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Geochemistry of Radioactive Isotopes

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Abstract

The chapter targeted the geochemistry of radioactive isotopes dealing with multidisciplinary topics and focusing on geochronology and tracer studies. The most common subjects are presented to include the basic principles of radioactive isotopes. The radioactive decay, the parent nuclide, the SI unit of radioactive decay as well as the historical discovery of radioactivity, the neutrons and protons in atomic nuclei, alpha and beta particles, gamma rays, electromagnetic radiation, decay and mode of decay, chain of decay, decay rates, decay timing, principle of dating, radiometric dating, isotope systems, the Rb/Sr System, the U, Th, Pb System, the age of the earth, Sm-Nd dating, K-Ar dating, ^{14}C Carbon dating, the geochron, all those were included overall.

Keywords: geochemistry, isotopes, radioactive isotope, parent nuclide, dating

1. Introduction

The process in which an unstable atomic nucleus loses energy by emitting radiation in the form of particles or electromagnetic waves known as radioactive decay that causes the energy loss from the parent nuclide converting it to daughter nuclide [1]. This chapter has been authorized based mainly on published reference focusing on some basic properties and principles of radiation and how to use this phenomenon for the estimation the absolute geological age depending on the isotope half-life and provides brief summary of only a very few examples of dating applications. Geochronology and tracer studies are two principle applications of geochemistry of radiogenic isotope. Geochronology goes to estimate the absolute time based on the radioactive rate decay from the beginning of decay to its daughter by knowing how much nuclides have decayed. Tracer application relies on the variation in ratio of the radiogenic daughter isotope to other isotopes of the element. The purpose of authoring this chapter is to help those who are interested in this field and to provide what is useful and brief in a simplified way away from the complexity.

2. Radioactive decay and natural radioactive isotopes

The radioactive decay (a phenomenon of natural and artificial) means loss of energy that results in an atom named the parent nuclide converting it to an atom of a different type, called the daughter nuclide. The ^{14}C is a parent, emits radiation and transforms to a ^{14}N representing a daughter [2]. Accordingly, it is easy to

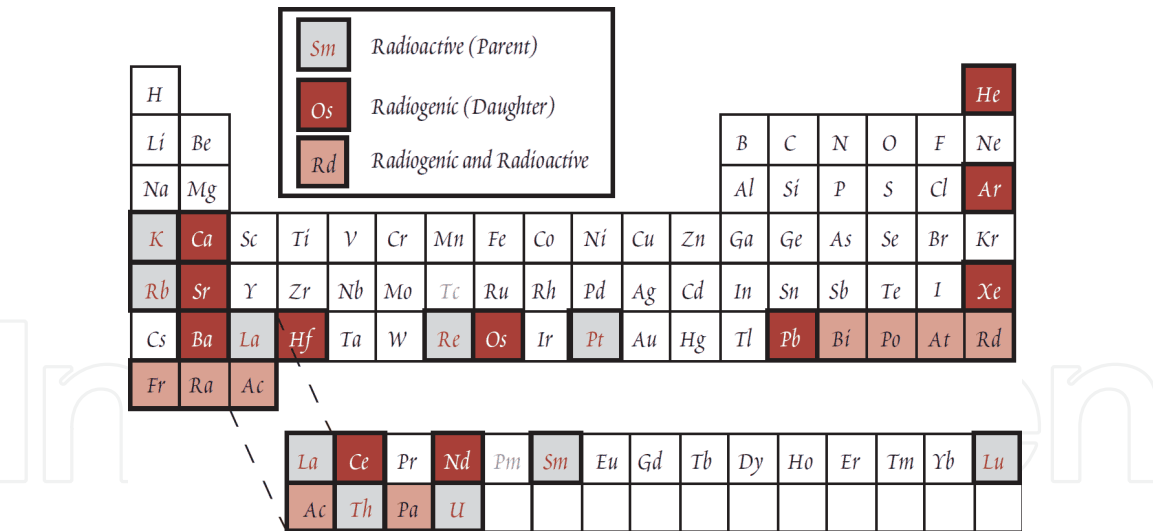


Figure 1.
Periodic table showing the elements of natural radioactive isotopes and their daughters.

understand that the radioactivity decay is that process by which an unstable atomic nucleus loses energy by emitting radiation in the form of particles or electromagnetic waves. Radioactive elements and their radiogenic daughters as well as the radiogenic and radioactive are illustrated in **Figure 1**.

3. Unit of radioactive decay and activity measurements

The becquerel (symbol Bq) is typically used as a SI unit of radioactive decay and it is defined as one decay/second. The Bq is just a tiny measure of activity; a small part of tera-becquerel (TBq) or giga-becquerel (GBq) that is commonly used. The curie (Ci) is an another unit of radioactivity that was basically defined as the activity of 1 g of pure radium ²²⁶Ra. Currently, The Bq is ordinary equal to number of disintegrations per second; where Ci is equal to 3.7 × 10¹⁰ disintegrations per second. Low activities are also measured in disintegrations per minute (dpm) [2]. The name of the unit “becquerel” is originated and belonging to the Henri Becquerel, a French scientist, who discovered radiation while he working on phosphorescent materials in 1896. Later, many contributions by Becquerel, Marie Curie, Pierre Curie, Ernest Rutherford and others discovered that radioactivity was significantly more complicated [2].

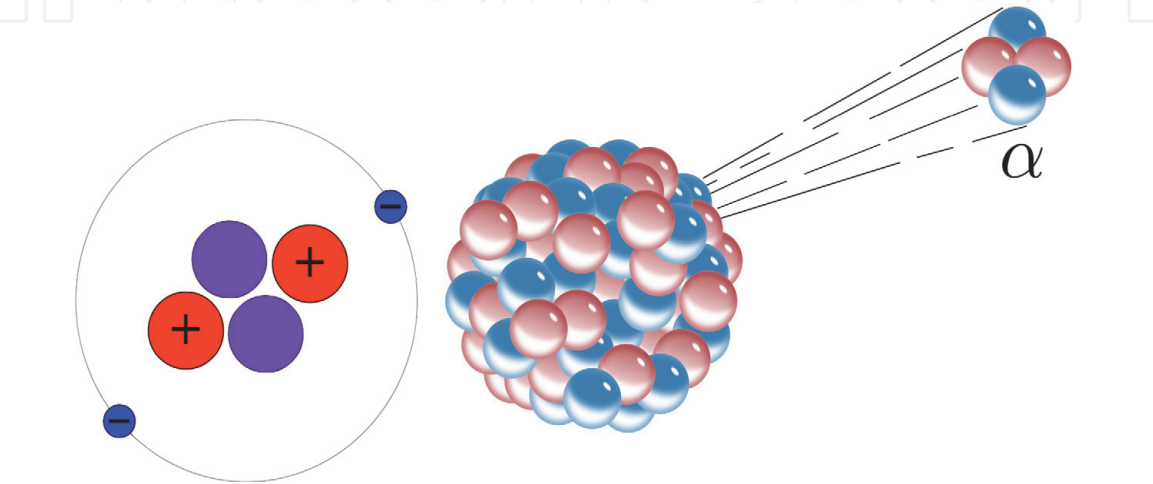


Figure 2.
Alpha particle represents the helium atom nuclei.

