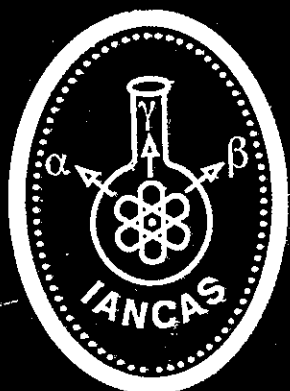


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IANCAS BULLETIN

RADIOISOTOPES IN EARTH SCIENCES

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ALLIED SCIENTISTS

Editorial

This issue of IANCAS bulletin covers the area of isotope applications in geology. Isotopic abundances or their ratio, of certain radioactive elements in geological samples act as chronometers for determining the age and are sensitive indicators for ore prospecting. Also, determination of isotopic abundances of hydrogen and oxygen in water samples helps immensely in water resources management and prospecting, a well developed discipline referred to as isotope hydrology.

Dr. K.L. Ramakumar, who is the guest editor for this issue, has nicely summed up the importance of this discipline in FOCUS.

I put on record my sincere thanks to all the authors, who constitute a spectrum of specialists from reputed organisations, for their contributions to this issue.

Our objective is to present a quality bulletin on a variety of interesting areas in science and technology. To maintain high quality and regularity, we need your active support. This support can come in the form of articles as well as comments. The latter is very important because your feedback will go a long way in helping us achieve our objectives. Our dream is to see the metamorphosis of the bulletin into a scientific journal of high standard. Today's dream can be made a reality tomorrow!

I wish all the members a happy and prosperous new year.

P.K. Pujari

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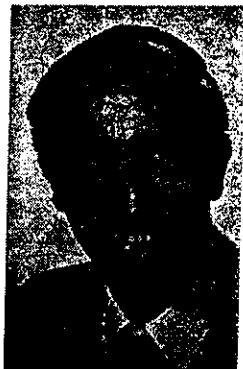
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Focus

Nuclear Geochemical Studies of Geological Waste Repositories



Dr John de Laeter is Professor of Physics and Deputy Vice-Chancellor of Research and Development at Curtin University of Technology. He is a Fellow of the Australian Academy of Technological Sciences and Engineering and the Australian and British Institutes of Physics. He is a past Chairman of the Commission of Atomic Weights and Isotopic Abundances and is a member of the Council of the Inorganic Chemistry Division of the International Union of Pure and Applied Chemistry. Professor de Laeter's major research interest is in the application of mass spectrometry to a range of astrophysical, chemical, geological and nuclear problems. He has played a major role in the development of geochronology in Western Australia, in analysing Western Australian meteorites, in radioactive waste containment studies and in the accurate determination of the isotopic abundances of numerous elements, many of which led to new values of their atomic weights. He has a long-standing interest in nuclear astrophysics and the origin of the chemical elements. He received the ANZAAS Medal in 1992 and the Royal Society Medal in 1993.

Introduction

The Oklo natural reactors provide a marvellous case study of the use of isotopic techniques in deciphering the nuclear characteristics and geochemical history of a geological waste repository. The variations in the isotopic composition of a large number of elements, caused by a combination of nuclear fission, neutron capture and radioactive decay, provide a powerful tool for investigating a unique geological environment. Mass spectrometric techniques have been applied to a range of elements at Oklo in order to measure the present day isotopic abundances, and from this isotopic information, to decipher the past history of the reactors.

Kuroda (1956) proposed that critical nuclear assemblages could have occurred in ancient uranium deposits. The subsequent discovery of a natural reactor at the Oklo mine site in Gabon, West Africa, in 1972 confirmed this hypothesis. The reactor sites consist of rich uranium ore in which ^{235}U has been depleted to as low a value as 0.29%, compared to its normal value of 0.72%. It has been demonstrated that the reactors operated some 2 billion years ago, consumed in excess of 6 tons of ^{235}U , generated approximately the same amount of fission products, and produced a total energy output of 10^{11} kWh (Naudet, 1978).

The Oklo deposit is located in the south-east part of Gabon, in the Precambrian sedimentary basin of Franceville. Uranium mineralisation occurs in a sandstone conglomerate lens as pitchblende, with an average concentration of 0.2%. By contrast, the reactor zones contain 25% to 60% uranium in the form of uraninite. The length of each reactor zone ranges from 10 to 20 m with a thickness of between 0.5 and 1 m. The size of the reactor zones was sufficiently large to exceed the critical mass at a time when the ^{235}U concentration was greater than 3%. Furthermore, the uranium ore is deficient in elements possessing large neutron capture cross-sections that would have "poisoned" the chain reactions. The Oklo uranium deposit is situated in a clay basin, which was periodically flooded with water. The water acted both as a moderator and coolant for the reactors. The exceptional character of Oklo is not so much that a nuclear reactor existed some time in the past, but in the fact that the repository still exists today.

The possibility of long-term storage of radioactive waste originating from nuclear reactors and reprocessing plants in natural geological repositories has been under consideration for some time. However a number of uncertainties exist about the safety of burying wastes in underground salt or rock formations. Most of the uncertainties involve a lack of knowledge about potential geophysical,

geochemical or hydrological interactions between the wastes and the geological structure in which they might be stored. Efforts to evaluate the effectiveness of geological media in containing radioactive wastes are severely constrained in that the time periods involved are greater than that recorded by human experience. Although many short-lived fission products decay to low levels in tens of years, a number of longer-lived radionuclides like ^{137}Cs and ^{90}Sr take approximately 600 years before they are effectively extinct. However, the actinides with their larger half-lives, may take 100,000 years or more to decay to low levels, so that no artificial repository can hope to provide definitive answers to the problems associated with the long-term storage of nuclear waste.

The Oklo reactors offer a unique opportunity to examine the fission products produced by the chain reactions at Oklo, and use them as isotopic tracers to examine the mobility-retentivity of numerous elements in the reactor zones themselves and in the surrounding geological formation. An assessment of the stability of the fission products at Oklo is a key factor in the assessment of the effectiveness of natural repositories in radioactive waste containment studies.

Mass spectrometry can be used to measure both the isotopic and elemental abundances of numerous elements from the reactor zones and peripheral rock samples from the Oklo deposit. A study of the cumulative fission yields of a number of key elements enable the nuclear parameters of the reactors to be established and, thus, the amount of fission products produced some 2 billion years ago to be estimated. Comparisons between the present, measured abundances of these fission products and the calculated abundances, provide a measure of the mobility/retentivity of the elements. The details of these changes provide an unprecedented opportunity to examine the effects of physiochemical processes on the various elements in this geological environment.

