RADIOMETRIC DATING

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Since the discovery of natural radioactivity in uranium, in the last decade of the nineteenth century, the nuclear property of radioactive decay of radionuclides at immutable rates has been effectively utilized in dating of varieties of naturally occurring geological matrices and the organisms which constantly replenish their ^{14}C supply through respiration when alive on earth. During the period, applications of radiometric dating techniques have been extensively diversified and have enabled the geologists to indicate the absolute time scales of geological formations and the evolution of the solar system, the earth, meteorites, lunar rocks, etc. and the archaeologists to record the facts of history of several important events like dinosaur era, Iceman, the Shroud in Turin and many other ancient artefacts. In the development of dating methods, varieties of naturally occurring radio-isotopic systems with favorable half-lives ranging from about 10 years to over 100 billion years have been used as radiometric clocks.

Introduction

The phenomenon of nuclear decay has been associated with the natural world since its formation some billions of years ago. After the discovery of radioactivity in natural uranium by Henri Becquerel in 1896, the nuclear property of radioactive decay has been fruitfully utilized in determining the ages and the history of the solar system, earth, rocks and meteorites, natural waters, the living things on earth and several ancient artefacts[1-7]. Ernest Rutherford[1] in 1905 was the first to suggest that the nuclear property of radioactive decay of naturally occurring uranium could be used to study the age of a mineral or the time elapsed since its solidification. Shortly afterwards, Bertram Boltwood[8] in 1907, through his pioneering work on lead as the end decay product of uranium, suggested that some specific radio-isotopic system could be used as internal clocks in dating or determining the absolute geological ages of rocks and minerals generally to be expressed in the ranges of hundreds and thousands of millions years. With the development of the concept of systematic nuclear dating, the opinions of the scientists, the geologists and archeologists in particular, regarding many geological and biological events occurring on earth, have been changed to a great extent.

Several naturally occurring radionuclides such as uranium-238, uranium-235, thorium-232, rubidium-87, potassium-40 and many others with long half-lives are effectively utilized in radiometric dating of geological materials. Willard Libby and his co-workers [9], in mid-1940s, suggested that the carbon in living matter might contain radioactive ^{14}C in addition to non-radioactive carbon-12 and the decay of ^{14}C at a constant rate in the atmosphere might provide a method of dating for organic matters and thus the method of radioactive carbon dating was initiated. Libby for his work on carbon–14 was awarded the Nobel Prize in Chemistry in 1960.

The development of the technique of Nuclear dating, Radiometric dating or Radioactive dating, as it is sometimes called, in general, provides important clues about the ages of geological matrices in which radioactive nuclides were selectively incorporated at the time of their formation in nature as well as of some specific materials of biological

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origins. In geochronology, a method of dating primarily compares the abundance of a naturally occurring radioactive parent isotope with favorable half-life to the abundance of its specific daughter product to estimate the geological time scales[10] for varieties of samples of geological origins including the age of the earth itself. The technique of radiocarbon dating is especially applied, unlike geological dating, to determine the ages of natural organisms which constantly replenish their ^{14}C supply along with carbon-12 through respiration when alive and and also to a wide range of man-made or artificial objects of archaeological interest. Studies on ^{14}C dating, provide information about the approximate dates at which the organisms were living and also help in predicting the past environmental conditions of carbon-bearing materials on earth.

Applications of different radiometric techniques in dating of a wide range of natural materials of geological origins and organisms, and also of mam-made objects like ancient artifacts, as a whole, provide information regarding the formation or evolution of the concerned matrices, for example, the creation of the earth billions of years ago. The coherency of results of radiocarbon dating of different carbon containing materials, both natural and artificial, is sometimes verified with those derived from non-radiometric dating methods.