4. Alpha particles

They are particles (α) emitted during the radioactive decay from the nucleus consisting of two protons and two neutrons tightly bound together (**Figure 2**). Such this decay is known as alpha-decay. All chemical elements above Pb, in the Periodic Table have at least one isotope which decays by emitting alpha particles. This process is relatively rare due it requires high energy to release two neutrons and two protons out of a nucleus. The alpha particle is expressed as an identical to a helium nucleus.

5. Beta particles

They are also known as beta ray or beta radiation, symbolized by β . Beta has high-energy, high-speed electron or positron emitted during decay process of a nuclei and give β^- and β^+ , which yield electrons and positrons respectively (**Figure 3**).

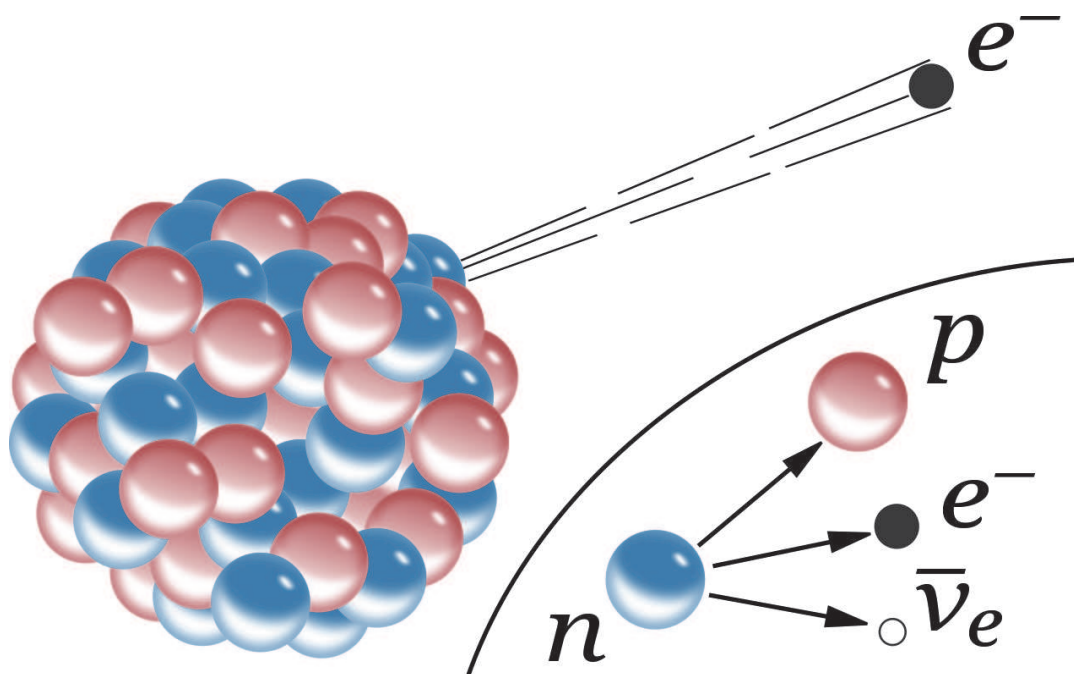


Figure 3.
Beta radiation.

6. Gamma ray

Gamma ray is also named gamma radiation symbolized with γ which is an electromagnetic radiation (**Figure 4**) emitting from the radioactive decay of atomic nuclei [3]. This type of radiation is very common.

7. Modes of decay

Different decay reactions of the radionuclides, the mass number A and atomic number Z of nucleus defined as A, Z are presented in **Table 1**. The column

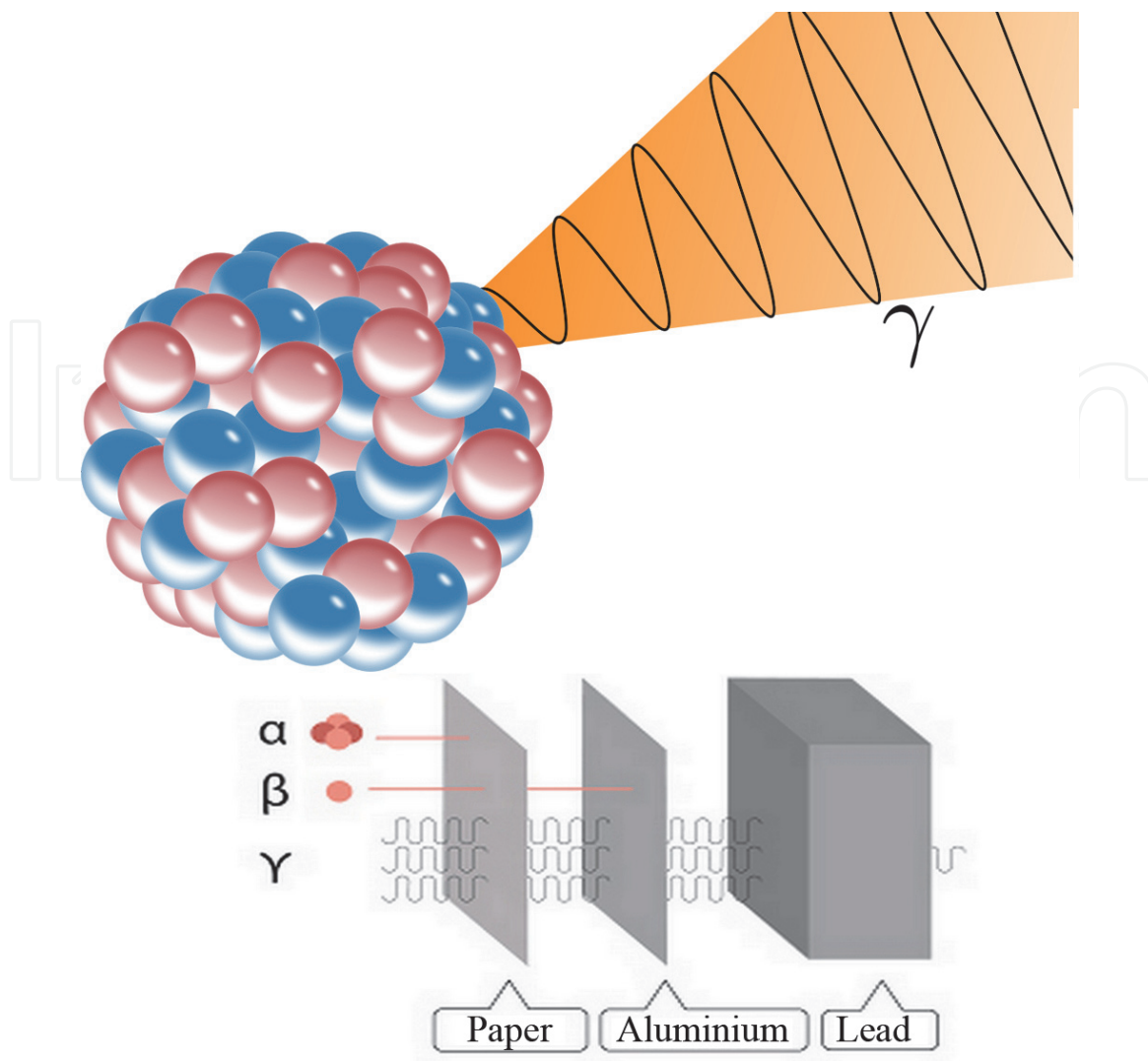


Figure 4.
Gamma radiation.