Nuclear Parameters

One of the most important parameters that needs to be determined is the proportion of ^{235}U , ^{239}Pu , and ^{238}U fuel involved in the fission process at Oklo. Plutonium-239 is produced by neutron

capture on ^{238}U . A proportion of the resultant nuclide undergoes fission, whereas the remainder decays to ^{235}U by alpha decay. Both ^{235}U and ^{239}Pu fission is induced by thermal neutrons, whereas ^{238}U fission is induced by high-energy neutrons. The Pd isotopes are particularly important in determining the relative proportions of ^{235}U , ^{239}Pu , and ^{238}U fission, because the low-mass hump in the asymmetric mass distribution of fission is shifted to higher masses for the heavier fissionable nuclides. The Pd fission yields are therefore sensitive indicators of the nuclides involved in the fission process.

Unfortunately the cumulative fission yields for Pd for the fast neutron fission of ^{238}U have not been measured, so they can only be estimated to an accuracy of $\pm 20\%$ compared to $\pm 5\%$ for ^{239}Pu and 2% for ^{235}U thermal neutron-induced fission yields (Shima et al., 1978). Loss et al. (1988) measured the isotopic composition of Ru, Mo, Pd, Cd, Ag, Sn, Te, Nd and U in Reactor Zone 9 samples, and from an examination of the Pd isotopes, showed that the nuclear fuel was 88%, 8%, and 4% for ^{235}U , ^{239}Pu and ^{238}U respectively. It can be shown that nearly 50% of the fissioning ^{235}U nuclides in reactor Zone 9 was produced from the decay of ^{239}Pu . During the period of criticality the average fission density was 0.92×10^{20} fissions cm^{-3} , which represents a total energy output of $4 \times 10^8 \text{ J g}^{-1}$ of sample, with an average power output of $8.1 \times 10^{-5} \text{ W g}^{-1}$ of sample (Loss et al., 1988).

Another important nuclear parameter is the integrated neutron flux of the various reactor zones. A number of nuclides with high neutron capture cross sections such as ^{113}Cd , ^{149}Sm , ^{155}Gd and ^{157}Gd can be used to determine this parameter by examining the change that has occurred in the isotopic composition of such nuclides in the Oklo material. For example Ruffenach et al. (1980) have calculated an integrated neutron flux in excess of $10^{21} \text{ n cm}^{-2}$ for Zone 2. It is also possible to calculate the energy spectrum of the neutron flux, by comparing the isotopic composition of a number of nuclides whose capture cross section varies with neutron energy. In fact the neutron spectrum at Oklo is well thermalised and Zone 2 has a spectral index of < 0.2 (Ruffenach et al., 1980).

Conventional geochronological decay schemes have been used to estimate the age of the reactors

themselves. Although these decay schemes (K-Ar, Rb-Sr, U-Pb, and Sm-Nd) must take into account the possible alteration of nuclides by the fission process itself, a number of determinations give the age of the reactors to be between 1.8 and 2.1×10^9 y (Gancarz, 1978).

The other major time interval involved in the Oklo reactors in the length of time the reactors were active. The small fission proportion of ^{239}Pu (as calculated from Pd fission yields) implies that most of the Pu that was formed decayed to ^{235}U , and this in turn means that the duration of the nuclear reactions was long compared to the half-life of ^{239}Pu (approximately 24,000 y). More precise calculations lead to a duration of about 800,000 y for the reactions in Zone 2, but the time interval varies from zone to zone, and some are as low as 100,000 y (Ruffenach et al., 1980).

Fission Product Retention

The most comprehensive study of element retentivity has been carried out on Reactor Zone 9 by Curtis et al. (1989). Figure 1 summaries the results in schematic form. The cumulative fission yields of the various nuclides measured by Curtis et al. (1989) are depicted from $95 \leq A \leq 150$. The predicted mass distribution curve has been calculated from the proportions of nuclear fuel determined for this reactor zone, and the measured values compared to this curve. Most of the Ru, Pd and Te were retained in the uraninite of the reactor zone whereas a significant fraction of Mo, Ag and Sn has been lost. Almost all the fission product Cd has escaped from the reactor and no ^{113}Cd was detected due to its high neutron capture cross section, although there was a comparative overabundance of ^{114}Cd due to the same neutron capture reaction.

The fission product abundances of elements (Mo, Ru, ^{99}Ru , Pd and Te) in the eight uraninite samples in Reactor Zone 9 show extremely well-defined linear correlations over concentrations that differ by an order of magnitude. This regularity is attributed to the primary retention at the site of production (Curtis et al., 1989). Based upon this interpretation, fixed proportions of Mo, Ru, ^{99}Ru and Pd have been removed from the reactor zone with respect to Te. By analogy with anthropogenic spent fuel, it can be argued that the degree of primary

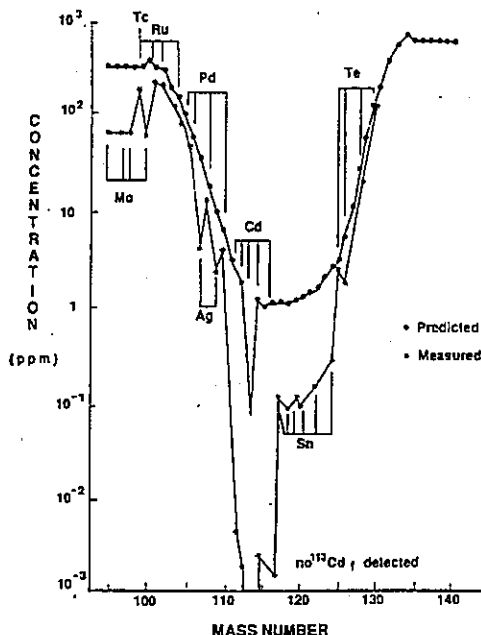


Fig. 1 Predicted and measured fission product abundances for an Oklo Reactor Zone 9 sample

retention was controlled by phase assemblages formed in the Oklo natural reactor fuel in response to micro scale conditions of pressure, temperature, and composition produced by the nuclear reactions. The ability of these putative minerals to retain nuclear products is a function of their stability under physiochemical conditions established by the geological environment over the past 2 billion years. Evidence of element fractionation is exhibited in the isotopic analyses of Ru in the reactor zone samples. A precursor to ^{99}Ru is ^{99}Tc , which has a half-life of 2.1×10^5 y. Thus for a geologically significant period of time the fission-produced isobars at mass 99 existed in two different chemical forms - Tc and Ru. Technetium was mobilised from Reactor Zone 9 to a more significant extent than Ru.