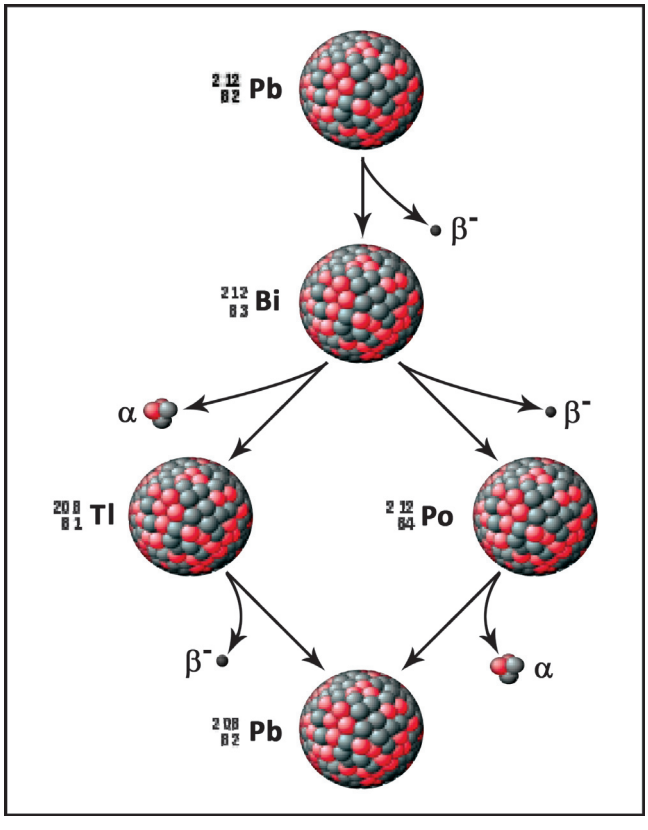

Figure 1. Radioactive Decay Chain of ^{212}Pb - ^{208}Pb

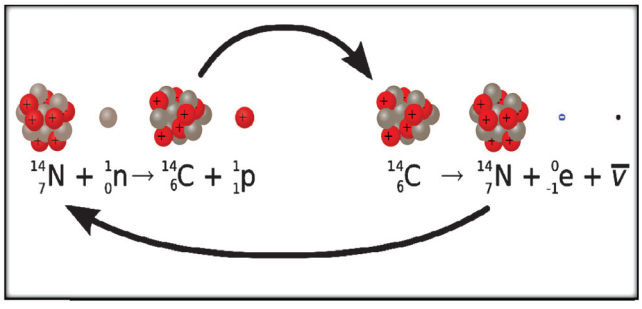

Figure 2. The Atmospheric Carbon – Nitrogen Cycle

Fundamentals of Nuclear Dating

In nature, all matters are made up of chemical elements, each of which may exist in its different isotopic or nuclidic forms. Most of these nuclides are stable but some of them are inherently unstable and radioactive. The radioactive nuclide spontaneously transforms into a different nuclide through a process called radioactive decay. The transformation of a radionuclide to another nuclide is accomplished in a number of ways, including alpha (α) – decay and beta (β-) – decay. For example, the radioactive decay chain, ^{212}Pb - ^{208}Pb, in which the parent nuclide, ^{212}Pb, spontaneously decays both via α – decay and β - decay to its final stable decay product, ^{208}Pb, can no longer undergo further radioactive decay[1], is presented in Figure 1.

The radioactive nuclide decays exponentially at a rate described by a parameter known as the half-life, usually expressed in unit of years in the dating process. In a radioactive decay process, the unstable radioactive isotope which decays at a fixed rate according to its half-life, is being effectively utilized in dating the age of a material. Generally, thenaturally occurring radio-isotopic systems with half-lives ranging from about 10 years (e.g.,^{3}H with half-life of 12.3 yr.) to over 100 billion years (e.g., ^{147}Sm with half-life of 106 billion yr.), are generally being utilized in radiometric dating processes [5].

The balance between the rates of production of a radionuclide and its decay becomes terminated when the sample is removed from the environment of its occurrence and hence its radioactivity will begin to decrease with time according to the simple radioactive decay law depending on its half-life. During the period, varieties of radiometric dating techniques [7] based on the basic principle of the **radioactive decay law**, as presented by the equation,

$$N_1 = N_0 \, e^{-\lambda (t_0 - t_1)},$$

where N_0 is the quantity of a radionuclide present at some time, t_0, in the past, and N_1 is the amount of the radionuclide remaining at some later time t_1 and λ is the

decay constant for the parent radionuclide, have been developed. If the amounts of the radionuclide, N_0 and N_1, respectively at times of t_0 and t_1, and the decay constant, λ, are known, the time interval $(t_0 - t_1)$ can be calculated. Generally, the dating scheme deals with the knowledge of the present abundances of the parent and daughter isotopes and thus if $t_1$is the present time that is $t_1 = 0$, then N_1 can be directly measured in a sample at hand. In the process of dating of a natural sample, the problem thus lies in knowing the amount of the radionuclide N_0 at the earlier time, t_0.

Again, different fractions of a mineral sample assumed to be formed by the same event are in equilibrium with the reservoir when they were formed and should form an isochron[7]. Thus, in calculating the age of a sample and its original composition, plotting of an isochron is sometimes used to solve the age equation graphically. In the study of an isochron, comparison of the current ratios of the parent and daughter isotopes to that of a standard isotopic system are merely used and it does not require information on the original compositions.

The half-lives of the radioactive isotopes excepting some nuclides like ^{7}Be,^{85}Sr and ^{89}Zr, which decay by the process of electron capture, are essentially constant. The nuclear property of half-life is very precise and is not affected by its physical or chemical form, temperature or presence of a magnetic or electric field. Thus, a radioactive sample continues to decay at a predictable rate and is used as a Radiometric Clock, sometimes referred to as an 'Atomic clock'[1,5,7]. In geological dating, the radioisotopes comparatively with longer half-lives are generally utilized as radiometric clock. Isotopes with relatively shorter half-lives are however not suitable to date very ancient events, but these are useful in dating shorter intervals, usually with greater accuracy. In a dating process, the radiometric clock starts when the specific radioactive isotope used for dating is removed from its source of replenishment.