(daughter nucleus) represents the difference between the produced nucleus and the parent. Thus, $(A-2, Z)$ means that the mass number is two less than before, but the atomic number is the same as before.

8. Decay chain and uranium isotopes

The daughter nuclide is a result of the radioactive decay of a certain radioactive element. Daughter is stable or may also be radioactive, so the chain still continues to decay. The resulting second and/or third daughter nuclide may be radioactive leading to sequential radiation, so the process known as decay chain. Uranium is very heavy element has 92 atomic number (**Figure 5**).

Three isotopes are most common of uranium; these are with their relative abundance and half-life ($t_{1/2}$):

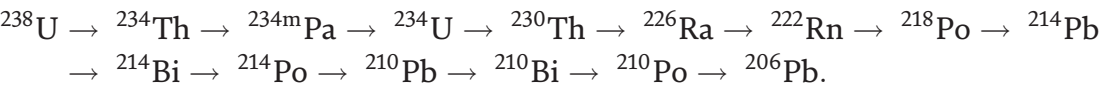
- ^{238}U has relative abundance 99.2739–99.2752% and half-life 4.4683×10^9 years.
- ^{235}U has relative abundance 0.7198–0.7202% and half-life 703.8 million years.
- ^{234}U has relative abundance 0.0050–0.0059% and half-life 245,500 years.

| Mode of decay | Participating particles | Daughter nucleus |
|--|---|-------------------------------|
| Decays with emission of nucleons | | |
| Alpha decay | An alpha particle ($A = 4, Z = 2$) emitted from nucleus | $(A-4, Z-2)$ |
| Proton emission | A proton ejected from nucleus | $(A-1, Z-1)$ |
| Neutron emission | A neutron ejected from nucleus | $(A-1, Z)$ |
| Double proton emission | Two protons ejected from nucleus simultaneously | $(A-2, Z-2)$ |
| Spontaneous fission | Nucleus disintegrates into two or more smaller nuclei and other particles | — |
| Cluster decay | Nucleus emits a specific type of smaller nucleus (A_1, Z_1) smaller than, or larger than, an alpha particle | $(A-A_1, Z-Z_1) + (A_1, Z_1)$ |
| Different modes of beta decay | | |
| Beta-negative decay | A nucleus emits an electron and an antineutrino | $(A, Z+1)$ |
| Positron emission, also beta-positive decay | A nucleus emits a positron and a neutrino | $(A, Z-1)$ |
| Electron capture | A nucleus captures an orbiting electron and emits a neutrino - The daughter nucleus is left in an excited and unstable state | $(A, Z-1)$ |
| Double beta decay | A nucleus emits two electrons and two antineutrinos | $(A, Z+2)$ |
| Double electron capture | A nucleus absorbs two orbital electrons and emits two neutrinos - The daughter nucleus is left in an excited and unstable state | $(A, Z-2)$ |
| Electron capture with positron emission | A nucleus absorbs one orbital electron, emits one positron and two neutrinos | $(A, Z-2)$ |
| Double positron emission | A nucleus emits two positrons and two neutrinos | $(A, Z-2)$ |
| Transitions between states of the same nucleus | | |
| Gamma decay | Excited nucleus releases a high-energy photon (gamma ray) | (A, Z) |
| Internal conversion | Excited nucleus transfers energy to an orbital electron and it is ejected from the atom | (A, Z) |

Table 1.
 Detailed radioactive decay reaction after [1].

Half-life (t) means the time required for a given amount of radionuclide to lose 50% of its activity, and can be expressed as the exponential relationship (**Figure 6**) represents the interval of time required for one-half of the atomic nuclei of a radioactive sample to decay and spontaneously changes into other element by emitting particles and energy.

The best example for the radioactive decay can be illustrating by the uranium decay chain (**Figure 7**) [4]. The natural decay chain of ^{238}U which eventually decays to ^{210}Po emitting alpha with a half-life of 140 days to produce finally a stable isotope which is ^{206}Pb .



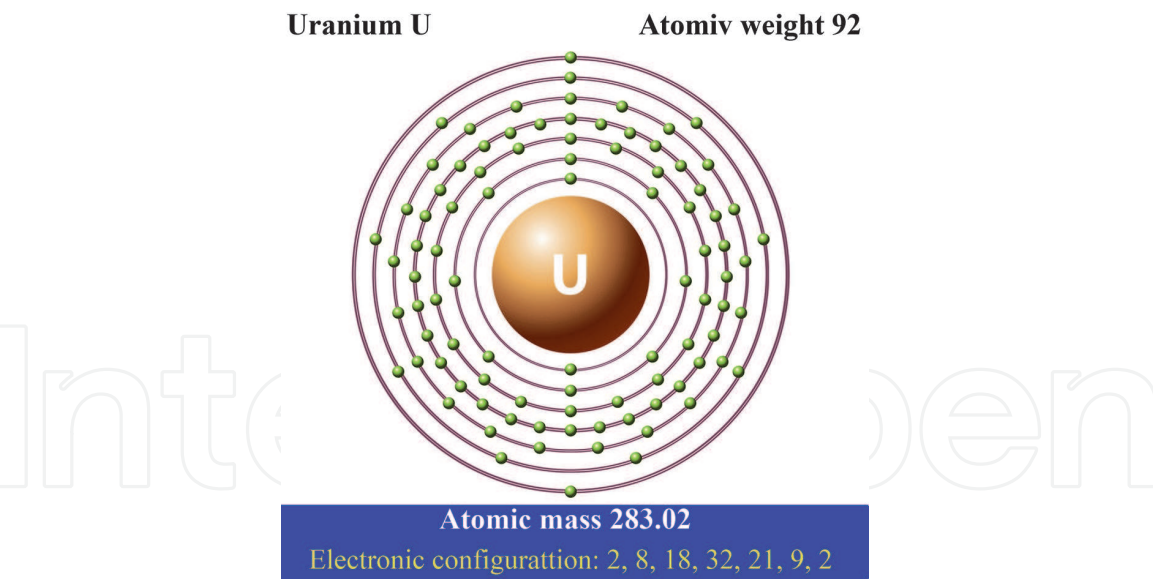


Figure 5.
Configuration of the uranium atom showing the atomic number and mass number.