In contrast, Cd and Sn have been depleted in some regions of the zone and enriched in others. In the mass 126 fission chain, ^{126}Sn (with a half-life of approximately 10^5 y) is a precursor to ^{126}Te . The mass 126 fission yields for Zone 9 samples show considerable scatter in comparison to the mass 125 and 128 yields, where the fission yields are normalised to ^{130}Te . The elemental abundance data demonstrate a similar effect in that Reactor Zone 9

samples are both enriched and depleted in ^{126}Te relative to the remainder of the Te (Curtis et al., 1989). This implies that Sn was mobile during the first million years or so of reactor criticality. However, the $^{126}\text{Sn} - ^{126}\text{Te}$ systematics imply that a proportion of the Sn must have been redistributed within Reactor Zone 9 itself and was not retained *in-situ*, as was the case for Mo, Ru, Tc, Pd and Te.

Thermal ionization mass spectrometry has also been used to measure the isotopic and elemental abundances of Mo, Ru, Pd, Ag, Cd, Sn and Te in a number of sandstones and shales in the immediate vicinity of Reactor Zone 9 (Loss et al., 1989). The data show that considerable amounts of fissionogenic Mo, Tc, Ru, Pd, Ag, Sn and Te that escaped from reactor Zone 9 have been retained in the peripheral rocks, the greatest proportion being retained within a few metres of the reactor zone itself. On the other hand Cd has not been retained to any significant extent.

Ruffenach et al. (1980) have examined the retentivity of a number of other elements at Oklo. They have shown that the rare gases, the halides and some of the alkali and alkali earths have escaped from the reactor zones. They have also shown that the transuranic elements, and in particular ^{239}Pu , have been retained almost in their entirety in the uraninite, as have the rare earth elements. Some of the nuclides that were altered by neutron capture can be effectively used as isotopic tracers to examine the mobility/retentivity of the elements in the reactor zones and in the rocks in the surrounding geological formation. For example, if one examines the isotopic composition of Pd in a reactor zone sample, a significant amount of ^{104}Pd will be found. This nuclide has been produced by neutron capture on ^{103}Rh , and the results indicate that rhodium was retained in the uraninite, at least for the duration of reactor criticality (Loss et al., 1984).

One of the most difficult problems so far encountered in deciphering the mobility/retentivity of fission products at Oklo has been to search for fissionogenic alkali and alkali earth elements such as Rb, Sr, Cs and Ba. A recent mass spectrometric study of Ba from uraninite samples from Reactor Zone 10 has revealed excess amounts of ^{135}Ba , ^{137}Ba and ^{138}Ba , which is presumably the result of nuclear fission, together with an enhancement in ^{134}Ba

resulting from neutron capture on ^{133}Cs (Hidaka et al., 1993). The data indicate evidence of the existence of fissionogenic Cs and Ba in the Oklo samples. However the retentivity of ^{135}Ba and ^{137}Ba is very low as compared with the retentivity of Nd, thus implying that migration of Cs in the early aqueous phase of reactor criticality has occurred. Hidaka et al. (1994) have carried out a similar study on the same Reactor Zone 10 samples for Rb, Sr and Zr. Excess ^{90}Zr indicates that a proportion of the precursor, ^{90}Sr (with a half life of 29.1 y), must have been retained in the reactor zone. The data indicate that chemical fractionation between Sr and Zr occurred whilst radioactive ^{90}Sr was still present during the early stages of criticality. This fractionation is similar to that observed between Ba and Cs (Hidaka et al., 1993).

Conclusion

Many of the elements in the symmetric region of fission have high ionization potentials and are therefore difficult to analyse by conventional solid source mass spectrometry. Silica gel activators and micro electrodeposition techniques have had to be developed to enable these elements to be analysed at the nanogram level. Furthermore, chemical extraction techniques with low blanks and high efficiencies are also required to enable small quantities of these elements to be extracted (Loss et al., 1990).

Isotopic measurements have enabled the nuclear parameters of Oklo Reactor Zone 9 to be characterised, although the lack of accurate cumulative yield data for Pd for ^{238}U fission is a limiting factor in calculating the proportion of fission that can be ascribed to the various fissile fuels. The errors in these values in turn limit the accuracy with which we can calculate a number of other reactor parameters. However, the essential nuclear features of the reactor zones have now been successfully delineated.

Although it must be acknowledged that an extrapolation of the results of the Oklo natural reactor to the storage of radioactive wastes in geological repositories is not a straightforward matter, nevertheless, the isotopic studies carried out at Oklo have demonstrated that the retention of many fission products in well-preserved crystalline lattices

has been achieved on a time scale far longer than is required for practical purposes. Again, the peripheral rocks surrounding the reactor zones have demonstrated their ability to act as effective "getters" for a number of elements. These observations must be viewed against a situation in which the uraninite zones at Oklo were exposed to high radiation doses, large thermal loadings, and hot circulating hydrothermal fluids, which would never be contemplated in a present-day repository. The natural reactors at Oklo offer a unique opportunity to study the geochemical processes involved in the transport of fission products through geological materials.

Acknowledgement

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Isotope Hydrology in Water Resources Management



Dr. S.M. Rao is Head, Isotope Division, Bhabha Atomic Research Centre, Bombay, India. He obtained his Master's degree in physics from Sri Venkateswara University, Tirupati and later his Ph.D. from the University of Bombay. He joined the Bhabha Atomic Research Centre, Bombay in 1960 and had his advanced training in isotope techniques in hydrology in the French nuclear centres at Saclay and Grenoble. He has over thirty years of experience in the application of isotope techniques in sediment transport studies, stream flow measurements, seepage investigations, groundwater studies and in industrial process control and trouble-shooting. He was the recipient of Dr. Vikram Sarabhai Award for Atmospheric Physics and Hydrology in 1983. Dr. Rao was a member of UNESCO/IAEA Working Group on nuclear techniques in hydrology during the International Hydrological Decade and also of several IAEA Advisory Groups on isotope hydrology and industrial applications of radioactive tracers. Dr. Rao was a project expert during 1987-89 for the UNDP/IAEA Regional Project on industrial applications of isotopes and radiation technology in Asia and the Pacific. He was recently in Jordan as an IAEA expert on industrial applications of radioisotopes and in Syria on isotope applications in hydrology. He has over 80 publications to his credit. He edited two books, one on "Industrial Applications of Radioisotopes and Radiation" published by Wiley Eastern in 1986 and the other on "Isotopes and Radiation Technology in Industry" published by NAARRI in 1995. He has also written a booklet on "Isotope Tracer Applications in Industry and Civil Engineering" in 1992.

