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Naturally occurring radionuclides and Earth sciences

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Abstract
Naturally occurring radionuclides are used in Earth sciences for two fundamental purposes: age determination of rocks and minerals and studies of variation of the isotopic composition of radiogenic nuclides. The methodologies that are in use today allow us to determine ages spanning from the Earth's age to the late Quaternary. The variations of isotopic composition of radiogenic nuclides can be applied to problems of mantle evolution, magma genesis and characterization with respect to different geodynamic situations and can provide valuable information not obtainable by elemental geochemistry.

Key words *radionuclides – isotopes – geochronology – isotope geochemistry*

1. Introduction

One hundred years after the discovery of radioactivity, hundreds of applications of this phenomenon have been found in numerous different fields of science including Earth sciences. Two major possibilities were offered to this discipline a few decades after the first Becquerel observations of the properties of radioactive substances in 1896. These new fields are isotope geochronology and isotope geochemistry (1); they represent the consequence of the decay of a natural radionuclide in a stable one.

The radioactive decay of a radionuclide P in a stable nuclide D is a time dependent event and in principle this can be used for time measurement; besides, the produced stable nuclide D represents an isotope of a previously existing element and thus the ratio of D to another isotope of the same element (D_i) not produced by radioactive decay will increase with time; from a given initial moment the ratio D/D_i in an isolated (closed) system will increase depending on the ratio P/D_i of the system itself.

The first impact of radioactivity on the Earth sciences was in 1903 with the discovery by Curie and Laborde that radioactive decay was characterized by emission of heat; this fact made Kelvin's calculations of the Earth's age (based on conductive cooling) meaningless, as another source of heat unknown to him, had to be taken into account.

Two years later (1906) Rutherford suggested that radioactivity of U can be used as a geological clock:

«The helium observed in the radioactive minerals is almost certainly due to its production from the radium and other radioactive substances contained therein. If the rate of production of helium from

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(1) These two fields of research, together with the geochemistry of stable isotopes and the study of cosmic ray produced radionuclides, represent what today is called «isotope geology».

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known weights of the different radioelements were experimentally known, it should thus be possible to determine the interval required for the production of the amount of helium observed in radioactive minerals or, in other words, to determine the age of the minerals».

This was the beginning of a series of measurements that rapidly produced a series of ages, still based on chemical ratios, that allowed Holmes in 1927 to write his popular book titled: *The Age of the Earth: an Introduction to Geological Ideas.*

From 1930 to 1950 the discovery of new radioactive elements and the precise measurement of their rate of decay provided new tools for the determination of ages in numerous rocks and minerals. Ages obtained with these new methods were often referred to as «absolute» ages compared to stratigraphic ones. In 1962 in a paper that appeared in Nature with the title *Absolute Age: a Meaningless Term* Holmes wrote:

> ... «An age does not become 'absolute' by virtue of being expressed in units of time such as a year. ... The term is not only redundant and both philosophically and scientifically without meaning: it is also misleading in its psychological suggestion of a higher degree of accuracy that can be justified... When it is desirable, as it sometimes is, to distinguish between geological age and the age expressed in years, the latter (except when measured by counting varves) can appropriately be called the 'radiometric age', a term that has already appeared occasionally in the literature of geochronology».

Thus the term «radiometric age» was used by most of the growing group of geochronologists but Faure in his book: *Principles of Isotope Geology* (1977) rejects this term as a «improper» suggesting the use of isotopic age:

> «Dates calculated from the abundances of radiogenic isotopes are often referred to as 'radiometric' dates. This practice is misleading and should be discouraged because it implies that the date was measured with a radiometer, which is an instrument for measuring the intensity of radiant energy. A more appropriate adjective for such dates might be 'isotopic', which at least suggests that they are based on the abundance of isotopes produced by radioactive decay».

Holmes' and Faure's criticism of the terms «absolute» and «radiometric» age should be considered valid; but up to now these different adjectives are still used by many experts in the field, together with the terms «isotopic» or even «nuclear» age.

2. Isotope geochronology and isotope geochemistry

It is beyond the aim of this paper to the discuss various methodologies and the details of their application; we can only attempt to give some examples of the contribution of these disciplines to the solution of several major problems in the earth sciences, that have been clarified or resolved mostly due to the application of these techniques.