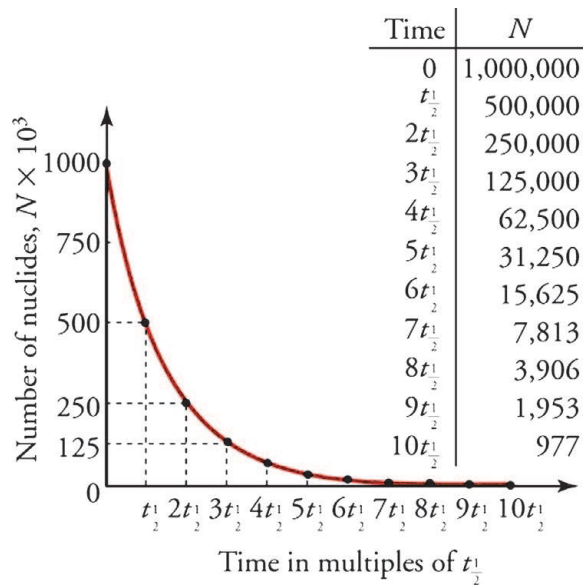


Figure 6.
The exponential relationship of half-life with radioactive decay.

9. Isotope systems in geological dating

Many isotope systems are mostly given as examples for dating geologic materials (Table 2).

It can be done to use this information to date rocks, for example; usually, the amount (N) of an isotope present today, and the amount of a daughter element produced by decay (D*), see Eqs. (1) and (2).

$D^* = N_0 - N$ (1)

$N = N_0 e^{-\lambda t}$ (2)

λ , the decay constant

$D^* = N e^{\lambda t} - N = N(e^{\lambda t} - 1)$ (3)

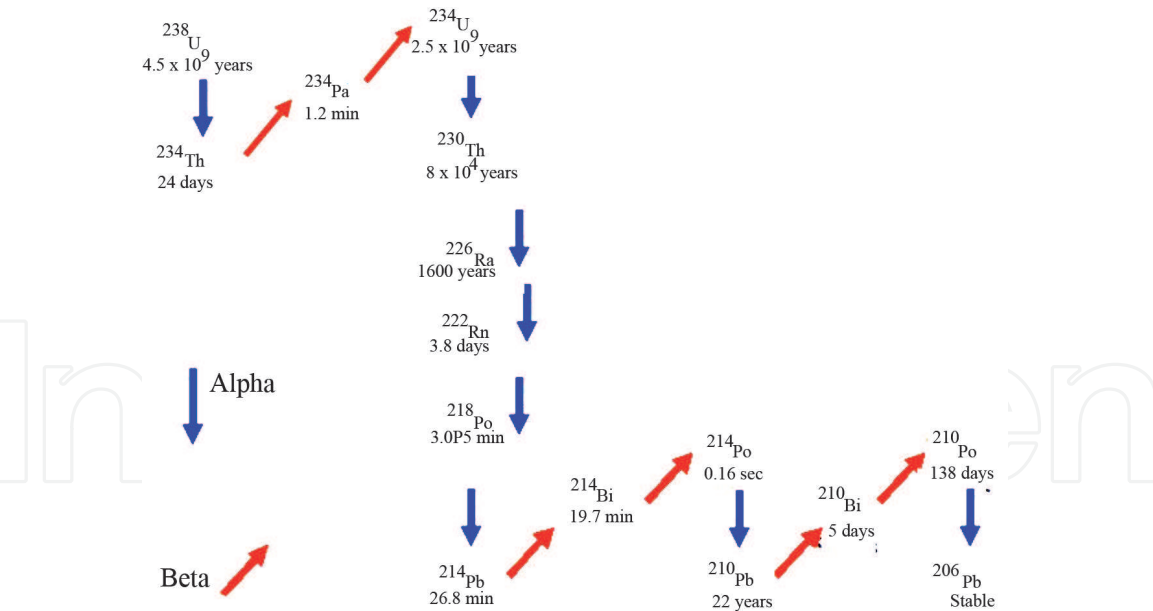


Figure 7.
Natural radioactive decay series of ^{238}U .

| Parent | Daughter | Half-life | Range available | Lithology type |
|-------------------|-------------------------------------|-----------|-----------------|--|
| ^{238}U | ^{206}Pb | 4.47 b.y | >10 m.y | Igneous & sometimes metamorphic rocks and minerals |
| ^{235}U | ^{207}Pb | 707 m.y | | |
| ^{232}Th | ^{208}Pb | 14 b.y | | |
| ^{40}K | ^{40}Ar & ^{40}Ca | 1.28 b.y | | |
| ^{87}Rb | ^{87}Sr | 48 b.y | >10 m.y | Organic Material |
| ^{147}Sm | ^{143}Nd | 106 b.y | | |
| ^{14}C | ^{14}N | 5730 y | 100 – 70,000 y | |

b.y = billion years; m.y = million years; y = year

Table 2.
Some radioactive elements with their daughters and dating application.

Consequently, it is possible to calculate the age if you have the number of daughter atoms produced by decay (D^*), while the number of parent atoms (N) is known now with should pay attention for the number of daughter atoms that may have been present prior to the start of our clock.

9.1 The Rb/Sr system

We can simplify our isochron equation somewhat by noting that if x is small [7],

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots = 1 + x \tag{4}$$

so that $(e^{\lambda t} - 1) = \lambda t$, when λt is small.

$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$ by β decay. The neutron emits an electron to become a proton.

For this decay reaction, $\lambda = 1.42 \times 10^{-11}/\text{y}$, $t_{1/2} = 4.8 \times 10^{10}$ y, at present, 27.85% of natural Rb is ^{87}Rb .

If we use this system to plug into Eq. (3), then

$$^{87}\text{Sr}^* = ^{87}\text{Rb} (e^{\lambda t} - 1) \quad (5)$$

but,

$$^{87}\text{Sr}_t = ^{87}\text{Sr}_0 + ^{87}\text{Sr}^* \quad (6)$$

or

$$^{87}\text{Sr}^* = ^{87}\text{Sr}_t - ^{87}\text{Sr}_0 \quad (7)$$

Plugging this into Eq. (5)

$$^{87}\text{Sr}_t = ^{87}\text{Sr}_0 + ^{87}\text{Rb} (e^{\lambda t} - 1) \quad (8)$$

We still do not know $^{87}\text{Sr}_0$, the amount of ^{87}Sr daughter element initially present. To account for this, we first note that there is an isotope of Sr, ^{86}Sr , that is:

1. non-radiogenic (not produced by another radioactive decay process),
2. non-radioactive (does not decay to anything else).

