

INTRODUCTION TO "ISOTOPIC SIGNATURES AND SEDIMENTARY RECORDS"

Urey's (1947) suggestion, that fractionations of oxygen and carbon isotopes between water and shells of different organisms may be used to determine paleotemperatures of ocean waters, marked the dawn of isotope geochemical research on sedimentary deposits. Soon after, Wickman's (1948) proposal of using strontium isotopic data as a means of defining ages for marine chemical sedimentary rocks opened another new frontier of isotopic research on sedimentary rocks. Wickman suggested that as the ^{87}Sr content in the crustal rocks has increased with time due to the decay of ^{87}Rb to ^{87}Sr , the ^{87}Sr content of sea water deriving its Sr from weathering of crustal rocks must have also increased with time. His suggestion implied that the Sr isotopic compositions of those Rb-poor but Sr-rich marine chemical sedimentary rocks, which formed at different times, should reflect the time-dependent increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the ocean waters. Although Wickman's predictions on the magnitude and the trend of the isotopic changes proved to be wrong some twenty years later, the works that followed have led to the development of a presently existing best-estimate Sr isotope-age curve which is being increasingly used for stratigraphic correlations and understanding of the processes of global crustal evolutions.

Since the works of Urey and Wickman, isotopic approaches to studies of geologic phenomena have diversified to new dimensions to produce a large body of knowledge giving a clear identity of a research field that may be called Isotopic Sedimentology, which is the study of evolutions of organic and inorganic sediments, sedimentary rocks, waters and atmosphere from a perspective of isotopic analyses. Isotopic solutions have been a major force in recent

advances to our understanding of such broad questions in the history of sedimentary cycles as:

- Ages of Sedimentary Rocks,
- Physical and Chemical Controls on Changes of Sediments to Sedimentary Rocks,
- Cycling of Sediments in the Continental Crustal Evolution,
- Tectonic and Climatic Controls on Fluxes of Chemical Elements from Different Sources into Oceans,
- Variations in Oceanic and Global Temperatures in the Past,
- Chemical Equilibria of the Present and Past Oceans,
- Evolution of Basinal Waters and their Dissolved Constituents,
- Source of Ore Fluids and Timing of Mineralization of Strata-Bound Ore Deposits,

and others. Increasing numbers of isotopic tools are coming into use providing new evidence for the resolution of these different problems and giving fresh perspectives on the dimensions of these problems. But promises from the use of isotopic tools cannot be fully realized unless the materials to be analyzed are also thoroughly characterized by relevant field, mineralogical, chemical, morphological studies.

A major aspect of the sedimentary cycle involves movements of materials of the lithosphere through many different reservoirs largely under the influence of forces of the hydrosphere, the biosphere and the atmosphere. The processes and products in this dynamic evolution are diverse and complex, and are too numerous to be covered in a single volume of texts. The limitation of space has forced us to be selective in the contents illustrating how isotopic analyses can shed much light on our understanding of these processes and products of the sedimentary cycles.

This book has endeavored to demonstrate for advanced undergraduate and beginning graduate students and interested professional geologists the values of some currently popular methods of isotope analyses in understanding a part of the sedimentary cycle which is governed largely by the interactions between the lithosphere and the hydrosphere. The topics covered here have not been meant to ignore the importance of interactions between any of these two spheres and the biosphere or the atmosphere, as influences of the

biosphere and the atmosphere in many instances are inextricable from processes governed by interactions between the lithosphere and the hydrosphere. The illustrations covered in this book are by no means all encompassing. For example, little or no reference has been made to the use of Pb and Ca isotopes in many of the discussions. Very limited work in these fields is the reason for the lack of coverage in the book, but the coming years will undoubtedly see changes in the scopes of isotopic research on sedimentary materials, as technical innovations for some yet untested methods are already in progress.

As our intent has been to focus on the application of isotopes in problems related to sedimentary systems, the basis of the isotopic principles used in such studies has not been discussed or developed. Several books have discussed rigorously and elegantly on the fundamental principles of different isotopic methods (e.g; Faure, 1986; Valley et al., 1986; Kyser, 1987). We will, therefore, mention briefly only those isotopic principles which have been dealt in this book.

