



S T A B L E I S O T O P E A N A L Y S I S

by

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"STABLE ISOTOPES IN HYDROCARBON EXPLORATION"

STABLE ISOTOPE ANALYSIS

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I was asked by the Seminar Committee to present a talk on the general and applied aspects of stable isotope analysis. They felt that the participants wanted a "how to" approach rather than a purely theoretical one. I hope that the talk will satisfy the wishes of the Committee and the audience.

The talk will be divided into five major parts:

- 1) Introduction; 2) Sample handling; 3) Analysis;
- 4) Data processing; 5) Future.

INTRODUCTION

Short history

Stable isotope chemistry is celebrating its fiftieth anniversary this year by the discovery of deuterium. Let us shortly review how isotopes were recognized.

The phenomenon of radioactivity was discovered less than 100 years ago. In the year 1900 Frederick Soddy and Ernest Rutherford suggested that the atoms of radioactive elements disintegrate spontaneously to form atoms of another element.

In 1931 careful determinations by an American chemist T. W. Richards showed that lead produced by the decay of uranium had a different atomic weight than ordinary lead. These problems were solved by a suggestion made by Soddy that the place occupied by a particular element in the periodic table could accommodate more than one kind of atom. He named these atoms "isotopes", which in Greek means "same place".

J. J. Thompson followed these ideas and made the same year observations of neon isotopes by a "positive-ray"

apparatus made by him. His assistant, F. W. Aston, improved Thompson's design and called it a "mass spectrograph". With this instrument Aston discovered 212 of the 287 naturally occurring isotopes.

In 1931 Harold C. Urey predicted on theoretical grounds that there should be a difference in the vapor pressures of the isotopes of hydrogen. The next year, by evaporating about 6 liters of liquid hydrogen, the twice-mass isotope of hydrogen, deuterium, was found 50 years ago by Urey and his coworkers Murphy and Brickwedde (the latter whom I had the pleasure of living next door to for 3 years in USA).

After the 2nd world war Urey turned his attention to the possibility that other stable isotopes may be fractionated by natural processes. His ideas were published in 1947 and started the science of stable isotope geochemistry.





The elements whose isotopes are especially susceptible to natural isotope fractionation are the lighter ones, including hydrogen, carbon, nitrogen, oxygen and sulfur. These are among the most abundant elements in the Earth. Furthermore, they play a major role in chemical reactions in the biosphere, the hydrosphere, and the lithosphere.

Isotope ratios

The four most commonly analysed stable isotopes are those of hydrogen, carbon, oxygen, and sulfur (see Table 1).

In most instances we are not interested in absolute isotope abundances, but rather to compare isotope ratios of a sample with the isotope abundance ratios of the same isotopes of a reference sample. 30 years ago geochemists used to compare the actual isotope ratios. The isotopic

Table 1. Commonly used stable isotopes.

Isotope	Average abundance in nature	Approx. isotope ratio
^1H	99.985 %	 $\frac{7000}{1}$
^2H (= D)	.015 %	
$[^3\text{H}$ (= T)]	radioactive, half-life 12.26 years	
^{12}C	98.89 %	 $\frac{90}{1}$
^{13}C	1.11 %	
$[^{14}\text{C}]$	radioactive, half-life 5730 years	
^{16}O	99.756 %	 $\frac{500}{1}$
^{17}O	.039 %	
^{18}O	.205 %	
^{32}S	95.02 %	 $\frac{22.57}{1}$
^{33}S	.75 %	
^{34}S	4.21 %	
^{36}S	.02 %	

ratios show fairly small variations in nature. It also became necessary to compare the measured isotope ratios versus an international "standard" or "reference sample".

Therefore the stable isotope ratios (R) are now expressed in the delta-notation:

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \cdot 1000 \text{ (o/oo)}$$

The isotope ratio R is now always written as the ratio of the heavy (rare) isotope to the light (common) isotope, i.e. $\delta(^{18}\text{O}/^{16}\text{O})$, or often expressed as $\delta^{18}\text{O}$, and so forth.

Negative δ values then indicate that the sample is depleted in the heavy isotope relative to the "standard".

"Standards" (reference samples)

While the precision of stable isotope analysis is good, the accuracy of our analyses may not be that good when compared with laboratories elsewhere in the world. The reason for such relative small discrepancies arise from problems with standardization.