Generally, two types of radiometric clocks, namely, the accumulation clock and the equilibrium decay clock, serve the purpose of radiometric dating. The accumulation clock in which there is no possibility of migration of the parent or its daughter (s) nuclides in or out of the sample material for the time period measured, is practically a closed system. The radionuclidic systems such as Uranium – Lead, Potassium – Argon, Rubidium – Strontium, etc., are some of the examples of radiometric accumulation clocks generally applied to geological materials.

Similarly, the radiocarbon dating and tritium dating are examples of equilibrium decay clocks. In these systems, the respective equilibrium specific activity levels of ^{14}C and ^{3}H for the carbon and hydrogen are established by continuous interactions of cosmic-rays with the atmosphere. However, this condition of equilibrium is terminated when a sample containing carbon in a living system or hydrogen usually in water is removed from the equilibrium contact with the atmosphere. For a living system, the input of ^{14}C terminates at its death, just like a living tree when dies, it no longer takes in ^{14}C - laden CO_2 from the atmosphere. Similarly, for ^{3}H, the input is stopped when water enters a deep aquifer or is bottled, as for wines, where further atmospheric exchange cannot occur. Some important naturally occurring radioactive parent - daughter pairs of isotopes with longer half-lives [11] are presented in Table I.

TABLE 1. Naturally Occurring Radioactive Isotopes Commonly Used in Radiometric Dating

Radioactive Isotope (Parent)	Decay Product (Daughter)	Half-Life (Years)
Samarium-147	Neodymium-143	106 billion
Rubidium-87	Strontium-87	48.8 billion
Rhenium-187	Osmium-187	42 billion
Lutetium-176	Hafnium-176	38 billion
Thorium-232	Lead-208	14 billion
Uranium-238	Lead+-206	4.5 billion
Potassium-40	Argon-40	1.26 billion
Uranium-235	Lead-207	0.7 billion
Beryllium-10	Boron-10	1.52 million
Chlorine-36	Argon-36	300,000
Carbon-14	Nitrogen-14	5715
Uranium-234	Thorium-230	2,48,000
Thorium-230	Radium-226	75,400

In a geological matrix, the chemical system becomes closed when the mineral solidifies from its melts. The transformation of a melt mineral into its crystalline form effectively prevents further diffusion of isotopes and becomes a closed system of rocks. The temperature at which this transformation occurs is termed as closure temperature and for a particular material and isotopic system it is specific. The absolute age as determined by radiometric dating is the time at which the rock or mineral sample cooled to its closure temperature [1,12].In most of the isotopic systems, the radioactive decay equation makes use of information on the composition of parent and daughter isotopes at the time of being cooled below its closure temperature. The closure temperature also acts as

a blocking temperature at which a radioactive material on heating selectively rejects the daughter nuclides that have been accumulated over the time through diffusion, setting the isotopic "clock" to zero.

Nuclear Dating Methods

The nuclear dating methods have been developed utilizing different radioactive isotopes with specific half-lives as radiometric clocks. Presently, there are well over forty different radioactive dating techniques generally applied to determine the absolute ages of geological materials and dating of samples of biological origins. Some of the important radiometric methods such as Uranium – lead, Rubidium – strontium, Potassium – argon, Argon – argon, Samarium – neodymium, Lutetium – hafnium, Rhenium – osmium, Carbon-14, etc., generally used in dating of different types of sample materials, are briefly cited.

Uranium - Lead and Related Methods of Dating: Radiometric dating with the accumulation clocks, uranium – lead and thorium – lead, are based on the measurement of Pb - isotopes, the decay products of the radioactive decay series of uranium, ^{238}U (4.47×10^{9} yr) $\rightarrow$ ^{206}Pb and ^{235}U (7.04×10^{8} yr) $\rightarrow$ ^{207}Pb and thorium, ^{232}Th (1.40×10^{10} yr) $\rightarrow$ ^{208}Pb. In nature, thus there are four isotopes of lead, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb, at variable concentrations. Of these four lead isotopes, the rarest ^{204}Pb is only non-radiogenic and the other three, ^{206}Pb, ^{207}Pb and ^{208}Pb, are the respective radiogenic end products of the ^{238}U, ^{235}U and ^{232}Th - series continually decaying all through the history of the earth. Studies on these dating techniques are often referred to as Plumbology [7].

In dating of the absolute age of a mineral containing uranium and thorium using radioactive decay equation, the knowledge of the present day amounts of the parent radionuclides, ^{235}U and ^{238}U and/or ^{232}Th and their corresponding stable decay products of lead in the concerned solidified samples are essentially needed. These dating methods are commonly used for dating the ages or time of solidification of geological samples as closed systems in which no further migration of the relevant parent or daughter into or out of the matrix occurred.