Nuclear Science and Water Resources! To many, it is indeed a strange and odd combination. Not so to the modern water resources engineer and scientist. On the other hand, for them it is already a successful and indispensable combination. Among the peaceful uses of atomic energy, other than the well known nuclear power, applications of isotopes and radiation technology in medicine, industry and hydrology are today silently yielding large socio-economic benefits beyond the purview of the man in the street. More silent are probably the applications in water resources management. Let us try and appreciate their value and potential in our national development.

India was the cradle of one of the most ancient civilisations in the world aided by the availability of plentiful water. Rains coming with clock-work precision, huge river courses and fertile lands promoted growth of settlements. With increasing demand for farm land, the settlements had to move away from perennial river courses. This, coupled with long dry season called for search of alternate

sources of water and development of methodologies for their exploitation. This science of hydrology in India like in other parts of the world, but unlike other sciences, grew more out of necessity rather than curiosity. Varahamihira, in the 4th century A.D. provided, in his Brihatsamhita, detailed guidelines for the exploration of groundwater resources. Ancient Indian kings tamed huge rivers by constructing dams to provide water for irrigation. These great traditions coupled with systematic surveys of surface and subsurface water resources in the last hundred years or more provided a very strong foundation for scientific hydrology in India. Our country is today a leader in water resources technology with rich experience in such modern areas as remote sensing and nuclear technology.

Let us first identify some typical areas in water resources work where one turns to nuclear science for help.

You intend to exploit groundwater resources in a desert region. Before you do that, you need to

know whether the resource is being replenished. If so, what is the quantum of recharge? If not, when was the source last recharged?

- A certain groundwater body is becoming saline. It is important to establish the source of salinity and decide on optimum conditions of operation of the wells so that further salinisation is controlled.
- In many cases, it would be necessary to establish the source of recharge to a given groundwater body in order to evaluate the potential and take necessary steps to protect the source.
- Water resources are often interconnected or interdependent. It often becomes necessary to identify the sections where a river loses water to an aquifer (water bearing strata underground) and where it gains water from the ground. Similarly one is often called upon to look at possible interconnections between aquifers and between a lake and groundwater body.
- Conventional techniques are either cumbersome or are not suitable for flow measurements in fast flowing hilly streams.
- Location of seepage (leakage) entry zones and delineation of seepage paths in operating dams are required to be done speedily for taking remedial measures. There are also situations when conventional procedures are not adequate to examine the soundness of bed rock foundations at dam sites.
- Seepage situations in canals and tunnels sometimes cannot be studied easily by normal engineering procedures.
- Investigation of sediment movement on sea bed is an essential prerequisite for deciding on suitable locations for dumping silt dredged from navigational channels and other areas in ports and harbours and also to decide on alignments of new navigational channels.

The list could continue, but the above is representative enough of the range of isotope hydrology, a discipline in its own right, combining nuclear science and water resources research.

How does this Isotope Hydrology work?

Isotopes are the species of a chemical element, differing only in nuclear mass from each other, but

otherwise maintaining the same chemical identity. Every school boy knows water is a chemical compound of hydrogen and oxygen (H-O-H). Hydrogen has three isotopes: ^1H : protium, ^2H : Deuterium, ^3H : Tritium as also oxygen: ^{16}O , ^{17}O , ^{18}O . These are all natural and out of them only tritium is radioactive whereas all the others are stable. So, it is possible to have many isotopic species of the water molecule. But, only the following four are of interest in hydrological investigations. In addition to the above, dissolved salts in natural waters have their own isotopic species which are of special interest in hydrological investigations. Isotopes of carbon (^{12}C , ^{13}C and ^{14}C) are of greatest interest.

$^1\text{H}-^{16}\text{O}-^1\text{H}$	stable	Most abundant (>997000 pm)
$^1\text{H}-^{16}\text{O}-^2\text{H}$	stable	2000 ppm
$^1\text{H}-^{18}\text{O}-^1\text{H}$	stable	150 ppm
$^1\text{H}-^{16}\text{O}-^3\text{H}$	radioactive (natural)	10^{-18} - 10^{-16}

Isotope hydrology is primarily application of all the above mentioned isotopes in natural waters as tracers to follow the behaviour of water in the hydrosphere; from the ocean-back to the ocean.

If you pick up a glass of water from a well, lake or a river, the levels of different isotopic species in that glass reflect the history of that water after it left the ocean. This glass of water was subjected to evaporation and condensation processes during its journey in the hydrological cycle till it was picked up. These processes modified its stable isotope picture as the heavier isotopes are sluggish and prefer to remain in the liquid phase.

The radioactive levels of tritium and carbon-14 in our glass of water represent the age of the water because each radioisotope is characterised by a specific rate of decay.

There is yet another way the nuclear science serves water resources management. It is in the use of radioactive isotopes produced in nuclear reactors. Chemical compounds incorporating some of these isotopes make excellent tracers. Tritiated water ($^1\text{H}^3\text{HO}$) is obviously the best choice. Others are bromine-82 as ammonium bromide and

cobalt-60/cobalt-58 as cobalticyanide complex. These are specially suited for localised investigations such as seepage (water loss) studies in dams and for flow measurements.

There are times when a water resources engineer would ask for a water-soluble, but bad water tracer which should leave the liquid phase and get attached to soil particles when it comes into contact with them. This is useful when locating seepage zones on reservoir beds. Gold-198 and lanthanum-140 are two isotopes often used in suitable chemical forms.

