0.5 Myr, in order of decreasing stability. Geological useful parent nuclides are marked. Some very long-lived radionuclides with no geological application are also marked, in brackets.

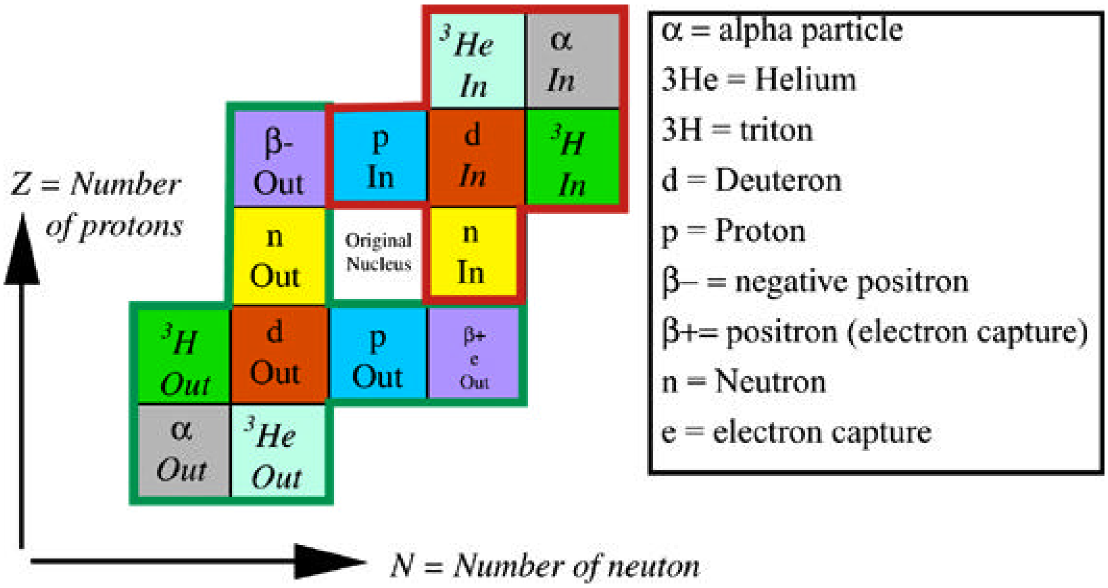


Figure 1.13: Possible decay scheme for an isotope.

*** Stable isotopes - Chemical fractionation**

Mass fractionation of stable isotope geochemistry is concerned with variations of the isotopic compositions of light elements arising from **chemical fractionations rather than nuclear processes**. The elements most commonly studied are H, Li, B, C, N, O, Si, S and Cl. Of these, O, H, C and S are by far the most important However recent development in MC-ICPMS allow the measurement, at high precision, of Cu, Zn, Fe and Ca isotopes.

These elements have several common characteristics:

- They have low atomic mass.
- The relative mass difference between the isotopes is large.
- They form bonds with a high degree of covalent character.
- The elements exist in more than one oxidation state (C, N, and S) and are important constituents of naturally occurring solids and fluids.

Each isotope is animated by a vibration movement and are therefore very tempted to change place. The frequency of that movement (vibration) is inversely proportional to the mass. Thus heavy molecules react less rapidly than light isotopes during a chemical reaction.
Stable isotope fractionation process occur during isotopic exchange reactions:

- **Equilibrium fractionation:**

Occurs because heavy isotopes form stronger bonds than (they don't vibrate as much as) light isotopes.

- **Kinetic fractionation:**
  - Given the same kinetic energy ($Ec = 1/2mv^2$), light isotopes have higher velocities and therefore diffuse and evaporate faster than heavy isotopes.
  - Heavy isotopes form stronger bonds, and therefore break bonds more slowly during chemical reactions. Molecules containing the light isotope react more rapidly. Thus, unidirectional chemical reactions effectively fractionate isotopes.

So as the mass of the isotope increase and as temperature increase, the fractionation decrease.

2- Definitions

Quantitative: Quantified concentration or abundance of an element
Qualitative (semi-quantitative): detectable but not quantified
Unit of concentration:
Chemistry: amount of a particular element per unit of **volume**: g/l^{-1}
Geochemistry: amount of a particular element per unit of **mass**:
% = g per 100 g
ppm = _ g / g
ppb = ng/g
ppt = pg/g
ppq = fg/g

Abundances:

Major element	> 1 % by mass
Minor element	1 – 0.1 % by mass
Trace element	< 0.1 % by mass

Bulk (large volume) versus **spatially resolved** (high-resolution, in-situ) analysis
Spectrometry (information on *abundances*) versus **Spectroscopy** (*spectral wavelength* after excitation of an element. Provide information on *chemical bounding* and *environment of the element).*

Acquired data using analytical techniques are always associated with errors. It is of paramount importance to estimate the magnitude of these errors in order to validate such and such data. Unfortunately there isn't any simple and general way to estimate them. Generally the time spent to acquire the data is equivalent to the time spent to estimate the errors attached to them. Two expressions are commonly used to discuss the error on a data set: precision and accuracy.