The difference in rates of radioactive decay of ^{235}U (704 million yr) and ^{238}U (4.47 billion yr) makes uranium-lead radiometric dating as one of the most reliable methods as it provides a built-in cross-check with two different decay clocks allowing more accurate determination of the absolute ages of geological materials. Again, ^{208}Pb is produced as the end product of ^{232}Th (14 billion yr) – decay series and thus with the knowledge of the isotopic composition of uranium, thorium and lead in a mineral, one can independently determine the age of a rock through these three different natural decay processes. Now, appropriate application of uranium-lead dating can provide the absolute ages of a rock within an error margin as low as less than two million years in two-and-a-half billion years and for an younger specimen like Mesozoic rocks, an error margin of 2–5% has been achieved [1,13].

The method has been applied to date different materials such as uranium-rich minerals like zircon ($ZrSiO_4$), deep-sea sediments, ancient lake beds, shells, bones and teeth [14]. The methods have also been used to date the lunar rocks and a wide variety of terrestrial rock systems with solidification ages in the range of several aeons (one aeon = 10^9 yr = 1 Gy or 1 Ga). However, because of the factors like metamorphic events, chemical weathering, etc., which can alter the chemical composition of the rocks, these ages may not always be concordant.

The method of Uranium-thorium dating, based on the decay of ^{234}U (0.0055% of natural abundance) to ^{230}Th, is always associated with a relatively short-range sister process in which ^{235}U decays to ^{231}Pr having a half-life of 34,300 years. In the process, ^{230}Th and ^{231}Pr, unlike water-soluble uranium, are selectively precipitated into ocean-floor sediments and their ratios are measured.

The two radiogenic lead isotopes, ^{206}Pb and ^{207}Pb, the respective decay products of the two ^{238}U and ^{235}U - decay series formed the basis for the development of the method of Lead – lead dating. The present atomic ratio of $^{235}U/^{238}U$ is equal to 1/138 and the ratio of radiogenic and non-radiogenic or primordial lead isotopes, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$, are 10.3 and 9.31 respectively. In dating, the isotopic ratios of the parents and daughters can be measured with a mass spectrometer. The method applied is known as the *Holmes – Houtermans Model*[7] for lead isotopic composition and the age equation is normally solved graphically (*isochron).*

The element helium, produced as an intermediate product through α - particle decay of both uranium and thorium in a geological sample, can be used for dating[7] as the Helium accumulation dating clock, often called as the Helium clock. The respective emissions of 8, 7 and 6 α - particles in the ^{238}U, ^{235}U and ^{232}Th - decay series, in each instance, can furnish a method for dating the age of the concerned mineral. In the process of dating, the amounts of uranium and thorium and the radiogenic ^{4}He released on heating of the sample are measured. The ^{4}He - contents in uranium-poor minerals and in samples of fossil, coral and mollusks from a given location, have been found to be directly proportional to the amount of uranium. The

possibility of escape or loss of helium gas through cracks, grain boundaries or on heating may sometimes cause problem in determination of the age of a rock.

Potassium-argon Dating: The Potassium-argon accumulation clock is suitably applied in dating of the oldest rocks[15]. Natural potassium is composed of 0.01% of radioactive ^{40}K (1.28 x 10 ^{4} yr) which spontaneously decays by two different routes to two daughter products, ^{40}Ca, by β-decay and inert ^{40}Ar by electron capture (EC) respectively following the single – step decay process,

^{40}K (0.01% of natural K) $\rightarrow$ ^{40}Ar (11.2%) + ^{40}Ca (88.8%).

The potassium minerals like micas and feldspars when solidified in their crystalline forms from molten states, the potassium-argon clock was clearly reset in an igneous rock formation and the new radiogenic ^{40}Ar, the decay product of ^{40}K, became trapped in the crystalline mineral matrix as tiny bubbles. In the dating process, the relative amounts of ^{40}K and ^{40}Ar are measured by chemical and mass spectrometric techniques. Loss of argon by slow diffusion in 'loose lattice' minerals, partial melting of rocks or through shocks may sometimes cause discordant in estimated ages of rocks. The method has been used to date volcanic layers above and below different fossils and artefacts in East Africa [4]. In case of dating of meteorites or lunar samples, there is the possibility of contamination of ^{40}Ar that may be produced in the samples by the action of cosmic rays. In Potassium – Calcium dating, with a fractional branching value of ~ 89% of ^{40}K to decay to ^{40}Ca and normalization to non-radiogenic ^{44}Ca, a working equation similar to that for potassium – argon dating is applied. Calcium is not volatile like argon and the method can be used to date potassium - rich and calcium - poor minerals such as micas at appropriate temperatures.

The Argon-argon dating clock, sometimes called as the Incremental heating or $^{40}Ar/^{39}Ar$ method[7], was first used by Merrihue and Turner[16] in dating of lunar rocks. In the process, the potassium mineral is irradiated with fast neutrons in a nuclear reactor to transform stable ^{39}K to ^{39}Ar (269 yr), a long lived β– emitter by the nuclear reaction, $^{39}K(n, p)^{39}Ar$. The irradiated rock when heated at incrementally higher temperatures, both ^{40}Ar and ^{39}Ar, respectively produced from decay of ^{40}K and irradiation of ^{39}K, come out of the rock in a constant proportion at different heating steps. The released ratio of $^{40}Ar/^{39}Ar$ at each step is analyzed with a mass spectrometer for dating of potassium mineral.