STABLE ISOTOPE COMPOSITIONS

The composition of the stable isotopes of an element in a sample is an expression, which is now followed by almost every laboratory, of the ratio of the abundance of a heavy to that of a light isotope. For example, the hydrogen-isotope composition is taken as the D/H ratio. Similarly, the oxygen-isotope composition is the $^{18}\text{O}/^{16}\text{O}$ ratio, the carbon-isotope composition is the $^{13}\text{C}/^{12}\text{C}$ ratio, and the sulfur isotope composition is the $^{34}\text{S}/^{32}\text{S}$ ratio. As the absolute abundance ratio of the heavy isotope is extremely small relative to that of the light isotope, for which the precision of the ratio measurement is not extremely high, any small difference in the particular isotope compositions among different samples is best described relative to individual differences with some accepted standard substance. This practice of expressing the isotope composition of a substance relative to a standard substance

is now an accepted mode in all investigations of stable isotope analyses. The specific isotope composition of a substance is expressed by its delta (δ) value given in per mil, which is stated as:

$$\delta = ((R_{\text{sample}} / R_{\text{standard}}) - 1) \times 1000,$$

where R is the ratio of the heavy to the light isotopes.

Differences in the physical and chemical properties among the isotopes can lead to varied degrees of partitioning of isotopes among different substances. The isotope ratio between two substances A and B is defined as the isotope fractionation factor α , which is expressed as:

$$\alpha_{A-B} = R_A / R_B$$

Since the R_A and the R_B are also expressed in terms of their δ -values, the fractionation factor α_{A-B} between the two substances is approximately related to the difference between their delta values by the following expression:

$$1000 \ln \alpha_{A-B} = \delta_A - \delta_B$$

Thermodynamic equilibrium factor and kinetic effect are major influences that cause isotope fractionation between two substances. At temperatures in excess of 1000°K the following relationship between fractionation factor and temperature exists:

$$\ln \alpha \approx 1/T^2$$

and consequently:

$$1000 \ln \alpha_{A-B} = C/T^2 + D \text{ or } \delta_A - \delta_B = C/T^2 + D$$

where C and D are constants and T is the temperature in degrees Kelvin. The above expression may be used to determine the temperature of the equilibrium crystallization of a solid phase provided all other parameters for the equation are known and the isotopic

composition of the solid phase was not altered since the equilibrium crystallization.

RADIOGENIC ISOTOPE COMPOSITIONS

The radiogenic isotope composition of an element in a substance is described by the ratio of the abundance of the radiogenic isotope to that of a non-radiogenic (or stable) isotope. For a high precision of the abundance ratio, a non-radiogenic isotope with an abundance not very greatly different from that of the radiogenic isotope, is selected and mass compared to other non-radiogenic isotopes to minimize the effect of analytical mass fractionation. Thus for Ar, the isotopic composition is expressed by $^{40}\text{Ar}/^{36}\text{Ar}$, for Sr by $^{87}\text{Sr}/^{86}\text{Sr}$, for Nd by $^{143}\text{Nd}/^{144}\text{Nd}$, for Pb by $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, and so forth.

The abundances of any radiogenic isotope of an element in sedimentary materials are varied, due to variations in the sources of the materials or in the chemical environments of their formation and in the growth of the radiogenic isotopes from time-dependent natural decay of the radioactive isotopes. The decay controlled growth of a radiogenic isotope is expressed by the well known equation for the decay of the radioactive isotope. The equation for the decay of a radioactive isotope is given as:

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

where N is the number of the radioactive parent isotope present in time t , N_0 is the number of the radioactive isotope present initially, and λ is the decay constant. But this equation cannot be used directly in most instances to calculate the time for geologic materials, as we will never know the value for N_0 . Hence the above equation is modified to express in such a way that we can calculate the value for t when all other parameters are known. The modified expression is given as:

$$D = N_0 - N = N e^{\lambda t} - N = N (e^{\lambda t} - 1)$$

where D is the number of the radiogenic daughter isotope and all other parameters are the same as in the equation above. Both sides of the equation for the growth of radiogenic isotope may be divided by a constant factor, or in this case by a non-radiogenic or stable isotope of the same element as that of the radiogenic isotope, without changing the mathematical relationship. The discussion which follows gives expressions for Ar, Sr and Nd isotopic compositions of natural materials.