Finally, we have solid radioactive tracers for sediment transport investigations on sea and river beds. The tracer is either specially prepared glass powder incorporating a suitable radioisotope like scandium-46 or natural sediment on to which a radioisotope like gold-198 has been absorbed.

Whereas environmental isotopes, both stable and radioactive, are naturally present in the hydrological system, artificial tracers like reactor produced isotopes have to be injected into a given water body using special procedures after a thorough review of the technical and radiological safety aspects of the investigation.

Isotope assays need special equipment. Stable isotopes like deuterium (^2H) and oxygen-18 are measured by mass spectrometers. Natural radioactive isotopes like tritium and carbon-14 are measured by liquid scintillation spectrometers. Artificially injected tracers are either assayed, in water samples, by liquid scintillation spectrometers as in the case of a beta ray emitter like tritium or insitu by crystal scintillator probes as in the case of such gamma ray emitters as bromine-82, cobalt-60, cobalt-58, gold-198, lanthanum-140 and scandium-46.

Real-life Examples

Cauvery Delta

This is the rice bowl of Tamil Nadu. Availability of adequate quantities of water for crops is often threatened by the vagaries of monsoon and consequent problems in inter-state river water transfer. Artificial recharge of the local groundwater bodies (aquifers) is considered to be one possible way of smoothening out of variations in the seasonal

availability of water i.e. put the water underground when available and extract it when there is shortage. To ensure the feasibility of such artificial recharge, the interconnection between the shallow and deep water-bearing zones needed to be studied.

An environmental isotope study was undertaken to compare the isotope pictures of waters from the two water-bearing zones and their seasonal variations. Deuterium (^2H) and oxygen-18 as well as chloride levels were measured and the data were interpreted along with the information available on the geology and geohydrology of the two zones.

It was concluded that the two zones were not connected at most places except at isolated places where the clay layer between the two zones was either absent or very thin.

Salal Hydroelectric Project, Jammu

During the construction of the tail race tunnel through a dolomite hill for the Salal Hydroelectric Project in Jammu and Kashmir, several seepages (water entering the tunnel from the rock) were encountered and one of them was so severe that the work had to be suspended for months. The obvious question was which was the source of seepage and whether it would be safe to continue with the tunneling work. Quick answers were needed as the Project was already running quite behind schedule.

A single set of samples were collected from the seepage points in the tunnel, the Chenab river, a stream and a pond in the dolomitic hill. They were analysed for stable isotopes (^2H and ^{18}O) and natural tritium as well as for conductivity. These measurements coupled with the geological information and rainfall tritium data for Kabul and Delhi for the last two decades from the WMO/IAEA Worldwide network, provided the required answers.

The seepage waters in the tunnel were not from the river Chenab, nor were they connected to the stream or the pond in the hill. Based on the stable isotope ratios and natural tritium levels, it was shown that the seepage waters were local precipitation (rainfall) waters, 10 to 15 years old, stored in the dolomite rock and found their way into the tunnel whenever a weak zone was pierced during tunneling. It was considered safe to go ahead with tunneling and

the Project had since been completed without any further problem in the tunnel.

Kudremukh Iron Ore Project

At the peak of construction activity of this prestigious project, a dam was being constructed to store tailings left over after the concentration of the iron ore. This was to prevent pollution of the river system. In the cut-off trench of the dam, a large fissure was noticed in the rock. Aerial survey indicated the possibility of the fissure being part of an extended geofault. The work in this time-bound project came to a standstill and the Isotope Division, BARC was called in for an urgent isotope based investigation of the geofault as it could endanger the safety of the project township.

A reactor produced radioisotope bromine-82 was used as an injected tracer in the form of bromide. The tracer was injected after achieving the desired hydraulic conditions by pumping water into the fissure which caused two seepage points to appear in the valley. Monitoring for radioactivity in the river and the seepage points indicated that the fissure was not connected to the river and it was localised, posing no danger to the future structure. The dam was then built as planned and today Kudremukh is full of activity.

Madras Port

Madras Port is in a continuous process of modernisation and upgrading like other major ports in the country. Bringing in bigger vessels need deeper navigational channels and consequent need to identify alternate dumping grounds for dredged silt which do not send the silt back to the channels and which provide for economy in operational costs.

The port requested the Bhabha Atomic Research Centre to carry out a radioisotope tracer study to investigate the suitability of a site north of the fishing harbour for dumping dredged silt and whether such dumping would aid beach replenishment.

The BARC had already accumulated large experience with over 35 such studies in almost all major ports along the Indian coastline. The radiotracer used in Madras was scandium-46 labelled glass powder matching the grain size

distribution and specific gravity of the natural sediment. After depositing the tracer on the sea bed at the point of interest, movement of the tracer was followed at regular intervals, using special underwater nuclear detectors. Interpretation of the tracer data indicated that -

- a) the sediment moved Southwards during the Northeast monsoon and the direction reversed in March.
- b) beach replenishment was possible.

In short, the radioisotope survey confirmed the suitability of the selected dumping site.

Chilla Hydel Channel

This waterway in the Garhwal Himalayas feeds the Chilla Power Station near Rishikesh. Immediately after commissioning, several springs were noticed on the right bank between the channel and the Ganga river. The lining of the channel was suspected to have failed and an isotope investigation was requested.

The water in the channel from the Veerabhadra Barage was derived from higher altitudes in the Himalayas and hence had a depleted heavier stable isotope composition compared to the local groundwater near the springs. A comparison of the isotopic compositions of the channel water, spring water and groundwater was undertaken. It could be unambiguously shown that the channel was sound and not seeping and the springs were the result of the hydrostatic pressure of the channel on shallow groundwater coupled with lowered ground level due to the earthwork during construction.

This is a typical example of the simplicity of the isotopic approach to a problem which would have no easy solution otherwise.

Groundwaters in Western Rajasthan

Any investigation on groundwater resources in the arid regions of Rajasthan would have to try and answer the question whether the resources are presently receiving recharge either from rainfall or by any other means. If so, how much and if not, when did the last replenishment occur? These are not easy questions to answer without isotope help.

The Bhabha Atomic Research Centre analysed shallow and deep groundwaters at Jalore, Barmer and Bikaner for stable isotopic compositions and for tritium and carbon-14 levels. In all the cases, deep groundwaters show depletion in heavier stable isotope content compared to present day rain water indicating that the replenishment occurred during an earlier pluvial episode, that is when Western Rajasthan was not arid and had substantial rainfall. Tritium is absent in these waters and carbon-14 levels are so low that they indicate an age of several thousands of years. Shallow groundwaters near river courses alone show some enrichment in deuterium and oxygen-18 indicating possible recharge to shallow groundwater from flash floods in the water courses.