Table I lists the radionuclides most frequently used either as geochronometers or isotopic tracers. In the first case, using the systematics at our disposal, we can assume (perhaps somewhat triumphantly) that any age value from the Earth's age to the late Quaternary can be measured in almost any kind of rock. A number of age determinations obtained on rocks and minerals up to now have been used to solve hundreds of problems of regional geology. They have permitted the construction of an accurate geological time scale and a paleomagnetic scale and have cast light on the problems of continental growth or measured the velocity of continental drift. Besides, isotopic geochronometers represent the only possibility for deciphering the past, because biostratigraphic methods will cease to function in the absence of life forms; biological fossils can be used for the last 700 million years of the Earth's history; geochronometers based on radioactive decay act as isotopic fossils and allow the entire Earth's history to be traced back; it is worth mentioning that lunar chronology as was made possible only by the use of these chronometers.

A schematic view of the major problems of the Earth's evolution is represented in fig. 1 that we can describe starting from the time of the Earth's formation.

Table I. List of the commonly used radioactive/radiogenic pairs in geochemistry and isotopic geochemistry. Except for ^{40}K-^{40}Ca, all the isotopic systematics refer to trace elements. Radiogenic nuclides represented by gases (^{40}Ar and ^{4}He) have not been discussed in the text but they are of major importance for the two fields.

Radioactive nuclide	Radiogenic nuclide	$T½$ 10^9 years	Isotopic ratio	Primeval isotopic composition
^{40}K	^{40}Ca	1.27	$^{40}Ca/^{42}Ca$	151.016 (1)
^{87}Rb	^{87}Sr	48.8	$^{87}Sr/^{86}Sr$	0.698990 (2)
^{147}Sm	^{143}Nd	106	$^{143}Nd/^{144}Nd$	0.506609 (3)
^{176}Lu	^{176}Hf	35.7	$^{176}Hf/^{177}Hf$	0.27978 (4)
^{187}Re	^{187}Os	44	$^{187}Os/^{186}Os$	0.807 (5)
^{232}Th	^{208}Pb	14	$^{208}Pb/^{204}Pb$	29.475 (6)
^{235}U	^{207}Pb	0.70	$^{207}Pb/^{204}Pb$	10.293 (6)
^{238}U	^{206}Pb	4.47	$^{206}Pb/^{204}Pb$	9.3066 (6)

1) Marshall and De Paolo (1982); 2) Papanastassiou and Wasserburg (1969); 3) Jacobson and Wasserburg (1980); 4) Patchett and Tatsumoto (1980); 5) Luck and Allegre (1983); 6) Chen and Wasserburg (1983).