Rubidium – Strontium Method: The rubidium-strontiumdating, like the uranium-lead clock, is an accurate and widely used method to determine the solidification ages of rocks with high closure temperatures. It is based on the â" decay of ^{87}Rb with a half-life of 4.8 x10^{10} years to ^{87}Sr, following the single-stage decay scheme,

^{87}Rb (27.84% of natural Rb) $\rightarrow$ ^{87}Sr

Formation of ^{87}Sr from ^{87}Rb results in increasing the ratio of ^{87}Sr to the stable ^{86}Sr, over the time. Both the parent and the daughter nuclides involved in dating are non-volatile and are easily mobilized. The method is manly based on the isotopic ratio measurements by mass spectrometry. Graphical methods are also often used to measure rubidium – strontium ages. The technique is used to date the ages of the old igneous and metamorphic rocksof billions of years and the lunar samples.

Samarium – Neodymium, Lutetium – Hafnium and Rhenium – Osmium Dating: These accumulation clocks**,** work very similarly to that of the rubidium-strontium method. In samarium - neodymium method, ^{147}Sm with a half-life of 105 billion years produces the daughter isotope, ^{143}Nd, through α - decay. The ratio of ^{143}Nd to another neodymium isotope, ^{144}Nd, is considered against the ratio of the parent, $^{147}Sm/^{144}Nd$ in determining the age of the minerals and an acuracy level of about twenty million years in two-and-a-half billion years has been achieved [17]. The lutetium-hafnium clock uses ^{176}Lu which with a half-life of 38 billion years decays to ^{176}Hf through β- emission by the process,

^{176}Lu (2.59% natural abundance) $\rightarrow$ ^{176}Hf

The dating system which in many ways is similar to samarium-neodymium clock, uses the non-radiogenic radionuclide ^{177}Hf for normalization and is sometimes used to date zircon rocks. In rhenium – osmium dating, the isotope, ^{187}Re with a half-life of 4.1 x 10^{10} yr decays to ^{187}Os through β- emission by the process,

^{187}Re (62.60% natural abundance) $\rightarrow$ ^{187}Os

In the dating process, the non-radiogenic isotopes, ^{186}Os and ^{188}Os, are being used for normalization and the isochron plots of $^{187}Os/^{186}Os$ against $^{187}Rb/^{186}Os$ are used for graphical computation of ages. The method is used primarily to date molybdenite (MoS_2) bearing vein deposits in rhenium-rich copper ores, minerals with low uranium, potassium and rubidium-contents and also the terrestrial rocks.

Dating with Short-lived Extinct Radionuclides

At the beginning of the solar system, the radionuclides formed in stellar nucleosynthesis with half-lives in the range

of million to tens of millions of years, although have survived through the early ages of formation of planetary bodies, but are not long enough to be survived to the present and have now become extinct[7]. Some of these important extinct natural radionuclides are ^{26}Al (7.3 x 10^{5} yr), ^{41}Ca (1.03 x 10^{5} yr), ^{53}Mn (3.7 x 10^{6} yr), ^{107}Pd (6.5 x 10^{6} yr), ^{129}I (1.57 x 10^{7} yr), ^{146}Sm (1.03 x 10^{8} yr), ^{244}Pu (8.0 x 10^{7} yr). Other similar extinct radionuclides are ^{60}Fe, ^{135}Cs, ^{205}Pb and ^{247}Cm. Studies on the decay products of these extinct radionuclides in meteoriteswith mass spectrometers or by isochron plots, have helped in determining the relative ages of very old geological matrices as well as getting information about the early history of the solar system.

In dating with the extinct radionuclides, the ^{129}I – ^{129}Xe radiometric clock is the mostly used chronometer [18]. It is an isochron technique based on β- decay of ^{129}I to ^{129}Xe with a half-life of ~16 million years.Similarly, the ^{26}Al – ^{26}Mg chronometer is another example of short-lived extinct radionuclide dating in which ^{26}Al decays to ^{26}Mg with a half-life of 7,20,000 years, has been used to estimate the relative ages of chondrules(~1.4 million years)[19].

Some of the oldest rocks of great ages on earth occurring in Western Greenland have been extensively studied and the ages of one particular rock formation in Western Greenland, the Amitsoq gneisses[6], derived through different dating methods are presented in Table 2.

TABLE 2. Age of a particular rock formation in Western Greenland, the Amitsoq gneisses.