Thus, ^{86}Sr is a stable isotope, and the amount of ^{86}Sr does not change through time. If we divide Eq. (8) through by the amount of ^{86}Sr , then we get

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t (e^{\lambda t} - 1) \quad (9)$$

This is known as the isochron equation. In case of Sr was isotopically homogeneous, the time (t equal 0). For instance, $^{87}\text{Sr}/^{86}\text{Sr}$ was the same in the igneous mineral at the time of crystallization. Typically, rock – forming minerals more may be have a different amount of ^{87}Rb [5], and accordingly, those minerals are ordinary have a different $^{87}\text{Rb}/^{86}\text{Sr}$ at the crystallization time. During the natural cooling, the ^{87}Rb in each mineral will decay to ^{87}Sr , and each mineral will have a different ^{87}Rb and ^{87}Sr over time [6].

And simplify to:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t \lambda t \quad (10)$$

Then time (t) can be computed as:

$$t = \frac{\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0}{\left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t \lambda} \quad (11)$$

The initial ratio $(^{87}\text{Sr}/^{86}\text{Sr})_0$, is useful to use as a geochemical tracer because Rb distributed unequally through the Earth over time [7]. The amount of Rb in the earth mantle is typically low (<0.1 ppm). The mantle thus has a low $^{87}\text{Rb}/^{86}\text{Sr}$ ratio and would not change its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio very much with time, whilst the earth crust has higher amounts of Rb (>20 ppm) and therefore start out with a relatively high $^{87}\text{Rb}/^{86}\text{Sr}$ ratio. Over time, this results in crustal rocks having a much higher $^{87}\text{Sr}/^{86}\text{Sr}$

ratio than mantle rocks. Thus, it will be expected if the mantle has a $^{87}\text{Sr}/^{86}\text{Sr}$ of say 0.7025, melting of the mantle would produce a magma with a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7025, and all rocks derived from that mantle would have an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7025.

On the other hand, if the crust with $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710 melts, then the resulting magma would have $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.710 and rocks derived from that magma would have an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710. So, the rock derived from the mantle or crust can determine its initial Sr isotopic ratio accordingly.

9.2 The U, Th, Pb system

Many Pb isotopes are produced from U and Th isotopes. ^{238}U and ^{235}U and ^{232}Th can produce Pb isotopes during their radioactive decay that can be described as follows:



$$\lambda_{238} = 1.551 \times 10^{-10}/\text{y}, t_{1/2} = 4.47 \times 10^9 \text{ y} \quad (13)$$



$$\lambda_{235} = 9.849 \times 10^{-10}/\text{y}, t_{1/2} = 0.707 \times 10^9 \text{ y} \quad (15)$$

$$\text{the present ratio of } \frac{^{235}\text{U}}{^{238}\text{U}} = \frac{1}{137.8} \quad (16)$$



$$\lambda_{232} = 4.948 \times 10^{-11}/\text{y}, t_{1/2} = 1.4 \times 10^{10} \text{ y} \quad (18)$$

^{232}Th does not used in dating.

^{204}Pb is a stable non-radiogenic isotope of Pb, the two isochron equations and get two independent dates from the U-Pb system can be written as:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_t = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_0 + \left(\frac{^{238}\text{U}}{^{204}\text{Pb}} \right)_0 (e^{\lambda_{238}t} - 1) \quad (19)$$

and

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_t = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_0 + \left(\frac{^{235}\text{U}}{^{204}\text{Pb}} \right)_0 (e^{\lambda_{235}t} - 1) \quad (20)$$

If these two independent dates are concordant, a concordia diagram will show the values of Pb isotopes that would give concordant dates and can plug in t and solve for the be calculated Eqs. (21) and (22) as follows:

$$\left(\frac{^{206}\text{Pb}^*}{^{238}\text{U}} \right) = \frac{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_t - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_0}{\left(\frac{^{238}\text{U}}{^{204}\text{Pb}} \right)_t} = (e^{\lambda_{238}t} - 1) \quad (21)$$

and

$$\left(\frac{^{207}\text{Pb}^*}{^{235}\text{U}} \right) = \frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_t - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_0}{\left(\frac{^{235}\text{U}}{^{204}\text{Pb}} \right)_t} = (e^{\lambda_{235}t} - 1) \quad (22)$$

The Concordia is particularly useful in dating of zircon, that usually contains a lot U and less amounts of Pb, so we expect it has large amounts of radiogenic Pb that can be produced. Apatite and sphene are the two minerals that are commonly can be used in radiometric dating as well. Zircon from the crystallization time to the present represents a closed system in case no loss or gain of uranium or lead. The age of the zircon can be determined from its position on the Concordia after plotting the $^{206}\text{Pb}^*/^{238}\text{U}$ and $^{207}\text{Pb}^*/^{235}\text{U}$ ratios on the Concordia diagram. The discordant dates fall out of the Concordia curve.

The both ends of the Discordia intersect are represented by t_0 , the older and t^* , the younger. Many reasons lead to Pb leakage. Metamorphism for example, could heat the crystal to the point where Pb will become mobile. Another possible reason cause U leakage, where the discordia is represented by the two points that would give two ages $-t^*$ representing the possible metamorphic event and t_0 representing the initial crystallization age of the zircon.

The Pb-Pb isochrons can be normally concluded from combining the two isochron Eqs. (19) and (20).

$$\frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_t - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0} = \left(\frac{^{235}\text{U}}{^{238}\text{U}}\right) \left[\frac{(e^{\lambda_{235}t} - 1)}{(e^{\lambda_{238}t} - 1)}\right] \quad (23)$$

$$\frac{^{235}\text{U}}{^{238}\text{U}} = \frac{1}{137.8} \quad (24)$$

Then, and by assuming that the ^{206}Pb and ^{207}Pb dates are the same, then Eq. (23) is the equation have a slope.

$$m = \frac{1}{137.88} \left[\frac{(e^{\lambda_{238}t} - 1)}{(e^{\lambda_{235}t} - 1)}\right] \quad (25)$$

that passes through the point.

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0, \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 \quad (26)$$

10. The age of the earth and dating

The oldest rock found in Canada, with an age of $3.962 \text{ b.y} \pm 3 \text{ m.y.}$ This provide only a minimum age of the Earth. The age of the earth can be computed based on the chemical concept that is the $^{235}\text{U}/^{238}\text{U}$ ratio may have been 1.0 when the elements formed. So, from:

$$N = N_0 e^{-\lambda t} \quad (27)$$

the

$$\frac{^{235}\text{U}}{^{238}\text{U}} = \frac{^{235}\text{U}_0 e^{-\lambda_{235}t}}{^{238}\text{U}_0 e^{-\lambda_{238}t}} \quad (28)$$

Finally, t is about 6 b.y.