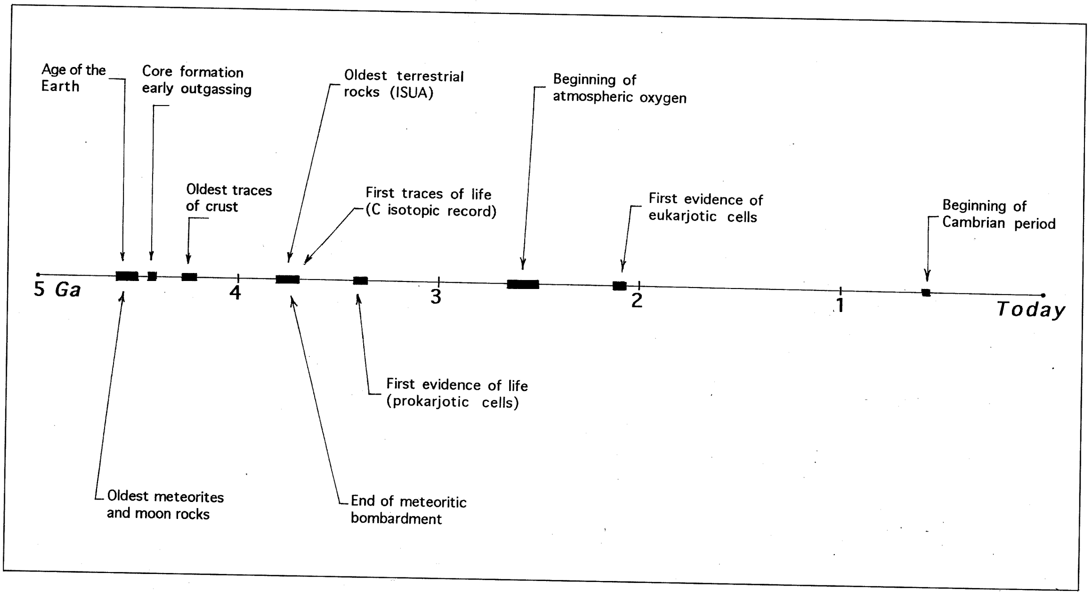

Fig. 1. Time scale of the most relevant events of the Earth's history dated by isotopic methods.

Direct measurement of the age of the Earth is impossible because none of the samples of rocks at our disposal are as old as the Earth itself; and, besides, what is the meaning of «age of the Earth»? Earth was not born instantaneously, but through a series of processes during a finite period of time; so when can we fix the time of its birth? The evidence that we have today suggests that the length of the period of Earth's formation was very short in comparison to the age of the Earth itself. We also have isotopic evidence that the core formation was an event that quickly followed the formation of the Earth, taking a relatively short time; it follows that the first age that we can possibly measure is the moment of iron-silicate separation.

Meteorites are the most important source of data for the determination of the age of the Earth and lead isotopes are the tools that permit this determination. The age of meteorites has been determined with all the isotopic methods in all the classes of these extraterrestrial bodies; the numerous results obtained up to now cluster around 4.5–4.6 Ga and these are the oldest data so far obtained for our solar system; a slightly lower range of values has been obtained for the oldest lunar rocks (4.4 to 4.5); thus, according to the commonly accepted theory of the formation of the solar system, the age of the Earth has to fall in the range of values 4.4 to 4.6 Ga.

Assuming this genetic link between earth and meteorites Patterson (1956), using the isotopic composition of lead from two iron meteorites, three stone meteorites and lead from modern ocean sediments, demonstrated that the data fall in a lead-lead isochron with an age of 4.5 ± 0.07 Ga. With the new decay constants the age will be 4.48 Ga.

Today the best value for the age of the Earth is assumed to be 4.54 Ga and was obtained using lead isotope data from ancient lead ores and from the Canon Diablo troilite. The age of the Earth thus can be defined as the age of the meteorite-Earth system and represents the last time the isotopic composition of lead was uniform throughout the solar system (Dalrymple, 1991). Assuming such an age for the Earth, let us explore what these methods of isotope geochronology can do to unveil the sequence of fundamental events that took place after the birth of the Earth.

All the data have been obtained using one or more methods of isotope geochronology and cannot be obtained in other ways.

The first event that took place after (and during) the Earth's formation was the separation of metallic core from silicate Earth; again, this is not an instantaneous phenomenon but took place at least during the first 100 million years of the Earth's history.

Soon after the core formation, the cooling of the silicatic phase certainly originated some primeval crust or protocrust; at this time we cannot determine any age reference for this event, and the only possible way to follow is the search for and age measurement of the oldest rocks that can be found. The oldest and most extensively studied rocks are the metamorphosed supracrustal rocks of Isua (Western Greenland) that have been dated using all the isotopic methods (Jacobsen and Dymek, 1988; Moorbath *et al.*, 1973, 1975; Moorbath and Whitehouse, 1996).

Ages from 3.7 to 3.8 Ga have been obtained and 3.8 represents the maximum value for the age of a rock formation today. Indirect evidence of the existence of an older differentiated crust (4.1–4.2 Ga) was obtained from zircons found in sedimentary units of Mt. Narriyer in the Ylgarn Archean Block of Western Australia using U/Pb methods with the SHRIMP ion microprobe (Froude *et al.*, 1983). The same type of sedimentary unit (Jak Hills Metasedimentary Belt) furnished zircons which measured with the same technique gave a maximum age of 4.27 Ga (Compston and Pidgeon, 1986). In spite of the fact that the source rocks have not yet been found we can tentatively assume this value (4.27 Ga) as representative of the trace of the oldest crust of the Earth.