Nuclear Dating Technique	Age Range (billion years)
Uranium-lead	3.60±0.05
Lead-lead	3.56±0.10
Lead-lead	3.74±0.12
Lead-lead	3.62±0.13
Rubidium-strontium	3.64±0.06
Rubidium-strontium	3.62±0.14
Rubidium-strontium	3.67±0.09
Rubidium-strontium	3.66±0.10
Rubidium-strontium	3.61±0.22
Rubidium-strontium	3.56±0.14
Lutetium-hafnium	3.55±0.22
Samarium-neodymium	3.56±0.20

(Compiled from Dalrymple, 1991)

Scientists are of the opinion that all the bodies in the solar system were created at about the same time and this would make the Earth 4.5 to 4.6 billion years old. Applications of radiometric dating to varieties of geological materials of different geological time scales also indicate the Age of the Earth to be approximately of four and a half billion years. Detailed studies on meteorites and other available materials like the chips off the asteroids, suggest that almost all of the meteorites are practically of identical ages of ~ 4.56 billion years. Characterization of uranium, thorium and lead isotopes also corroborates the Earth's age with that of the meteorites. The consistency in results regarding the ages of some specific samples of a particular rock formation estimated through different dating methods, as evident from Table 2, itself proves the efficiency of the nuclear dating techniques. Thus, the technique of nuclear dating has been found to be a key concept in determining the age of the earth [6].

Dating with Cosmogenic Radionuclides

Several cosmogenic radionuclides such as ^{3}H, ^{10}B, ^{14}C, ^{36}Cl are continuously being produced by the interactions of the high energy particles like neutrons and protons present in cosmic-rays with the nuclides of the concerned elements in space and remain at a constant levels on earth. Amongst these cosmogenic radioisotopes, the ^{14}C nuclide has been extensively applied in radiocarbon dating of organisms.

Radiocarbon Dating: The radioactive carbon, ^{14}C, is formed by the interactions of cosmic-ray neutrons with nuclides of nitrogen, ^{14}N, in the atmosphere following the nuclear reaction,$^{14}N(n, p)^{14}C$. ^{14}C, with a half-life of 5730 years decays spontaneously to ^{14}N by the emission of the β - particle of energy 0.016 MeV [1,20,21]. Since ^{14}C is constantly being produced and undergoes radioactive decay to ^{14}N, an equilibrium level of the carbon–nitrogen cycle is eventually established in the atmosphere. The rate of production of ^{14}C in the atmosphere seems to be fairly constant and the ratio of ^{14}C to^{12}C is in the order of 1.3 x 10^{-12}. Knowledge of the ratio of ^{14}C to total carbon in a dead organism which ingested ^{14}C along with ^{12}C while living helps in determining the age of the sample concerned [22].

^{14}C produced as hot atom by $^{14}N(n, p)^{14}C$ reaction promptly reacts chemically with oxygen in the atmosphere like ordinary carbon-12 to produce radioactive $^{14}CO_2$ which is then incorporated along with ordinary CO_2 in the plants by photosynthesis, into animals that eat plants and eventually in all living things. When the organism dies,

the body stops incorporation of all carbon including ^{14}C from food or air and the concentration of ^{14}C in the once-living thing gradually declines due to radioactive decay of the existing ^{14}C with its characteristic half-life as time goes on. Once an organism is decoupled from the carbon-nitrogen cycles (i.e., death), the ^{14}C decays until essentially gone. The atmospheric carbon- nitrogen cycle [21] is presented in Figure 2.

The technique of Radiocarbon dating, also known as Carbon-14 or simply Carbon dating, is an example of the equilibrium decay clock, essentially used to determine the age of a sample organic in nature by measuring the radioactivity due to its ^{14}C - content. The technique of radiocarbon dating was developed by Willard Libby along with his collaborators [9] in 1949. They accurately estimated the ages of woods from a series of samples including an ancient Egyptian Royal barge of 1850 BCE, the age of which was already known.

The process of radiocarbon dating was originally based on the conversion of an organic sample to $CO_2$and its precipitation as $BaCO_3$ which was counted with thin-window gas filled counters. However, the emission of the weak β- of an E_{max} of only 157 keV by ^{14}C and its self-absorption in the solid sample, cause problems in counting. To achieve better results, the radiocarbon dating is now mostly performed by converting the organic matter into a gaseous form such as acetylene (C_2H_2), methane (CH_4) or CO_2 and is directly used as counting gases in pressurized internal sample proportional counters with much higher counting efficiencies (> 90%) for the β- emitted by ^{14}C. Sometimes, the organic matter is converted to its liquid form such as benzene (C_6H_6) and is counted with high efficiency liquid-scintillation counting systems. The basic decay equation generally applied to calculate the radiocarbon age (t) can be presented as, $SA_{now} = SA_{eq} e^{-\lambda t}$, where SA_{now} and $SA_{eq.}$ represent the present and original equilibrium specific activities of ^{14}C.