The BARC also tried an injected tracer technique to follow the downward transport of soil moisture to look for any possible recharge from the present day rainfall. No such recharge process has been detected indicating that the rainfall is normally too meagre to have any influence on groundwater recharge.

Groundwater Salinisation and Recharge in Midnapore, West Bengal

In the Midnapore district, groundwater occurs in three distinct zones; saline in some areas, fresh in some others without any apparent relation zone-wise or to distance from the sea. At the request of West Bengal authorities, BARC conducted an isotope investigation to understand the salinisation processes and to identify the area of recharge.

Analyses of Midnapore groundwaters for isotopes and chemical ion species followed by interpretation along with geological and geohydrological data indicate that -

- there is only one limited present day sea water intrusion into the coastal groundwaters.
- Salinity in most places is due to past sea water entrapped in the sediments.
- the effect of saline river channels on the salinity in the top zone groundwaters is evident and
- the recharge to the groundwaters occurs in the rock outcrops in the northern part of Midnapore district.

In addition to the examples given above, isotope techniques have been applied to a host of other problems which include

- investigations on seepage conditions in Srisailem and Sathnala dams in Andhra Pradesh, Bhadra and Supa dams in Karnataka, Aliyar dam in Tamil Nadu, Kadana dam in Gujarat as well as Poip and Dimbhe in Maharashtra.
- estimation of beneficial effect of seven percolation tanks in Maharashtra (a very important component of minor irrigation schemes and rural development programmes).
- identification of sites where Ganga river loses to or gains water from the ground in the Harwar-Narora sector and quantification of such loss or gain.
- study of sea water intrusion into coastal Minjur aquifer near Madras leading to the conclusion, among other things, that past salt pan activity on the Madras coast was responsible for pockets of hypersaline water (groundwater more saline than sea water).
- investigation on the salinisation mechanisms in the shallow and deep groundwaters in Haryana.
- recent studies on sediment transport off Karwar coast for Project Sea Bird and in the ports of Calcutta, Mangalore and Kandla.
- flow measurements in many rivers and canals including Tapi and Beas rivers and Ganga Canal.
- estimation of seepage losses from unlined Ganga canal near Roorkee.
- identification of direction of transport of deep geothermal waters in the Manikaran geothermal field in Himachal Pradesh and also the study on the mixing of deep geothermal waters with shallow cold waters, in Tattapani geothermal area in Madhya Pradesh.

Well, no further proof may be necessary that nuclear science and water resources are not after all such an odd combination. You may also agree that it is in fact a natural alliance and is already indispensable in our quest for better water resources management.

Isotope Geology



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Introduction

Isotopic abundances of elements in geological and cosmological substances carry finger print information and tell tale signatures of their origin and processes of formation. The investigations of rocks and their constituent minerals and of ores with respect to variations in isotopic composition have helped in estimating the time periods elapsed since their occurrence or formation. This possibility led to the development of geochronology, another fascinating branch of isotope geology. Methods and techniques used for this purpose are termed dating. The purpose of this article is to give a brief description of different dating methods available which can be used to date a given geological specimen or fossil and estimate its age ranging between a few 100 years and the age of the earth (4.5×10^9 years).

Dating Methods

A number of dating methods are available at the disposal of geoscientist. These include the radioactive dating methods as well as more conventional non-radioactive methods such as tree ring counting method (dendrochronology), amino acid racemisation. A brief description of some of the dating techniques follows.

Radioactive Dating

This type of dating technique utilises the radioactive decay of certain long-lived, naturally occurring isotopes of elements to stable daughter products. At times even the spontaneous fission of an isotope of a heavy element such as uranium-238

can also be used for dating. Radiometric methods are the most accurate dating methods.

All radiometric dating methods are based on the general formula for the decay of a radioactive isotope with its characteristic half-life. ^{147}Sm , for example, decays with a half-life ($t_{1/2}$) of 1.1×10^{11} years to ^{143}Nd . The total number of ^{143}Nd atoms present in a typical rare earth bearing rock sample is given by

$$(^{143}\text{Nd})_t = (^{143}\text{Nd})_0 + (^{147}\text{Sm})_t(e^{\lambda t} - 1)$$

where λ is the decay constant of ^{147}Sm ($\lambda = 0.693/t_{1/2}$) and $(^{143}\text{Nd})_0$ is the number of atoms at $t=0$ (present initially)

Dividing through out by ^{144}Nd atoms, we have

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

We thus need to determine $^{143}\text{Nd}/^{144}\text{Nd}$ atom ratio and ^{147}Sm and ^{144}Nd atoms in the given amount of rock or mineral sample. A plot of $^{143}\text{Nd}/^{144}\text{Nd}$ atom ratio Vs. $^{147}\text{Sm}/^{144}\text{Nd}$ atom ratio from a given amount of specimen results in a straight line with intercept equal to initial $(^{143}\text{Nd}/^{144}\text{Nd})$ at $t = 0$ and the slope equal to $e^{\lambda t} - 1$ from which it is possible to calculate t , the age of the mineral or rock. Mass spectrometry is invariably employed to determine the isotopic ratios. For concentration determination, isotope dilution mass spectrometry or even conventional analytical techniques are used.

An important requirement for dating is that the system must remain isolated from the time it forms until the measurements are made. Any gain or loss of either parent or daughter will result in an incorrect

value for t . Ideally all minerals of a rock should indicate the same date which can be regarded as the age of the rock. The data from all rock samples belonging to a suite of cogenetic rocks generally fall on a straight line which is called "Isochron". When mineral dates obtained from one rock specimen or from a suite of cogenetic rocks are in agreement, they are said to be concordant otherwise discordant.

Table. Suitable radionuclides for dating techniques.