An international standard used as the zero-point for a scale of isotope ratios should be easily available in relatively large amounts, be homogenous in composition, be easy to handle for chemical preparation, and have an isotopic ratio near the middle of the natural variation range. Among the reference samples now used relatively few meet all these requirements.

The internationally adopted reference sample for carbon- and oxygen isotope ratios is "PDB", Pee Dee Belemnite. The supply of this standard was exhausted long time ago.

It was a sample of Cretaceous belemnite (Belemnitella Americana) guard from the Peedee Formation in North Carolina. Note that the standard is the solid carbonate, not its acid-liberated CO₂. In the oxygen isotope analysis of carbonates it is important that identical physical and chemical conditions must be operative during preparation of "standard" and sample so that systematic errors will cancel. The reason for this is that only 2/3 of the carbonate's oxygen is released with the CO₂ during acid dissolution.

The internationally adopted standard for oxygen- and hydrogen isotope ratios is "SMOW", Standard Mean Ocean Water. It was originally a hypothetical water sample with isotope ratios of oxygen and hydrogen similar to those of an average sample of ocean water. It was defined in terms of a National Bureau of Standards reference water sample, NBS-1. Later two additional SMOW standards have appeared. Taylor and Epstein at California Institute of Technology established their own SMOW lot, while a large quantity of "V-SMOW" was prepared by the International Atomic Energy Agency in Vienna. This latter reference sample has a ¹⁸O value of 0.00 ± 0.05 o/oo, which is within the limits of analytical uncertainty. Inhomogeneities (resulting from different degrees of vaporization?) have been found for the NBS-1 and V-SMOW standards with respect to hydrogen isotope ratios. Another hydrogen isotope reference sample called "SLAP" (Standard Light Antarctic Precipitation) is also frequently used when working with samples showing light hydrogen isotope ratios.

The internationally adopted standard for sulfur-isotope ratios is "CDT", the Canyon Diablo meteorite's iron sulfide

troilite.

In most cases the samples with unknown isotope ratios are not analysed directly against the internationally adopted standard. Instead the samples are analysed against a "working standard" with a precisely determined isotope ratio. The sample's delta-value can now be determined versus the "working standard" on a scale defined by the latter. To obtain the sample's delta-value on the international standard's scale one can use the expression

$$\delta_{\text{samp(STD)}} = \delta_{\text{samp(WS)}} + \delta_{\text{WS(STD)}} + (\delta_{\text{samp(WS)}} \cdot \delta_{\text{WS(STD)}} / 1000)$$

where $\delta_{\text{samp(STD)}}$ and $\delta_{\text{WS(STD)}}$ are the deltas of the sample and the working standard, respectively, on the international standard's scale; $\delta_{\text{samp(WS)}}$ is the delta of the sample on the working standard's scale.

It is also desirable from time to time to compare oxygen isotope ratios on the PDB and SMOW scales. The relationship between these two standard's scales is governed by the chemical equilibrium fractionation factors between CO₂ and water, for phosphoric-acid-liberated CO₂ from the carbonate in question, and for the standard PDB in equilibrium with SMOW, all at a given temperature.

These relationships are for calcite based on the following fractionation factors at 25°C: 1.0412 for CO₂ - H₂O; 1.01025 for H₃PO₄-liberated CO₂ from calcite; 1.00022 for H₃PO₄-liberated CO₂ from PDB-CO₂ in equilibrium with SMOW (Friedman & O'Neil, 1977):

$$\delta_{\text{samp(SMOW)}}^{18\text{O}} = (1.03086 \cdot \delta_{\text{samp(PDB)}}^{18\text{O}}) + 30.86$$

$$\delta_{\text{samp(PDB)}}^{18\text{O}} = (0.97006 \cdot \delta_{\text{samp(SMOW)}}^{18\text{O}}) - 29.94$$

Many stable isotope geochemists still use 1.0407 for

CO₂-H₂O giving slightly different numeric relations:

$$\delta^{18}\text{O}_{\text{samp(SMOW)}} = (1.03037 \cdot \delta^{18}\text{O}_{\text{samp(PDB)}}) + 30.37$$

$$\delta^{18}\text{O}_{\text{samp(PDB)}} = (0.97053 \cdot \delta^{18}\text{O}_{\text{samp(SMOW)}}) - 29.47$$

Isotope fractionation

Differences in atomic mass of an element causes its compounds to have differences in chemical and physical properties. Table 2 shows some characteristic properties of water; H_2^{16}O , D_2^{16}O , and H_2^{18}O .