The applicationof tandem Van de Graaff accelerator to introduce carbon ions for mass analysis into a specially designed mass spectrometer is one of the most innovative attempts made in radiocarbon dating. Since the half-life of ^{14}C is less than 6,000 years, the dating limit of the method lies around 60,000 years or ten half-lives by the counting techniques[1,3]. The range of radiocarbon dating can sometimes be extended to about 100,000 years by the use of accelerator techniques allowing a conventional mass spectrometer to separate ^{12}C and ^{14}C.For precise and accurate dating, normally, the procedure like isotope ratio mass spectrometry[23] is preferred. The mass spectrometer technique can be applied with a sample as small as a milligram.

Radiocarbon dating is an ideal technique to date ages of the remains of old organisms[1] like plants and animals which absorb ^{12}C and ^{14}C at a constant ratio as food in the form of carbohydrates, proteins and fats from the atmosphere while living. The radiocarbon dating of the samples of bones, hair, grass boots and leather belongings of once alive Iceman whose frozen body was chipped out of glacial ice in 1991, helped in determining the age of the Iceman to be of about 5,300 years old. Similarly, the dating of ages of the fossilized remains, such as dinosaur bones or the relics like the Dead Sea Scrolls and the Shroud of Turin claimed to have been used to wrap the body of the Prophet of Christianity after his crucifixion, have been effectively determined [6]. Radiocarbon dating encourages authentication of important documents and the ages of various rare archaeological artefacts. Studies on radiocarbon dating of different objects from the historically dated or marked graves and tombs, enable to estimate the level of ^{14}C in the atmosphere at that time and so partial calibration of the "clock" is possible. Currently, a clever forgery might be indistinguishable from a real artefact without radioactive dating. Investigation on "Radiocarbon dates of a layer of peat beneath the glacial sediments provided an age of only 11,400 years", although the age of sediments deposited by the last ice age was originally surmised to be about 25,000 years old [3,24].

The cosmic ray flux in the atmosphere, although assumed to be constant, has been found to be significantly altered in ^{14}C specific activity due to man-made activities in the twentieth century [25]. In 1955, H. Suess in his 'Suess Effect' [7,26] concluded that massive release of non-active carbon-12 into the biosphere by burning of fossil fuels in this era of industrialization, has resulted considerable depletion in ^{14}C - content in the atmosphere. On the contrary, atmospheric testing of thermonuclear weapons since World War II has the opposite effect, raising the equilibrium specific activity of ^{14}C by a factor of ~ 2. The effects of these human activities can make the radiocarbon dating scale sometimes inaccurate[1]. Similarly, the effects of natural phenomenon like isotopic fractionation of carbon by chemical, biological and physical processes, climatic variations, eruption of a volcano, changing in solar activity or earth's magnetic field, etc. which can alter the carbon isotopic mix in the atmosphere [6] must be considered in the process of accurate radiocarbon dating.

The accuracy of carbon-14 dates is sometimes cross-checked by comparing the same with those derived from

some non-radiometric indicators[6,7] of known ages. The specific specimens such as, the wood from interior tree-ring growths (Dendrochronology) of bristlecone pines from Western U. S. and Scandinavia, the underwater sediment "varves" (organic matter deposited in sediments of glacial lakes), ice cores, etc. with historical records of known ages are counted as reliable non-radiometric indicators in dating.

Tritium Dating: Tritium (^3H), produced by cosmic rays exists in equilibrium in all atmospheric and surface waters as HTO compound. **Tritium dating,** a method of equilibrium dating, was originally proposed by W. F Libby and others [7,9] utilizing French wines. ^3H with a half-life 12.3 years, is a weak β- emitter of 18.6 keV. Water while flowing in a deep aquifer or underground water that has been isolated from atmospheric equilibrium for a longer period will always exhibit lower levels of tritium activity depending on its time of isolation. The sensitivity of tritium dating can be enhanced by partial evaporation or electrolysis of water resulting in increment of ^3H with respect to ^1H in the residual liquid water. The equilibrium level of ^3H in the hydrosphere has been enhanced to thousands of time from its pre-test level after the thermonuclear tests depending on geological location. Ground water circulation and turnover rates of water in oceans and lakes have been studied by using the technique.

Dating of Terrestrial Ages of Meteorites: The terrestrial age of a meteorite [7] is the time interval between its landing on earth to the present. During the flight of a meteorite in space, varieties of radionuclides like ^3H, ^{10}B, ^{14}C, ^{26}Al, ^{36}Cl, ^{54}Mn, ^{60}Co and some isotopes of the noble gases, are produced in it due to its interactions with cosmic-ray particles. Once a meteorite falls on earth, the production of the radionuclides in meteorites almost stops and the activity of the radionuclides will decrease with time due to its shielding from cosmic-rays by the atmosphere, crater ejecta, ice in the polar region or water if the fall is in the ocean. Sometimes, simple radiocarbon dating of a dead tree buried by the ejecta from a large cater caused by the impact of landing of a meteorite, is used in dating the terrestrial age of the meteorite and the time of the cater formation. The ages of meteorites are most often determined by the simple equation, $A_{now} = A_{eq} e^{-\lambda t}$, where the present equilibrium activity, A_{eq} of the freshly fallen meteorite is the initial activity and A_{now}, is the activity in an older terrestrial age meteorite with similar chemistry after a decay time, t, on the earth's surface. D. Laul and J. R. Arnold [27] have developed a method of dating with the cosmic-ray produced ^{10}B and ^{26}Al in buried quartz vein of a meteorite by direct atom counting through a tandem Van de Graaff cyclotron mass spectrometry.