The lack of evidence of rocks older than 3.8 Ga is probably due to the fact that at the beginning of the Earth's history the forming protocrust was quickly recycled and consumed into the primitive mantle because of the much more energetic Earth's internal engine, also due to the radioactivity of such short-lived radionuclides as ^{26}Al and ^{244}Pu and the relatively long-lived ^{40}K and ^{235}U. It is assumed that the heat production from radioactive decay in the first hundred million years was about 8 times that of today (O'Nions *et al.*, 1978).

Another interpretation stems from the numerous age data gathered from the lunar rocks.

It is clear from these data that the Moon was subject to an intense meteoritic bombardment that ended at 3.8 Ga; due to its larger gravity field the same event would have involved (with much more intensity) the Earth's surface. The meteoritic bombardment will wipe out any trace of preexisting crust till 3.8 Ga ago; in fact the most realistic possibility is that a combination of the two events was responsible for the lack of existence of a crust older than 3.8 Ga.

Determination of the oldest limit for the crustal rocks is not only necessary for the study of the evolution of the early Earth, but is of paramount importance for the problem of the origin and beginning of life on Earth. It is beyond the scope of this article to discuss such a fundamental problem; again, we only want to show what information can be obtained with the methods of isotopic chronology and isotope geochemistry. The Isua supracrustal (sedimentary and volcanic) rocks have been deposited in shallow marine basins (Moorbat and Whitehouse, 1996) in conditions similar to the sedimentary rocks of Western Australia (3.45 Ga) where preserved microfossils have been discovered in a bedded chert unit (Schopf, 1993). The Isua supracrustal rocks have undergone an intense metamorphic event that has cancelled any possible presence of microfossils. The only indication of the existence of biological activity resides in the carbon isotopic determination (^{13}C/^{12}C).

Schidlowski *et al.* (1979) analyzed the isotopic composition of carbonate samples from the metasedimentary sequence of Isua supracrustal belt as well as kerogens and their graphitic derivatives (Schidlowski, 1998). The most positive data obtained with respect to the expected values for biological carbon have been explained due to the amphibolitic grade metamorphism that took place on the Isua rocks. This interpretation has been challenged (Moorbath, 1994) and a clear conclusion is still subject to debate. Very recently Mojzsis *et al.* (1996) using carbon isotopic data obtained from carbonaceous inclusions within grains of apatite extracted from the banded iron formation of the Isua supracrustal belt, claimed evidence of biological activity 3.8 Ga ago. As the authors state:

> «Unless some unknown abiotic process exists which is able both to create much isotopically light carbon and then selectively incorporate it into apatite grains, our results provide evidence for the emergence of life on Earth at least 3800 Myr before present».

Another basic event in the Earth's history is represented by the appearance of oxygen in the atmosphere; in this case too, determinations of and, possibly, dating this event are very difficult because it is evident that the passage from an anoxygenic to an oxygenate atmosphere has been a long-lasting event. Isotope geochronology can be used to determine the limit of the last anoxygenic period, thus setting a lower limit for the beginning of the oxygenated atmosphere. This has been made possible using U/Pb methods to measure the age of old sedimentary rocks containing uraninite (UO_2) grains, sediments that cannot be formed in the presence of even a low atmospheric oxygen level because UO_2 will be quickly oxidized to exavalent uranium.

The two most studied uranium ores containing uraninite, are Witwatersrand in South Africa and Blind River-Elliot lake (Ontario, Canada). Age measurements with the U/Pb method using ion microprobe give an age of at least 2.5 Ga for the Elliot lake formation setting a limit for the anoxygenic atmosphere.

Another important point for the history of life on Earth is represented by the recent discovery of megascopic eukaryotic algae from an iron formation in Michigan (Han and Runnegar, 1992). The formation was directly dated with the Sm/Nd method (Gerlach *et al.*, 1988) giving an age of 2.11 Ga; these fossils are the oldest known remains of megascopic organisms.