The K-Ar Method

The argon isotopes in natural materials consist essentially of ^{36}Ar , ^{38}Ar , and ^{40}Ar . Of these three, the ^{40}Ar is produced from the branched decay (electron capture) of ^{40}K which also decays to produce ^{40}Ca with beta emission. The decay constants for ^{40}K are: $\lambda_{ec} = 0.581 \times 10^{-10} \text{ yr}^{-1}$, and $\lambda_{\text{total}} = 5.543 \times 10^{-10} \text{ yr}^{-1}$. The radiogenic growth of ^{40}Ar is expressed as:

$$^{40}\text{Ar}_{\text{rad}} = (\lambda_{ec} / \lambda_{\text{total}}) ^{40}\text{K} (e^{\lambda t} - 1).$$

The K-Ar age is calculated from the ratio of the radiogenic ^{40}Ar to ^{40}K , after subtracting any atmospheric Ar component. For the calculated age to be geologically meaningful, the sample should not have contained any extraneous ^{40}Ar and must have remained closed to both argon and potassium since the time of its formation.

The Rb-Sr Method

In natural materials, strontium consists of four isotopes: ^{84}Sr , ^{86}Sr , ^{87}Sr , and ^{88}Sr . The isotopic composition of strontium in natural materials is described by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. As ^{87}Rb , one of the two isotopes of rubidium in natural materials and the other being ^{85}Rb , decays with beta emission to produce ^{87}Sr , the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of natural materials are varied. The decay constant of ^{87}Rb is considered to be $1.42 \times 10^{-11} \text{ yr}^{-1}$. Following the common mode of

expression for the growth of radiogenic isotopic composition of an element, the growth of the radiogenic Sr is given as:

$$(^{87}\text{Sr}/^{86}\text{Sr}) = (^{87}\text{Rb}/^{86}\text{Sr}) (e^{\lambda t} - 1)$$

But for an age determination of any natural material which is always likely to contain some amount of strontium at the time of its formation, we must know their initial strontium isotopic composition, in which case the equation for the strontium isotopic composition can be written as:

$$(^{87}\text{Sr}/^{86}\text{Sr})_{\text{total}} = (^{87}\text{Sr}/^{86}\text{Sr})_{\text{initial}} + ^{87}\text{Rb}/^{86}\text{Sr} (e^{\lambda t} - 1)$$

In the absence of knowledge of the initial isotopic composition of any mass of analyzed natural material, the age can be calculated only when different components or minerals of the same material have sufficiently different $^{87}\text{Rb}/^{86}\text{Sr}$ (or Rb/Sr) ratios, but had the same initial $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio. The age can be determined graphically by plotting the analyzed data in the co-ordinates of $^{87}\text{Sr}/^{86}\text{Sr}$ as the Y-axis and $^{87}\text{Rb}/^{86}\text{Sr}$ as the X-axis. A least-square fit of the data gives the best slope of the line from which the age can be calculated (Fig. 1). The line is known as an isochron and the method of calculating an age by such a method is commonly called isochron method.