Nuclide	Origin	Half-life (y)
H-3	Cosmogenic and man-made	17.3
Be-10	Cosmogenic	2.7×10^6
C-14	Cosmogenic and man-made	5730
Na-22	Cosmogenic	2.6
Al-26	Cosmogenic	7.4×10^5
Si-32	Cosmogenic	650
Cl-36	Cosmogenic	3.07×10^5
Ar-39	Cosmogenic	269
K-40	Primordial	1.3×10^9
Rb-87	Primordial	5×10^{10}
I-129	Primordial	1.6×10^6
Sm-147	Primordial	1.1×10^{11}
Lu-176	Primordial	3.5×10^{10}
Re-187	Primordial	4.3×10^{10}
Pb-210	Radiogenic	22
Pa-231	Radiogenic	3.2×10^4
Th-232	Primordial	1.4×10^{10}
U-234	Radiogenic	2.5×10^5
U-235	Primordial	7.1×10^8
U-238	Primordial	4.5×10^9

Widely employed dating techniques are briefly described below :

K-Ar dating

The K-Ar method of dating is based on the decay of naturally occurring ^{40}K to stable ^{40}Ar . Established methods such as flame photometry, atomic absorption spectrometry, isotope dilution, neutron activation have been employed for the determination of potassium. For ^{40}Ar determination, isotope dilution is employed. K-Ar dating method has been quite useful in the case of volcanic and metamorphic rocks and minerals such as feldspar, biotite, muscovite, and hornblende. K-Ar dates derived from young volcanic rocks have been used to construct a time scale for reversals of the earth's magnetic field. Dating of basalt from the floor of the oceans and the interpretation of magnetic anomaly patterns in the ocean basins have provided direct evidence for sea floor spreading and the resulting drift of continents. As a complement to K-Ar dating, $^{40}\text{Ar}/^{39}\text{Ar}$ method of dating can be used. This is based on production of ^{39}Ar from ^{39}K by an (n,p) reaction during neutron irradiation. The age of a specimen is then given by

$$t = \frac{1}{\lambda} \ln \left[\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} J + 1 \right]$$

where λ is total decay constant of ^{40}K and J is a parameter related to neutron flux density and capture cross section for $^{39}\text{K}(n,p)^{39}\text{Ar}$ reaction. The value of J is determined by a flux monitor of known age. The ^{39}Ar abundance needs corrections for interfering nuclear reactions with isotopes of calcium, potassium, argon and chlorine. The advantages of this method of dating are (i) it needs only the measurement of isotopic ratios of argon. Separate determination of potassium concentration is eliminated, (ii) argon can be released partially by step-wise heating of irradiated samples. In this way, a spectrum of dates can be calculated from the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of each fraction indicating the time of metamorphism and the time of initial cooling or crystallisation. The range of applicability is from 1,00,000 years to the age of the earth (4.5×10^9 years).

Rb-Sr dating

The Rb-Sr method of dating is based on the decay of naturally occurring ^{87}Rb to stable ^{87}Sr . It is applied to igneous and metamorphic rocks and minerals and the method is applicable only to those minerals with a large Rb value and significantly less Sr, so that initial Sr is negligible. Most commonly, Rb-Sr method is applied by using the isochron technique. This isochron technique requires isotopic analysis of three or more minerals from the same rock or of three or more cogenetic rocks. Sr-87/Sr-86 Vs. Rb-87/Sr-86 plot forms an isochron, whose slope is a direct function of the age. The range of applicability is 5×10^7 years to the age of the earth.

Dating with lead isotopes

The third widely used geological dating method is actually a family of methods based on the decay of U and Th to stable isotopes of lead. These are used on minerals such as zircon that contains a relatively large amount of uranium but negligible amount of lead. The most common of these schemes is based on the U-238 and U-235 decays resulting in stable daughter products of ^{206}Pb and ^{207}Pb respectively. In this method, the Pb-206/U-238 and Pb-207/U-235 ratios plot on a curved line known as concordia. The position of the point on concordia depends only on the age of the sample. This method also works on samples that lost lead due to postformational heating, a common phenomenon in many metamorphic rocks. In such rocks the method yields both the age of formation and the age of reheating. The effect of lead loss on U-Pb dates can be minimised by calculating a date based on $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. This ratio is insensitive to lead loss. Another advantage of this method of dating is that only the lead isotopic ratios need be measured and there is no need to determine separately lead and uranium concentrations. However, graphical methods are needed to arrive at the ages as the dating equation $^{207}\text{Pb}/^{206}\text{Pb}$ is transcendental. The range of applicability is from about 10^8 years to the age of the earth.

The U-series disequilibrium methods of dating

The decay chains formed by U-238 and U-235 are broken by geological processes because the daughters of uranium are isotopes of different

elements and therefore have different geochemical properties. The resulting radioactive disequilibrium can be used for dating over time periods ranging from a few tens of years or less to one million years or more. These geochronometers therefore provide information about the earth's history during the last million years. The disequilibrium methods of dating have been most useful in the study of sediment and calcium carbonate deposited in the oceans and in lakes. The relevant geochronometers are based on measurements of the activity ratios of $^{230}\text{Th}/^{232}\text{Th}$ (Ionium method), $^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{238}\text{U}$, and $^{230}\text{Tl}/^{234}\text{U}$. Another daughter in the decay series of U namely ^{210}Pb is useful in dating snow and ice and marine and lacustrine sediment deposits.

Sm-Nd, Re-Os, Lu-Hf methods of dating

The $^{147}\text{Sm}-^{143}\text{Nd}$ couple has recently attracted the attention of geochronologists and is useful in the case of granite and ultramafic rocks. The Re-Os method has been used to date iron meteorites which cannot be dated by other methods. This method was also used for molybdenites and sulphide ore deposits. The Lu-Hf is useful for dating certain Lu bearing minerals such as apatite, garnet, and monazite.

Carbon-14 method of dating

The carbon-14 method of dating, which was developed around 1950 by W. Libby is based on measurement of the activity of ^{14}C in carbon bearing materials that originally were in communication with CO_2 gas of the atmosphere. Carbon-14 is produced in the atmosphere by the interaction of cosmic ray produced neutrons and ^{14}N and forms $^{14}\text{CO}_2$ which is rapidly mixed through out the atmosphere. This atmospheric CO_2 containing ^{14}C is absorbed by the plants during photosynthesis and absorption by roots. The concentrations of ^{14}C in living plants is maintained constant by its continuous absorption and decay. When the plant dies, the activity due to ^{14}C decreases with a characteristic half life of 5730 years. In actual practice, the carbon content of the specimen is converted into CO_2 or any suitable gas (methane or acetylene) which is then counted in a well shielded counting arrangement. The age is calculated using the formula

$$t = 8.265 \times 10^3 \ln \frac{A_0}{A}$$

where A_0 is the initial equilibrium activity of ^{14}C (13.56 dpm/g of C) when the plant was alive and A is the measured activity. It is customary to express the ^{14}C ages in terms of years before the present (B.P.) where the present is taken to be 1950. With ^{14}C dating it is possible to calculate ages of 60,000 years. With accelerator mass spectrometric technique, this date can be pushed back well beyond 1,00,000 years into the past.