If the first age measurements with «isotopic» methods started very soon after the discovery of natural radioactivity, the possibility of applications of the isotopic variations of radionuclides in Earth sciences had to wait a little longer. The first paper dealing with the interpretation of the variations of isotopic composition of lead in galenas can be considered Nier's classic paper of 1938. For the first time the concept of primeval lead was introduced and reliable and precise lead isotope measurements have been produced.

It was only in the 1950's that the other systematics started to be used due to a substantial refinement in mass spectrometric techniques, that obtained a further notable impulse in view of the analysis of lunar rocks. A new mass spectrometer was developed (Wasserburg *et al.*, 1969) and from then on the improvement of this instrument, which is fundamental for isotopic geology, has reached levels that allow today very small amounts of substance to be measured with a high degree of accuracy.

The time evolution of the isotopic composition of a given radionuclide can schematically be represented in fig. 2, for an ideal system, such as the entire Earth.

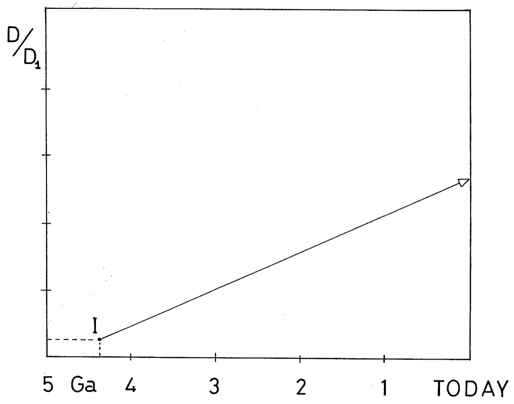

fig. 2

Fig. 2. Evolution line for the isotopic composition D/D_i with time. Starting from a point I (with coordinates age of the Earth-primeval isotopic composition) the ratio D/D_i in a closed system will increase with time with a slope depending on the P/D_i ratio of the system and P decay constraint.

Starting 4.54 Ga ago from an initial primeval isotopic composition $(D/D_i)p$, which represents the isotopic composition of the Earth at the time of its formation, the ratio D/D_i will increase in time up to the present value; the slope of the line, for any given radionuclide, is proportional to the P/D_i ratio of the system. Primeval isotopic compositions are obtained from meteorites; mean chondritic values are also assumed for P/D_i ratios, providing that no fractionation between P and D_i has taken place during the initial stages of the Earth *i.e.*, the high temperature stage and the core formation. These two events do not modify the isotopic compositions but can operate an elemental fractionation from the chondritic ratios due to the different geochemical character of the elements used as geochronometers. If we analyse the geochemical properties of the elements in table I, Sm/Nd and Lu/Hf and Re/Os are refractory elements and their original chondritic ratio will be not affected during the first stage of condensation. On the contrary, Rb is more volatile than Sr and Pb is more volatile than U and Th and this will cause the first elemental fractionation; besides Sm, Nd, Lu and Hf are lithophile elements so the core formation again will not affect their ratios. U and Th are lithophile but, on the contrary, Pb is both calcophile and lithophile and also Rb (and K) can behave as a calcophile if a sulfide phase is present in the core (Murthy and Hall, 1970; Lewis, 1971). In this case the core formation will be another factor of fractionation. Re and Os are strongly siderophile and will be concentrated in the core and depleted in the silicate phase but their ratio will still be chondritic in a silicate Earth. This situation will generate a silicate Earth depleted in Rb and Pb with respect to the chondritic values (fig. 3).

Figure 2 is an oversimplification and cannot represent the true evolution of the Earth's system because the formation of the Earth's crust has operated a substantial differentiation from the initial conditions. The formation of the Earth's crust is a continuous process that cannot be defined with a single age value, but using the data of the most ancient rocks and considering the age data distribution of the oldest rocks (between 3.5 and 2.5 Ga) we can as-