Such differences in physicochemical properties of isotopes are a consequence of quantum mechanical effects. The vibrational frequency of a molecule depends inversely on the masses of the atoms in a molecule. Hence the chemical bonds formed by the light isotope are weaker than the bonds involving the heavy isotope. During chemical reactions, therefore, the molecules of the light isotope will tend to react slightly more readily than those of the heavy isotope. This is an example on how the isotopes may be fractionated by a chemical reaction, but isotope effects will also occur at phase-transitions, like for the liquid/vapor-transition, and at simple isotopic exchange reactions.

For chemical reactions and phase transitions between two phases there will, in most cases, be an isotopic exchange-equilibrium established between them. The equilibrium fractionation factor α is defined as the ratio of the numbers of any two isotopes in one phase divided by the corresponding ratio for another phase. It should at this point, however, be noted that kinetic effects of the chemical reactions or phase transitions operate and modify our concept of the simple equilibrium approach.

The equilibrium fractionation factor is dependent on temperature. Isotope fractionation in nature is then in

Table 2. Characteristic properties of water (after Hoefs, 1980).

Properties	H_2^{16}O	D_2^{16}O	H_2^{18}O
Density (20°C, g/cm ³)	0.9979	1.1051	1.1106
Temperature of greatest density	3.98	11.24	4.30°C
Melting point (760 Torr)	0.00	3.81	0.28°C
Boiling point (760 Torr)	100.00	101.42	100.14°C
Vapor pressure (100°C, Torr)	760.00	721.60	
Viscosity (20°C, centipoise)	1.002	1.247	1.056

many cases interpretable in terms of environmental temperatures.

In addition to geothermometry the isotope ratios can be used with great success in the genetic research of geological processes. If the environmental temperature is known the isotope ratios of the reactants can be calculated from the knowledge of the isotope ratios of the products and the equilibrium fractionation factors, assuming equilibrium conditions.

SAMPLE HANDLING

Sampling

As we have seen the isotopic differences between samples to be analysed are often extremely small. Furthermore, the samples used in the analyses are also quite small, samples weighing in the 5 to 40 mg range are commonly used as starting material.

Therefore, great care has to be taken to avoid any isotope fractionation during chemical or physical treatment of the sample. Many different preparation techniques are used, but they have one thing in common: they must give a yield of 100%, which should be checked for each and every sample. Since different isotopic species have different reaction rates a yield less than 100% may indicate that the reaction product is isotopically different from the original specimen.

Contamination is the next thing we want to avoid. This may result from incomplete evacuation of the vacuum system.

Other sources of unwanted isotope exchange should also be avoided, such as degassing, isotope exchange with water, vapor, atmosphere, etc.

Of course the type of sample that we choose for analysis is extremely important, if we want to use the data most efficiently. The isotope analysis should be preceded by careful mineralogical investigation, grinding, homogenization or (instead) mineral separation, or chemical purification. One often finds that the pre-treatment of the sample involves, say, 5 to 10 times more work than the mass spectrometric isotope analysis.

Gas separation, purification, vacuum lines

In general, this is the story of the hot and cold. The samples are often led to react at very high temperatures (up to more than 1000°C) and the gases trapped (condensed) at very low temperatures (as low as -196°C). The gas separation and purifications are most often done in vacuum lines, made out of material that will withstand the conditions we apply to the samples. Such vacuum lines are often made out of metal (stainless steel or nickel) or glass. The vacuum is often of the order of 10^{-4} Torr obtained with mechanical plus diffusion vacuum pumps and adequate vacuum monitoring systems such as vacuum gauges and manometers.

The analysis of D/H ratios is usually performed on hydrogen gas. Water is converted to hydrogen by passage over hot zinc or hot uranium. Hydrogen and water in silicate minerals can be released by heating the sample in vacuum inside an induction furnace. The hydrogen gas can first be converted to water by reaction with hot cupric oxide, and

then all water be converted to hydrogen as described earlier.