This age represents the maximum age of the Earth. From the Pb-Pb isochron Eq. (23) and based on meteorites that may have been formed at the same time the solar system in which basically the Earth formed as well. The thing to be needed to date meteorites is knowing the initial ratios of the Pb isotopes. Two major types of meteorites are recognized; Fe- meteorites and stony (or chondritic) meteorites. The Fe-meteorites contain troilite (FeS) that has no U. Since the mineral troilite contains no U, all of the Pb present in the troilite is the Pb originally present, and none of it has been produced by U decay. Thus, the troilite in the Fe-meteorites will provide with the initial ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$.

The Pb ratios can be determined in other meteorites and check if they fall on the isochron of Pb-Pb that passes through the initial ratios determined from troilite in Fe-meteorites. The slope of this isochron (Geochron) estimated the earth age is of $4.55 \pm 0.07 \times 10^9$ yr. Consequently, the best estimation of the age of the Earth is 4.55 billion years.

10.1 Sm-Nd dating

^{147}Sm decays to ^{143}Nd by alpha decay with half-life of 106 ± 2 b.y. [8], ^{147}Sm , ^{148}Sm , ^{149}Sm , and ^{144}Nd are radioactive, three nuclides accordingly generated ^{144}Nd , ^{145}Nd , and ^{140}Ce [9].



$$\lambda = 6.54 \times 10^{-12}/\text{yr}, t_{1/2} = 1.06 \times 10^{11} \text{ y} \quad (30)$$

The isochron equation is described based on whether the ^{144}Nd is stable and non-radiogenic as:

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_t (e^{\lambda t} - 1) \quad (31)$$

The age of the rock can be estimated later from the isochron equation that basically can be drawn by the determination of the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for several minerals.

10.2 K-Ar dating

In the nature, ^{40}K makes up 0.119% of natural K, as it is a radioactive element, its decay can be presented as follows [10]:



The equation above is not used, because ^{40}Ca can be present as both radiogenic and non-radiogenic Ca [10].



For the combined process,

$$\lambda = 5.305 \times 10^{-10}/\text{y}, t_{1/2} = 1.31 \times 10^9 \text{ y} \quad (34)$$

and for the Ar branch of the decay scheme

$$\lambda_e = 0.585 \times 10^{-10}/\text{y} \quad (35)$$

Argon is a gas easily can escape from a magma or liquid, therefore, the percentage of initial ^{40}Ar is expressed as zero; during the rapid cooling of magma, quantity of the Ar may be trapped. The date consequently obtained will be older than the date at which the magma erupted.

The dating equation used for K-Ar is:

$$^{40}\text{Ar} = \frac{\lambda_e}{\lambda} {}^{40}\text{K}(e^{\lambda t} - 1) \tag{36}$$

where $\frac{\lambda_e}{\lambda} = 0.11$ and refers to fraction of ^{40}K that decays to ^{40}Ar .

Many points need to have attention when use K-Ar dating, the use of minerals like sanidine or biotite is better to use whole rocks because minerals not contain excess Ar. Other thing, some atmospheric argon originated from volcanic eruptions could be absorbed onto the sample surface, ^{40}Ar should be corrected for accordingly. Additionally, most minerals lose Ar during metamorphism due to high temperature, so the date will represent the metamorphic event (**Table 3**).

10.3 ^{14}C dating

Radiocarbon dating is different than the other methods of dating because it cannot be used to directly date rocks, but can only be used to date organic material produced by once living organisms [12]. Radiocarbon (^{14}C) has a short half-life (5730 y), it is therefore only used to date materials younger than about 70,000 years. The ratio of ^{14}C to ^{14}N in the Earth’s atmosphere is constant and the organism have the same ratio of ^{14}C to ^{14}N as the atmosphere. When an organism dies, the ^{14}C decays back to ^{14}N , with a half-life of 5730 years. Measuring the amount of ^{14}C in this dead material thus enables the determination of the time elapsed since the organism died. Bones, teeth, charcoal, fossilized wood, and shells are materials can be used for dating.

10.4 Re-Os dating

Rhenium has stable ^{185}Re and the radioactive ^{187}Re . The latter is the most abundant (62.6%) and decays to ^{187}Os based on beta decay, typically with a half-life of 41.6×10^9 y [13]. Osmium has seven isotopes; only two are the product of natural decay of radioactive isotopes: ^{186}Os is produced from ^{190}Pt by α -decay (half-life 4.7×10^{11} y, [14]) and ^{187}Os by β -decay of ^{187}Re . The two radiogenic isotopes ^{187}Os (~2%) and ^{186}Os (~1.6%) are typically normalized to the stable ^{188}Os (13.24%). Rhenium-osmium (Re-Os), an applicable method was first applied to meteorites [15]; it provides a chronometer for directly dating both of sulfides and oxides ore minerals.

| Decay | Decay factor | value |
|---|--|---|
| $^{40}\text{K} \rightarrow ^{40}\text{Ca}$ by β^- | $\lambda\beta^-$ | $4.962 \times 10^{-10} \text{ a}^{-1}$ |
| $^{40}\text{K} \rightarrow ^{40}\text{Ar}$ by electron capture and γ | λ_e | $0.572 \times 10^{-10} \text{ a}^{-1}$ |
| $^{40}\text{K} \rightarrow ^{40}\text{Ar}$ by electron capture | $\lambda' e$ | $0.0088 \times 10^{-10} \text{ a}^{-1}$ |
| combined value | $\lambda = \lambda\beta^- + \lambda_{ec} + \lambda' e$ | $5.543 \times 10^{-10} \text{ a}^{-1}$ |
| | present day $^{40}\text{K}/\text{K}$ | 0.0001167 |

Table 3.
Decay constants for K-Ar and Ar-Ar dating [11].