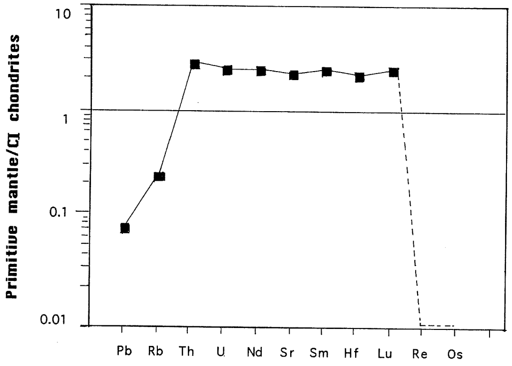

Fig. 3. Chondritic normalized ratios of the primitive mantle for the nuclides used in geochronology and isotope geochemistry. Pb and Rb are depleted with respect to chondrites due to high temperatures at the beginning of the Earth's formation, Re and Os are strongly depleted after the core formation, but preserve their chondritic ratio. Data from the primitive mantle are from Hofmann (1988); data relative to Re and Os in Newsom *et al.* (1986).

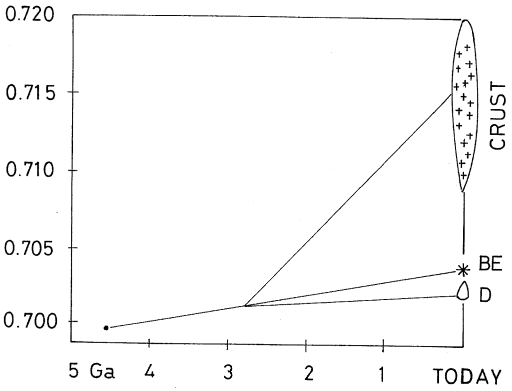

Fig. 4. Evolution of Sr isotopic composition. Starting from an initial point (age at the Earth-primeval Sr isotopic composition), the evolution of the Sr isotopic composition in the Bulk Earth (BE) at present reaches the value of 0.7045, possibly represented by some OIBS. Assuming a crust extraction 2.8 Ga ago, two lines of development are possible: one represents the evolution of the crust (enriched system) pointing to high values of isotopic composition; at the same time the extraction of a differentiated crust produces a depleted reservoir (depleted mantle) source of the MORBS with an isotopic composition of 0.7025.

sume a conventional value of 2.8 for the mean age of the crust formation in order to develop the diagram of fig. 2 more realistically.

Let us consider, for example, the $^{87}Sr/^{86}Sr$ isotopic evolution (fig. 4).

For the age of the Earth we will assume the already previously discussed data of 4.54 Ga; for primeval Sr isotopic composition the value of 0.698990 (BABI) will be used (Papanastassiou and Wasserburg, 1969) and for the silicate Earth a Rb/Sr ratio value is assumed as in Zindler *et al.* (1982). Only the formation of the crust has an effect on the Rb/Sr ratio because of the higher incompatibility of Rb. The Rb/Sr ratio will be higher in the crust resulting in a steeper line for the Sr evolution. At the same time the portion of the mantle from which the crust has been extracted will assume a Rb/Sr ratio lower than the undifferentiated Earth and the evolution line will be less steep than the whole Earth one. Material balance considerations allow us to calculate the amount of mantle involved in the crust evolution. It results that about one third of the total mantle has been used for the formation of continental crust. This leaves two thirds of the mantle with a primitive composition and corresponds to a boundary of 650 km equal to the position of the seismic discontinuity.

At the present time we have three different reservoirs characterized by different $^{87}Sr/^{86}Sr$ ratios. They are: the depleted mantle source of the MORB type basalts with a mean ratio of 0.7025, a primitive mantle, possibly represented by some OIB type basalts with a mean value of 0.7045, and a crust which cannot be represented by a mean Sr isotopic value because of its heterogeneity but which is characterized by high $^{87}Sr/^{86}Sr$ values (in fig. 5 a cartoon depicts how subcrustal magmas are characterized by different Sr/Sr isotopic composition depending on their geological settings). This kind of diagram can be constructed for all the decay schemes of table I taking into account the geochemical behaviour of the different pairs of elements during the formation of the crust. An example of evolution diagram in which the two elements behave in an opposite way to the Rb/Sr with respect to the crust formation is represented in fig. 6 which shows the