Precision: Errors on the repetition of an analytical procedure several time under the same condition
Accuracy: Deviation of a single observation from the TRUE value
Bias: Deviation of the mean of a series of analysis from the TRUE value

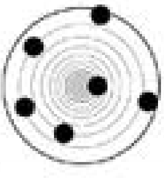
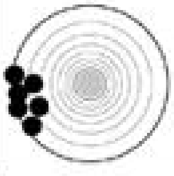
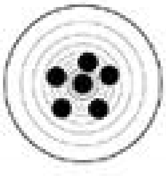
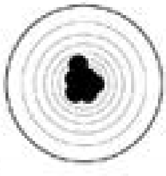
				
Precision	**No**	**Yes**	**No**	**Yes**
Accuracy	**No**	**No**	**Yes**	**Yes**

Figure 1.14: Difference between precision and accuracy.

3- Errors

Uncertainties associated with the measurement are separated in 2 groups:

1- **Systematic errors**: they are of known origins and usually the analyst can estimate them and correct them as well:

1. Instrumental errors
2. Drift of the detector because of increase in temperature of the lab
3. Unstability of the current
4. Oxidation of the electrical contacts which modify resistances for example

This type of error could be corrected and identifies during the calibration of the instrument.

5. Errors associated with the method chosen
6. Chemical and physical non ideal behaviour of the reagents and chemical reactions
7. Unstability of the reagents
8. Chemical interferences

Those errors are hard to find and correct

9. Errors associated with the analyst
10. Wrong reading of the display
11. Error in the transcription
12. Exchange of samples

Not so easy to correct

2- **Random errors**: These errors are very hard to correct and are usually termed NOISE. They represent the accumulation of a series of small fluctuations and depends on the instrument you are using. They can't be detected individually. Their primary characteristics are their random nature. For a full description of error in analytical chemistry see **Begley and Sharp 1994 (**Occurrence and reduction of noise in inductively coupled plasma mass spectrometry for enhanced precision in isotope ratio **JAAS, 6:** 171-176**)**

Before talking about error associated with the measurement of a series of data, it is important to find a value representative of this population:

1- **raw data**: direct from the instrument.

2- **Average**: A value characteristic of the population.

1. Arithmetic error:

$$\bar{X} = \frac{X_1 + X_2 + X_3 ..... + X_n}{N}$$

2. Harmonic average

$$H = \frac{N}{\sum \frac{1}{X}}$$

3. Quadratic average:

$$M.Q. = \sqrt{\frac{\sum X^2}{N}}$$

4. Geometrical average

$$G = \sqrt[N]{X_1 * X_2 * X_3 \ldots\ldots X_N}$$

The relation between the different average is: H ≤ G ≤ X
The arythmical average is the one most widely used.

3- Median
The median from a population of data sorted by increasing number is the middle value
4- Mode
The mode of a population is the number for frequently encounter, with the highest frequency. There could be more than one mode.

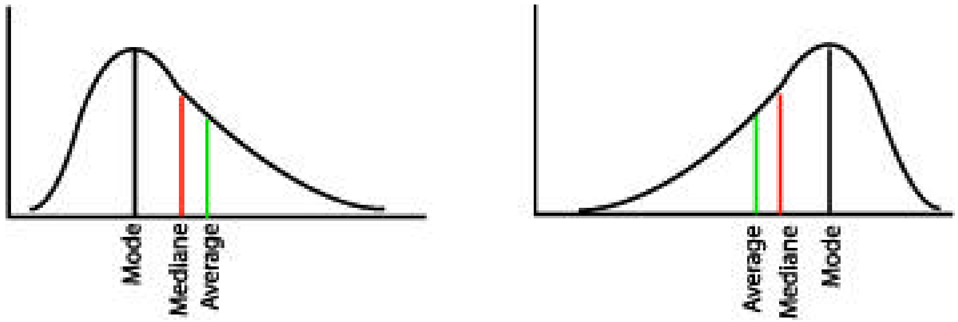


Figure 1.15: Comparison between average, mode and mediane

3- Measure of the dispersion:
There are different ways to estimate the dispertion:

1-The spread: difference between maximum to minimum value
2- Deviation from the mean

$$\frac{\sum \left| X - \bar{X} \right|}{N}$$

3- Standard deviation:

$$S = \sqrt{\frac{\sum (X - \bar{X})^2}{N}}$$