11. Discussion and conclusions

This chapter deals with the various types of radiation emitted by radioactive nuclides with principles of radionuclide decay and its radiations. Here an overview of some of the many dating radioactive techniques that play a significant role in our day-to-day lives. The dating techniques developed for defining reliable ages of geologic events other geochronological studies are recording of the isotope concentrations. All radiometric clocks depend on a radioactive “parent” isotope that decays to a daughter stable isotope of another element at a constant rate on geologic timescales. This process may take single step, or it may involve many stages of decay products before reaching the final stable daughter isotope. The half-life of the initial quantity of parent isotope to decay must be on the same order of magnitude as the time span to be measured. The Concordia–Discordia model has been developed for the U and Pb isotopes. The ^{235}U transforms to ^{207}Pb through a chain of radioactive nuclides, releasing $(235-207)/4 = 7\alpha$ -particles with the constant $\lambda_5 = 9.8 \cdot 10^{-10}$. The ^{238}U turns to ^{206}Pb releasing $(238-206)/4 = 8\alpha$ -particles with the constant $\lambda_8 = 1.55 \cdot 10^{-10}$ [16]. Currently, the ratio of $^{238}\text{U}/^{235}\text{U}$ (137.88) is growing. Both isotopes of uranium are closely connected to each other in kinetic processes due to the value $\sqrt{238/235} = 1.0063$, which is close to 1. The Discordant values can be obtained from the development of the Concordia–Discordia model as an open system with losses of radiogenic lead in accessory minerals such as zircon, monazite, apatite etc. [17]. A very wide time range, not only the 12 b.y. of the Universe age and the 4.5 b.y. of the Earth’s age can be explore, but also the details related paleontology through the history of the Earth and recent events of the last millennia [12]. The K-Ar dating technique developed soon after the discovery of ^{40}K and provided an important dating tool beside U-Pb and U-He dating methods. The half-life (1250 m.y) made this method is most popular for dating geological events [18]. The K-Ar dating are based on the decay of a ^{40}K to an isotope of ^{40}Ar by a branching process; 10.48% of ^{40}K decays to ^{40}Ar by $\beta +$ decay, and 89.52% decays to ^{40}Ca by β^- to the ground state [10]. The age measured by K-Ar techniques reflects the time since radiogenic argon produced by decay of ^{40}K , became trapped in the mineral or rock. The radiogenic noble gas daughter nuclides provide many methods for determining not only the chronology of events but also thermal histories combined with U-Pb and Rb-Sr dating techniques. This technique uses to conclude the cooling history based on use mineral closure or field estimates [19]. It can be applied for dating young volcanic eruptions and for low-temperature phases such as clay minerals like illite. In addition, they can be used for exploring. Despite the Rhenium–osmium (Re-Os), an applicable method was first applied to meteorites [15]; it also provides a chronometer for directly dating both of sulfides and oxides ore minerals. Recently, this technique is developed and become capable to estimate dating via dealing with very low content of Re and Os. The relative abundance of Osmium is the earth’s core and extraterrestrial material with a very leaser amount (ppt) in the mantle and it can be stored in sulfide and oxide minerals in the crust. It is best method for dating the age of gold in auriferous pyrites, it also used for dating marine shale containing coal.

It is difficult to obtain good precision and accuracy for radiocarbon due to its abundancy in the environment and it is possible to contaminate from material of a different age. Consequently, the methods for radiocarbon measuring are well tested, reproduced and carefully controlled under specific lab conditions. Recently, the radiocarbon methods have been developed, over the last 30 years to cover most of the materials suitable for radiocarbon measurement. The AMS system at Oxford was built with very high precision and accuracy for radiocarbon dating by High Voltage Engineering Europa BV. For high precious in situ age dating of Pb-U, Hf

and U-Th isotope ratios in very small minerals like zircons, it is recommended to use the Thermo Scientific Neptune XT MC-ICP-MS or Thermo Scientific Element 2 and Thermo Scientific Element XR High-Resolution ICP-MS, combined with a laser ablation system. The Thermo Scientific Triton XT Multicollector Thermal Ionization Mass Spectrometer (TIMS), provides the ultimate precision for U-Pb geochronology, while The Triton XT TIMS is an equipment with high-quality age dating for Rb-Sr, Sm-Nd and Re-Os.

To be useful, result must be accurate, so uncertainty must always be taken into account. The geochronological result is influenced by uncertainty. So, if it does not be known well, result is scientifically meaningless. The uncertainty is coming from error in sampling, laboratory procedure; adaption of methods to the problem in question [12]. Overall, the source of uncertainty obtained from:

- a. collecting samples
- b. Parent decay methods
- c. Long half-life parent daughter methods
- d. Age calculations

11.1 Analytical methods

The radiogenic isotopes are typically separated from the no-radiogenic isotopes using spectrometer whenever they used as dating tools or tracers. Sample is ionized normally in thermal-ionization mass spectrometer (TIMS). Recently, the induced coupled plasma (ICP) is technique used for the chemical purification before mass spectrometry method. The laser ablation is also used for analyzing mineral with high concentration of radiogenic elements. However, in samples of whole-rocks, in which the concentration of radiogenic isotope is mostly low, it is necessary to pre-concentrate after dissolution and chemical extraction. The silicate geological samples are routinely dissolved in hot method using either concentrated HF acid or HClO_4 acid at atmospheric pressure; so, the most rock-forming minerals are dissolved, but the resistant minerals like zircon must be dissolved under pressure in a bomb at 220°C . The bomb liner and beaker are made of poly-fluorinated ethylene [20]. The formation of fluoride is the most common problem that may encounter after dissolution in HF as an insoluble in HCl acid. Consequently, the refluxing with HNO_3 is needed [21]. The additional adding of HNO_3 before completely evaporation of HF leads to promote process [22]. If at some stage, complete digestion is not achieved, decant off the solution is recommended and return to undissolved fraction at the previous stage for a second acid attack [23]. Thereafter, the solution rich in isotope is split for isotope-dilution analysis and for accurate-isotope ratio analysis.

11.2 Dating of igneous rocks

11.2.1 Sr-model ages

The Rb-Sr is used widely as a method provides a great information of igneous rock dating. The naturel process begins from the decay of ^{87}Rb occurred in minerals to ^{87}Sr , so the number of ^{87}Sr daughters produced informs us about t years ago:

$$^{87}\text{Sr} = ^{87}\text{Sr}_1 + ^{87}\text{Rb}(e^{\lambda t} - 1) \quad (37)$$

Where the $^{87}\text{Sr}_1$ is the number of the initial ^{87}Sr atoms. The given nuclides are of so difficult to measure their absolute abundance, so, it is suitable to find isotope ratio by dividing by ^{86}Sr which is not radiogenic and accordingly still constant with time as follows:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_p = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_I + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1) \quad (38)$$

Currently, strontium isotope ratio (p) can be measured by mass spectrometry, and the $^{87}\text{Rb}/^{86}\text{Sr}$ is calculated from Rb/Sr weigh ratio. From the initial ratio $(^{87}\text{Rb}/^{86}\text{Sr})_I$ estimated, time (t) can be computed as:

$$t = \frac{1}{\lambda} \ln \left\{ 1 + \frac{^{86}\text{Sr}}{^{87}\text{Rb}} \left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_p - \left(\frac{^{86}\text{Sr}}{^{87}\text{Sr}}\right)_I \right] \right\} \quad (39)$$

Over geological time, Rb-rich minerals “like lepidolite” develop ratio (0.712) of $^{87}\text{Rb}/^{86}\text{Sr}$ and may use in chronological studies without error. The Rb-Sr method was extended to include other mineral such as mica (biotite and muscovite) as well as potash feldspar that have lower Rb/Sr ratios. The discordant dates are suggested based on the initial ration (0.712) when the real initial ratio was higher. This expressed as a problem and was overcome by the isochron diagram designed by [24] who developed a new way for treating Rb-Sr data based on the principle of linear equation:

$$y = c + xm \quad (40)$$

In this way, $^{87}\text{Sr}/^{86}\text{Sr}$ (y) is plotted versus $^{87}\text{Rb}/^{86}\text{Sr}$ (x), then the intercept *c* is the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (**Figure 8**).