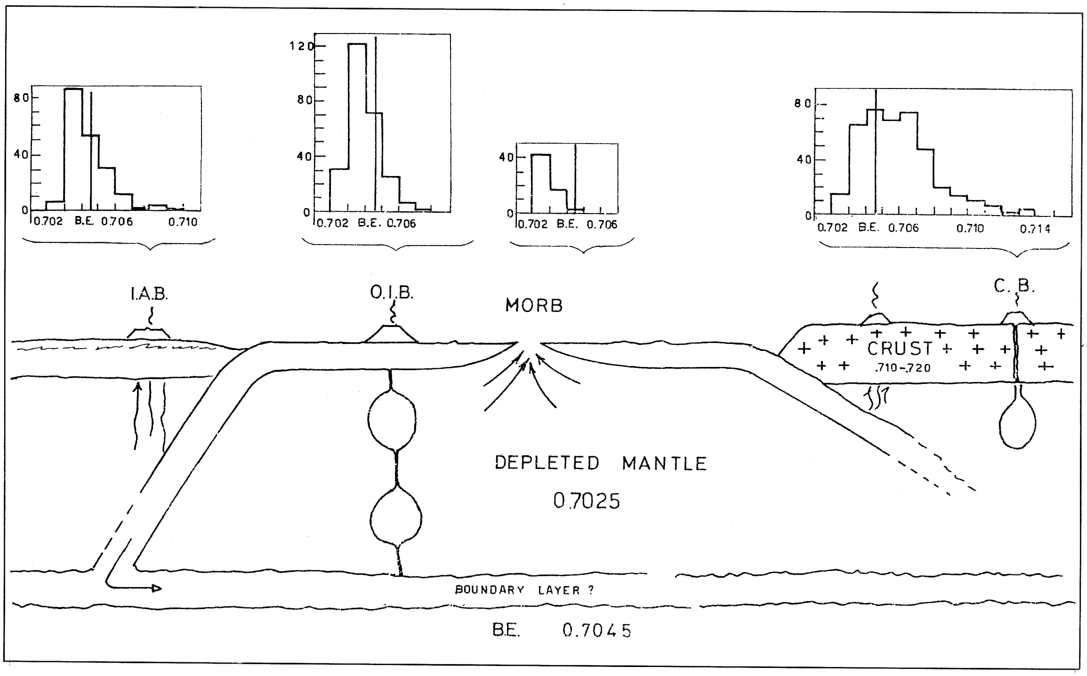

Fig. 5. Variations of $^{87}Sr/^{86}Sr$ ratios of subcrustal magmas in relation to their tectonic settings. MORBS directly derived from depleted mantle show minimum variations of isotopic composition around a mean value of 0.7025. OIBS, possibly derived from undepleted mantle, show a relatively larger spread of values, some lower and some higher than 0.7045. Low values can be interpreted as contamination of blobs of undepleted mantle with depleted MORB reservoir; higher values have recently been interpreted supposing that OIBS magma originates from a boundary layer at the bottom of the upper mantle (White and Hofmann, 1982). This hypothesis explains the OIBS heterogeneity (and especially its shift from values higher than 0.7045) as due to the collection at the boundary layer of different materials such as subduced continental debris and altered oceanic crust. IABS basalts exhibit an even larger variation of Sr isotopic composition that can be interpreted as the consequence of the participation of altered oceanic crust and oceanic sediments to the subduction process. Sea water strontium ($^{87}Sr/^{86}Sr = 0.70906$) is responsible for the higher isotopic composition of the altered oceanic crust; besides oceanic sediments can also have high isotopic composition depending on their nature and origin. Finally, Continental Basalts (CB) show the maximum spread in Sr isotopic composition because of the possibility of crustal contamination during their ascent to the surface through the continental crust. Depending on the age, thickness and composition of the crust, the «en route» contamination can increase the lower original isotopic composition of the CB to values up to 0.714.

isotopic evolution of Nd, another widely used isotopic systematic. The two isotopic systematics can be combined in a unique $^{87}Sr/^{86}Sr$-$^{143}Nd/^{144}Nd$ plot which defines the fields of existence of the three standard reservoirs (fig. 7)(²).