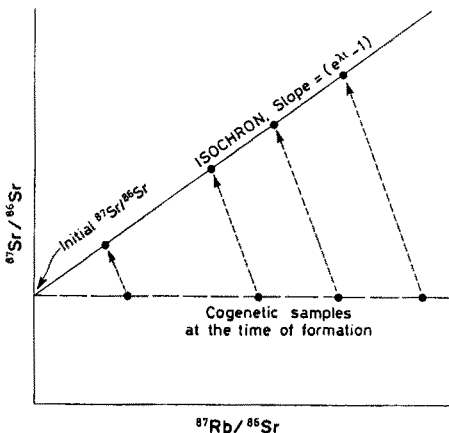


Figure 1: Sketch of a Rb-Sr isochron diagram

The Sm-Nd Method

Samarium and neodymium each has seven isotopes in natural materials. ^{147}Sm decays by alpha emission to ^{143}Nd with a decay constant, λ , of $6.54 \times 10^{-12} \text{ yr}^{-1}$. The isotopic composition of neodymium in a geologic material is expressed by the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, and the growth of the Nd isotopic ratio from the decay of ^{147}Sm through time is expressed by:

$$(^{143}\text{Nd}/^{144}\text{Nd})_{\text{total}} = (^{143}\text{Nd}/^{144}\text{Nd})_{\text{initial}} + (^{147}\text{Sm}/^{144}\text{Nd}) (e^{\lambda t} - 1)$$

Both samarium and neodymium belong to the group of rare-earth elements, and their geochemical behaviors in natural crustal systems are quite similar. Consequently, the Sm/Nd ratios did not fractionate significantly in crustal materials.

The neodymium isotopic composition of the "bulk" earth has been commonly assumed to have evolved in a uniform reservoir whose Sm/Nd ratio is equal to that of chondritic meteorites, and this uniform reservoir is known as the "Chondritic Uniform Reservoir" (CHUR). The present-day ratios of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ for the CHUR are considered to be 0.512638 and 0.1967, respectively, using a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219 for fractionation correction. The differences in Nd isotopic compositions can also be expressed in terms of ϵ -values, which are deviations in parts per 10,000 from the CHUR evolution. The ϵ_{Nd} expression for a sample relative to the CHUR today is as follows:

$$\epsilon_{\text{Nd}}(0) = ((^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1) \times 10^4$$

Positive ϵ_{Nd} values point to mantle-type sources for the samples with Sm/Nd ratios higher than that of CHUR and negative ϵ_{Nd} values indicate that the samples originated from crustal sources with Sm/Nd ratios lower than that of CHUR.

The Sm-Nd isotopic data on sediments can be used to calculate a "model" age for the provenance of the sediments. This "model" age expresses the time when the neodymium in the sediment had the same isotopic ratio as that of the reference reservoir, which could be

the depleted mantle reservoir or the CHUR. Therefore, this model age or so-called crustal residence age is an estimation of how long the Nd of a rock resided in the crust. Model ages are calculated by:

$$t = 1/\lambda \ln [(D_{\text{sample}} - D_{\text{CHUR}}) / (P_{\text{sample}} - P_{\text{CHUR}}) + 1]$$

where D refers to the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, P refers to the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio and subscripts sample and CHUR to the analyzed sample and the CHUR reservoir, respectively.

The U-Th-Pb Method

Naturally occurring materials have three isotopes of uranium: ^{238}U , ^{235}U , and ^{234}U and one isotope of thorium, ^{232}Th , which are all radioactive. Each with a long chain of decays, ^{238}U , ^{235}U , and ^{232}Th are transformed to stable isotopes of ^{206}Pb , ^{207}Pb , and ^{208}Pb , respectively. ^{234}U is an intermediate daughter product in the decay scheme of ^{238}U . The time-dependent growths of lead isotopes from radioactive decays of the uranium and thorium isotopes are expressed as:

$$\begin{aligned} (^{206}\text{Pb}/^{204}\text{Pb}) &= (^{206}\text{Pb}/^{204}\text{Pb})_{\text{initial}} + (^{238}\text{U}/^{204}\text{Pb}) (e^{xt}-1), \\ (^{207}\text{Pb}/^{204}\text{Pb}) &= (^{207}\text{Pb}/^{204}\text{Pb})_{\text{initial}} + (^{235}\text{U}/^{204}\text{Pb}) (e^{yt}-1), \\ (^{208}\text{Pb}/^{204}\text{Pb}) &= (^{208}\text{Pb}/^{204}\text{Pb})_{\text{initial}} + (^{232}\text{Th}/^{204}\text{Pb}) (e^{zt}-1), \end{aligned}$$

where x, y, and z are decay constants of ^{238}U ($1.55125 \times 10^{-10} \text{yr}^{-1}$), ^{235}U ($9.8485 \times 10^{-10} \text{yr}^{-1}$), and ^{232}Th ($4.9475 \times 10^{-10} \text{yr}^{-1}$), respectively.