This figure presents a suite of co-magmatic minerals of same age and initial of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, forming a line called isochron. From slop of isochron, $m = e^{\lambda t} - 1$, the mineral age can be determined. The mineral with very low Pb may yield the

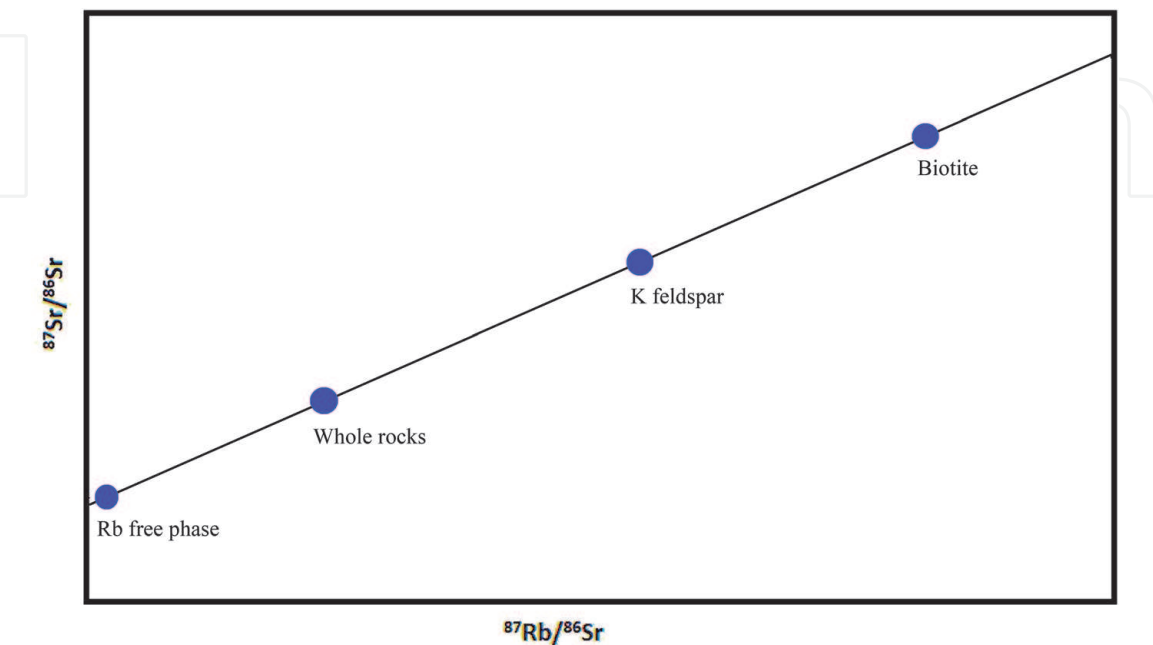


Figure 8.
Schematic Rb-Sr isochron diagram for a suit of co-magmatic igneous minerals [25].

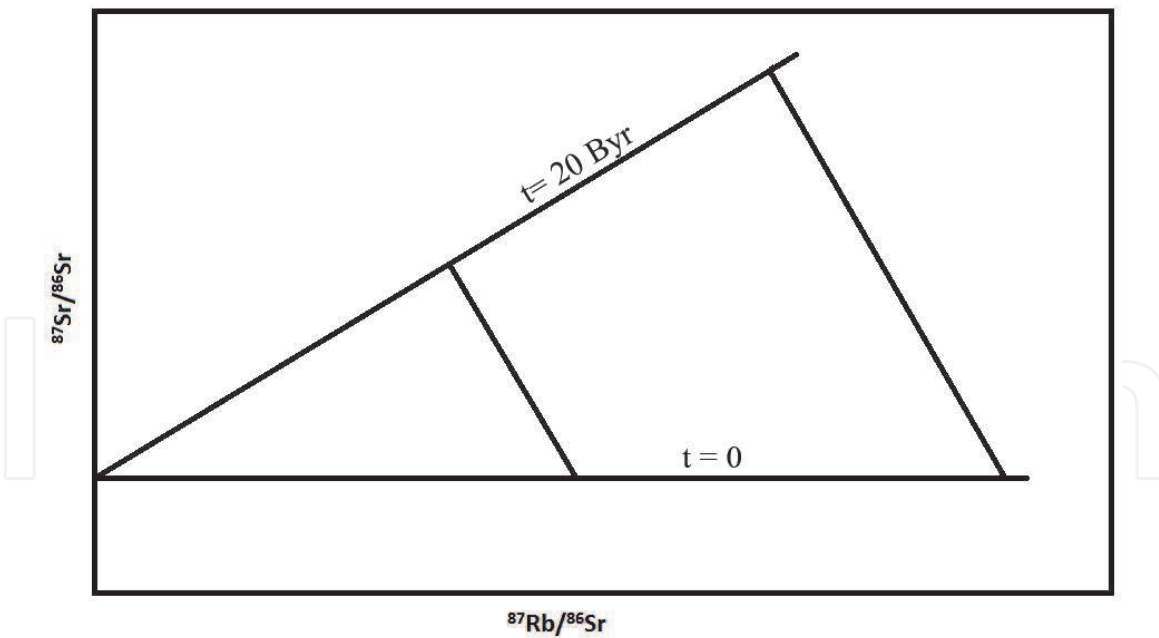


Figure 9.

Rb-Sr isochron diagram on axis of equal magnitude showing production of ^{87}Sr as ^{87}Rb is consumed in two hypothetical samples [25].

initial ratio directly on y-axis. On **Figure 9**, the $^{87}\text{Sr}/^{86}\text{Sr}$ increase with decrease $^{87}\text{Rb}/^{86}\text{Sr}$ due to decay Rb over time. The slope of isochron is increased accordingly with time. Practically, the y-axis is expanded much to displays rocks of geological time clearly, and the growth lines become vertical accordingly.

11.3 Erupted isochro

The original isotopic composition of mantle is basically inherited in the primary basic magma. The alkali ocean-island basalts were investigated for the Rb-Sr system [26]. The results of fourteen wide range type of ocean- island basalt samples plotted on an isochron displayed a proportional correlation to a slop age of about 2B.y representing the time of mantle isolation [25]. This age is known as a mantle isochrones that is also extended to continental igneous rocks [27]. The ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ should correct back to initial ratio at the time of magmatism before plotting versus $^{87}\text{Rb}/^{86}\text{Sr}$, so these are termed as pesud-oisochrons. Data of plotting 30 samples from both volcanic and plutonic continental igneous rock suits formed a roughly linear array. The pesud-oisochrons generates from two lines representing crustal contamination of mantle-derived basaltic magma, Scientist replaced that by timing the mantle differentiation events that established mantle domains of different ratio of Rb/Sr in subcontinental lithosphere. This suggestion does not provide reliable results to ascribe age significantly to erupted isochrones. However, the only isotope-isotope mantle isochrones is reliable and can be interpreted and used significantly as tool for dating the age of mantle differentiation events.

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