Assuming this standard model of the Earth (Jacobsen and Wasserburg, 1979; Allegre, 1987), the three reservoirs can be modified by two fundamental facts, *i.e.*, differentiation and mixing. Differentiation will modify the Pi/D_i

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(²) The existence of three large scale reservoirs is now in doubt and a more complex situation has been evidenced using different isotopic systematics; Zindler and Hart (1986) have modified this standard model that, in any case, is a useful starting point for the interpretation of the mantle crust history.

ratios but not the isotopic composition D/D_i of the system; mixing will modify both P/D_i and D/D_i ratios. The preservation of the original isotopic composition during the differentiation process makes this parameter unique among all the geochemical tracers; the change of the isotopic composition in a mixing process can be used to define the end members of the mixing event. The geochemical diversity of the different isotopic tracers and the different time constants allow us to tackle basic problems of Earth sciences with completely new tools. Fundamental progress in the knowledge of mantle properties and mantle and crust magma genesis have been made possible only by the use of integrated different radiogenic tracers. Problems of Earth structure and earth dynamics can be solved with these isotopic geochemical techniques, so that large-scale events can be envisaged from the isotopic analysis of very small rock samples.

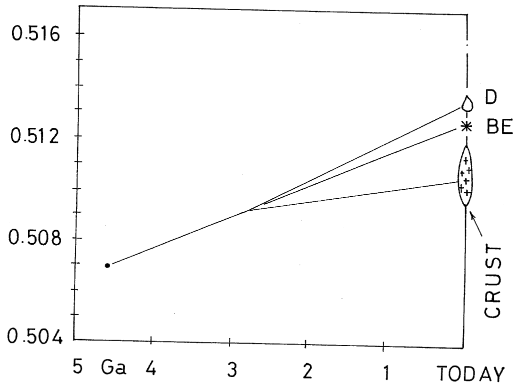

Fig. 6. Evolution of Nd isotopic composition. Starting from the initial parameters (age of the Earth-primeval isotopic composition), the formation of the crust 2.8 Ga ago is characterized by a lower Sm/Nd ratio with respect to the initial BE and lower ^{143}Nd/^{144}Nd ratios which characterize the crustal products, while MORBS are characterized by higher ^{143}Nd/^{144}Nd ratios.

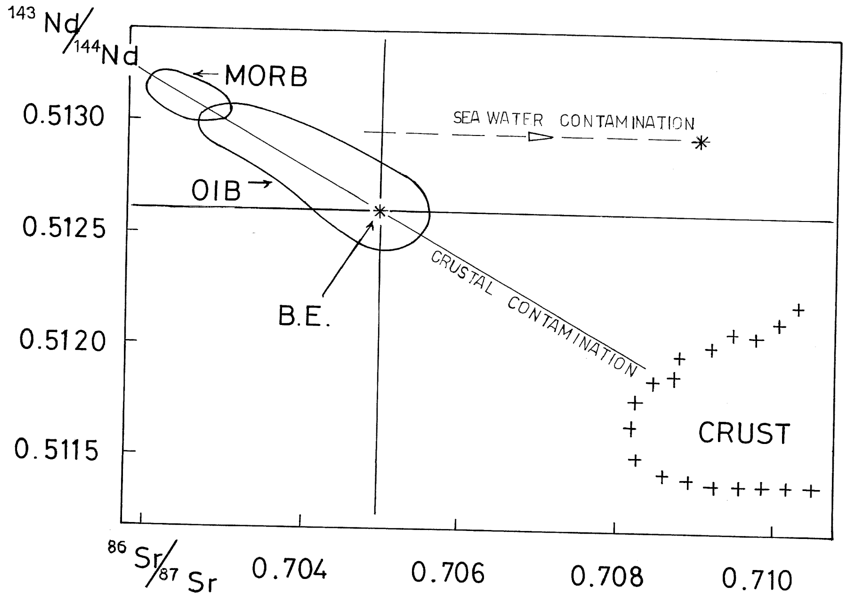

Fig. 7. ^{143}Nd/^{144}Nd *versus* ^{86}Sr/ ^{86}Sr. This diagram shows the position of the three reservoirs previously defined; most of the depleted sources are plotted in the upper left quadrant; crustal rocks are plotted in the lower right quadrant. Effects of sea water contamination or crustal contamination on magmas originated from sub-crustal sources are shown.

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