Fission track method of dating

When charged particles travel through a solid medium, they leave a trail of damage resulting from the transfer of energy from the particle to the atoms of the medium. Price and Walker showed that fission tracks in natural minerals are due primarily to spontaneous fission of ^{238}U and proposed that the density of such tracks could be used to date samples of biotite, phlogopite, muscovite and lapidolite minerals. In order to date a specimen of glass or mineral by this method, an interior surface is exposed by grinding which is then polished and etched with a suitable solvent under appropriate conditions. After etching, the polished surface is examined with a petrographic microscope equipped with a flat-filed eyepiece with a graticule to permit counting of tracks in a known area. Fission tracks are readily distinguished by their characteristic tubular shape from other etch pits that result from interferences or other causes. The observed track density (no. of tracks/cm²) is related to length of the time during which tracks have accumulated and to the uranium concentration of the specimen. In actual procedure, two samples from the mineral to be dated are taken. From the first sample, the spontaneous fission track density due to U-238 is measured. From the second specimen, the spontaneous tracks are destroyed by heating to cause annealing. The specimen is then exposed to thermal neutrons in a nuclear reactor in order to produce new tracks by induced fission of U-235. The age equation is then written as

$$t = 6.446 \times 10^9 \ln \left[1 + 7.744 \times 10^{-18} \left[\frac{p_s}{p_i} \right] \phi \right]$$

where p_s = spontaneous fission track density, p_i = induced fission track density and ϕ = neutron flux (neutrons/cm²).

With fission track method, measurements are possible even on minute specimens such as chips of meteoritic minerals or fragments of glass from the ocean bottom. This method is now widely used for dating a variety of minerals and both natural and synthetic glass. It is especially applicable to relatively young samples (ages $< = 500$ million years) that have not been reheated since the time of their formation and is therefore of potential interest in archeology and geology. This allows fission track dating to fill the gap that previously existed between the upper limit of 50,000 years in which C-14 dating is applicable and the lower limit of roughly 1 million years below which K-Ar dating becomes excessively laborious. This method also provides useful information about the thermal histories of older rocks because the preservation of fission tracks is temperature dependent and different minerals lose their tracks at different temperatures.

Non-radioactive Methods

Non-radioactive methods include dendrochronology and amino acid racemisation and are of historical significance only. Dendrochronology relies on the annual rings produced by the growth of certain trees in subtropical climates. By cutting the tree and counting the number of rings backwards one can get an estimate of age of the specimen. In ideal cases, dendrochronology can take us to about 7000 years into the past. Another technique known as varve counting utilises the supposed annual sediment layers deposited in glacial lakes.

Amino acid dating is a chemical method of dating. With the exception of glycine, the amino acids found in proteins can exist in two isomeric forms called D- and L- enantiomers. Under conditions of equilibrium, equal amounts of both enantiomers are present. It was discovered by L. Pasteur around 1850 that only L- amino acids take part in metabolism in living organisms. Living organisms maintain a state of disequilibrium through a system of enzymes that selectively utilise only L-enantiomers. Once a protein has been synthesised and isolated from active metabolic processes, racemisation reaction sets in.

$$\ln \left[\frac{1+(D/L)}{1-(D/L)} \right] - \ln \left[\frac{1+(D/L)}{1-(D/L)} \right]_{t=0} = 2K_1 t$$

(D/L) is the ratio of the amino acid at time t . $t=0$ term is necessary to account for some racemisation that occurs during sample preparation.

Since racemisation is a chemical process, the extent of racemisation is dependent not only on the time that has elapsed since the L-amino acids were synthesised but also on the exposure temperature; the higher the temperature, the faster the rate of racemisation. For e.g., the half life of racemisation (for D/L to become 0.33) at neutral pH for aspartic acid is 3500 years at 25°C but is only 35 days at 100°C.

A variety of analytical procedures can be used to separate amino acid enantiomers; gas chromatography and HPLC are the most widely used. Samples are first hydrolysed in HCl acid to breakdown the proteins into free amino acids, which are then isolated by cation exchange chromatography.

Geochemical uses of amino acid racemisation include the dating of fossils, or in the case of known age specimens, the determination of their temperature history. Fossil types such as bones, teeth, and shells have been studied, and racemisation has been found to be particularly useful for dating specimens that were difficult to date by other means. These dating methods depend on chemical changes that progress with increasing time. Although the measurements themselves contain no inherent age information, they can yield useful ages if calibrated with quantitative methods. The Olduvai gorge region in the north central Tanzanian rift valley in Africa offered an excellent opportunity to study the racemisation reaction of amino acids in fossil bones and teeth over a time period extending back to several million years.

Instrumental Techniques

Thermal ionisation mass spectrometry (TIMS) has been extensively and invariably employed for determining ages of different minerals and rocks. Atom ratios required for solving the dating equation can be precisely and accurately determined by TIMS even at subppm levels. Isotope dilution in conjunction with TIMS is an established and well recognised technique for precise and accurate concentration measurements. The capability of determining small changes in the isotopic composition and carrying out measurements on subppm amounts of samples makes TIMS an indispensable tool in geochronology. This feature is especially useful in ^{147}Sm - ^{143}Nd couple. Because of very large half life of ^{147}Sm ($\approx 10^{11}$ years), the changes in isotopic composition will be extremely small and the precision and accuracy requirements are at ppm level. TIMS has also been used for dating sulphide ores, and iron meteorites using ^{187}Re - ^{187}Os couple. These ores are not generally amenable to other geochronometers and the difficulties in separating Re and Os to eliminate the isobaric interferences could be overcome by measuring negative ions ReO_4^- and OsO_3^- ions. The advent of accelerator mass spectrometry (AMS), resonance ionisation mass spectrometry (RIMS), and secondary ion mass spectrometry (SIMS) have further extended the scope of isotope geology.

Suggested Reading

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