The equations for the growths of ^{207}Pb and ^{206}Pb may be combined to express the ^{207}Pb - ^{206}Pb equation:

$$(^{207}\text{Pb}/^{206}\text{Pb})_{\text{radiogenic}} = (^{235}\text{U}/^{238}\text{U}) (e^{yt}-1)/(e^{xt}-1)$$

where the ratio of $^{235}\text{U}/^{238}\text{U}$ is a constant with the value of 1/137.88 for terrestrial materials with normal U isotopic composition.

The dating of geologic materials by individual U-Pb isotope

method gives highly discordant ages, probably as a result of differential loss of radiogenic lead during the geologic history of the materials. A reliable age may be obtained by the use of the combined ^{207}Pb - ^{206}Pb data.

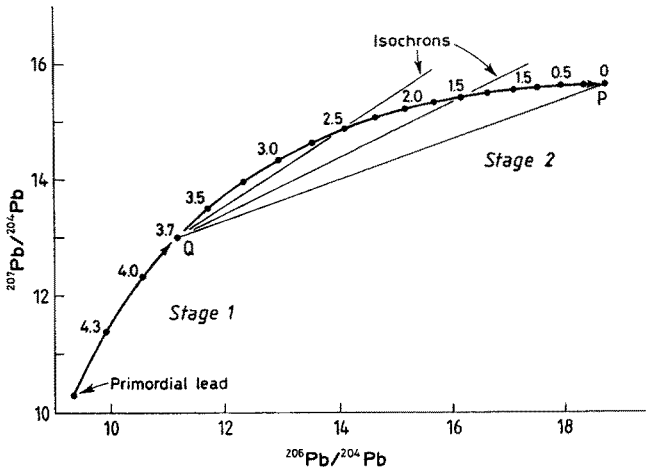


Figure 2: Two-stage evolution of Pb isotopes (Stacey and Kramers, 1975). Stage 1 involves evolution from 4.57 to 3.7 Ga in a reservoir with $^{238}\text{U}/^{204}\text{Pb}$ of 7.192. The evolution then continues from 3.7 Ga, Q, to the Present, P, in a reservoir with $^{238}\text{U}/^{204}\text{Pb}$ changed to 9.735 by chemical differentiation. The straight lines between 3.7 Ga and the Present are isochrons (Adopted from Faure, 1986)

Ore minerals, whose lead has been separated from uranium and thorium at the time of their formation so that their isotopic composition has been conserved, may be dated by one of several models with single or multiple stage evolution which has been proposed for the common lead. A single stage model assumes that the isotopic compositions of common lead in all samples evolved in different environments with different U/Pb and Th/Pb ratios from the same primordial isotopic value at 4.55×10^9 yr until the lead is separated from these different sources to form lead ore minerals. The lead isotopic compositions of different samples of ore deposits would then define an isochron in the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ coordinates, and an age can be calculated from slope of the line. A frequently used multi-stage model is one of two stage evolution model (Stacey and Kramers, 1975) which assumes that the lead evolved first from primordial isotopic value between 4.55 and 3.7 Ga in a reservoir with $^{238}\text{U}/^{204}\text{Pb}$ of 7.19 and $^{232}\text{Th}/^{204}\text{Pb}$ of 32.21,

and then as a result of differentiation at 3.7 Ga, in an reservoir with $^{238}\text{U}/^{204}\text{Pb}$ ratio of 9.735 and $^{232}\text{Th}/^{204}\text{Pb}$ ratio of 36.937 until the leads were separated from these sources. An isochron defined by the $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ data relate to the time elapsed since the lead in a sample was isolated from second reservoir (Fig. 2).

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Sam CHAUDHURI

Norbert CLAUSER