Interactions of cosmic-rays with meteorites result in the formation of appreciable quantities of ^3He and ^4He through spallation reactions [7]. It has been observed that In iron meteorites, all the helium is practically produced by cosmic-ray induced spallation reactions, whereas in stone meteorites in which the uranium content is significantly higher than that of iron meteorites, helium is produced partly due to decay of uranium and partly due to action of cosmic-rays. Thus, studies on cosmic rays – meteorite interactions have provided essential information regarding the origin and the history of the meteorites in the solar system.

Dating on Background Radiation

The effects of radiation, especially from á - particles or fission fragments, on the surrounding materials over a very longer period of time are either more or less uniformly distributed as in the case of Thermo-luminescence or is localized as in cases of Pleochroic halos and Fission tracks depending on the specific properties of the concerned materials.

The thermo-luminescence produced by radioactivity can be used as a method for determination of the age or a thermal history of the surrounding minerals including archaeological samples [6,7]. The technique is useful in dating of pottery shards, sediment layers, minerals like lime-stones, granites, quartz, sodium potassium feldsparsor fine-grained volcanic dust and the thermal history of meteorites.The related techniques like optically stimulated luminescence (OSL) and infrared stimulated luminescence (IRSL) are sometimes used to determine the age of some specific unheated sediments.

Similarly, when a minute crystal of a radioactive mineral like uranite having high content of uranium or thorium is surrounded by another mineral like biotite, quartz, calcite, apatite or plagioclase, the energetic á - particles emitted by the decay of uranium or thorium and their daughters cause radiation damage in the host materials producing dark halos, known as pleochroic halos[7] and the extent of darkening is a function of the total dose of radiation. The process can provide information concerning the relative ages or the thermal history of geologic sub-systems having common origins. The technique of fission track dating mainly deals with the radiation damage caused by the two energetic spontaneous fission fragments of uranium-238 impurities as double 'track' markings in the polished glasses and crystalline materials [1,7]. It has got effective applications [28] in dating of meteorites and the thermal history of varieties of old geological deposits ranging from over a few decades to billions of years and

also in relatively young archeological glass samples that have been protected from heating since their production.

Applicability and Accuracy of Radiometric Dating

The applicability of the techniques of radiometric dating depends on the time scales over which they are accurate and with the materials for which they can be effectively used. In dating of geological time scale, the effects of loss or gain of either of the radioactive parent or the daughter, the possibility of contamination or any other parameter which can alter [29] the composition of the geological materials since its creation, are of serious concern. Similarly, precise radiocarbon dating of samples of dead organisms or ancient artefacts demands precautionary measures against surrounding environment which can change or affect the $^{14}C/^{12}C$ ratio in the atmosphere due to natural or man-made activities over the time. Generally, analysis of multiple fractions from different parts of the samples of rocks or of biological origins like plants and animals results in enhancement of accuracy in dating. In addition, a correlation between different dating methods appropriately applied for dating of a specific material may be more effective in confirming the age of the concerned sample. For example, twelve samples of Amitsoq gneisses from Western Greenland, as presented in Table 2, have been studied through five different radiometric dating methods to achieve agreement in dating within 30 Ma for an age of 3,640 Ma (mega-annum; million years)[6,30]. Since each of the dating techniques has its specific applicability, advantages and disadvantages, aco-relation of dates with multiple specimens via different dating methods provides a highest degree of reliability in dating. Radiocarbon dating correlates well with the non-radiometric dating techniques and has been accepted as an accurate dating tool especially for Pleistocene and Holocene period analysis.

Conclusions

The characteristic nuclear property of radioactive decay of radionuclides at almost immutable rates has been effectively utilized to develop over forty different radiometric techniques for dating of varieties of materials of geological and biological origins since its initiation about 100 years back. With gradual improvement in nuclear techniques, in general,the methods of absolute dating as analytical tools have undergone continual refinement resulting in enhancement in accurate and precise dating of important geological events as well as the history of organisms once living on earth.

Application of efficient radiometric dating enables the geologists to record the time sequence of different geological formations involving the age of the earth, meteorites, lunar rocks, etc., within the geologic time scales and also encourages the archaeologists to study ancients events of biological origins such as dinosaur era, age of the Iceman, the Shroud in Turin and also in authentication of important archaeological materials along with their evolutionary changes. In dating, absolute age is just a fancy way of presenting the definitive or specific age of a material against the relative age which only refers to how old or young a substance is in comparison to something else. Close agreement in dating of the age of the earth derived through different dating methods, for example, is a hallmark of nuclear or radiometric dating. In fact, the radioactive decay constitutes a 'clock' provided by nature. ❐

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