The analysis of $^{13}\text{C}/^{12}\text{C}$ ratios is done on carbon dioxide gas. Carbonates are reacted with 100% phosphoric acid, normally at 25°C . Calcite is usually left to react for a day, dolomite 3 days, magnesite and siderite about a week. Organic compounds or reduced-carbon compounds are generally oxidized at 1000°C in a stream of oxygen or by an oxidizing agent like cupric oxide. Adjoining sulfur, halogens and nitrogen are removed by leading the liberated gas through hot silver wires, hot copper, hot manganese dioxide, and finally hot lead dioxide.

The analysis of $^{18}\text{O}/^{16}\text{O}$ ratios is also done on carbon dioxide gas. Carbonates was mentioned earlier. Sulfates are reduced at 1000°C with carbon to CO_2 and CO . The CO is converted to CO_2 by sparking between platinum electrodes. Oxides and silicates are usually fluorinated with fluorine or bromine pentafluoride at $500 - 600^{\circ}\text{C}$ in nickel vessels for a day. The released oxygen gas is then being converted to CO_2 by reacting it with hot graphite. Water can also be prepared by the CO_2 - water equilibration technique at 25°C .

The analysis of $^{34}\text{S}/^{32}\text{S}$ ratios is usually done on sulfur dioxide gas. Some are finding advantages using sulfur hexafluoride gas. Most often pure sulfides are converted to SO_2 by reaction with an oxidizing agent like CuO at high temperature. Sulfates can be mixed with silica and heated to produce $\text{SO}_2 + \text{SO}_3$. SO_3 is being reduced to SO_2 by leading the gas over hot copper. Any CO_2 produced can be selectively pumped away by for instance freezing the SO_2 in a cold finger submerged in frozen alcohol.

For both CO_2 and SO_2 preparation any accompanying water

is removed by a dry ice + acetone cold trap. Iso-propanol can be used instead of acetone. It is less volatile and does not dissolve the styrofoam cups commonly used for liquid nitrogen.

Chemical techniques are attractive in extraction of sulfur from rocks. The "Thode"-solution is a mixture of HCl , H_3PO_2 , and HI releasing all sulfate as H_2S which can precipitate silver sulfide in a silver solution. The "Kiba"-solution is a tin-phosphoric acid solution releasing all sulfur in igneous rocks as H_2S .

ANALYSIS

Mass spectrometry

A mass spectrometer separates charged atoms and molecules on the basis of their masses when they move in magnetic and electric fields. Aston's mass spectrograph construction was later improved for light stable isotopic analysis by Nier and McKinney. The mass spectrometer may be divided into four parts: 1) Inlet system; 2) Ion source; 3) Mass analyser; 4) Ion detector.

The mass spectrometric analysis of stable isotopes normally is made so that a sample gas and a working gas (of known isotopic composition) are alternately led into the mass spec. several times. The two gas reservoirs are held at similar pressures with the help of mercury columns or compressable bellows.

To avoid mass discrimination in the inlet system the gas is being led into the mass spec. utilizing viscous gas flow (contrary to molecular flow) through capillary leaks.

gas valves have now been replaced by double sets of pneumatic valves.

Before the advent of high-resolution and high-precision digital electronics the isotope ratio measurement system consisted of a Wheatstone's Bridge-type of arrangement in which the amplified voltages from the two ion beams could be adjusted to a null with a high precision variable resistor. Another variable resistor could be switched in with the help of a relay when switching the inlet system from the sample gas to the standard gas. The isotopic mass ratios would then be proportional to the resistance used to obtain a null in each case.

DATA PROCESSING

Correction factors

When analysing a gas in the mass spectrometer we are analysing the ratio of the ionized gas molecules that enter the different collector cups. This may not directly give the atomic ratios that we want to express as our delta-values.

For example, in CO₂ gas we collect the masses 44, 45, and 46, but we want to know the $\delta(^{13}\text{C}/^{12}\text{C})$ and the $\delta(^{18}\text{O}/^{16}\text{O})$. However, oxygen-17 is also present in some of the CO₂ molecules (Table 3).

The ion source is where ions are formed, accelerated and focused. In most gas-source mass spectrometers today the electron bombardment ion source is used. A beam of electrons is emitted by a heated tungsten filament, and positive ions are formed as the electrons collide with the gas atoms or molecules. These ions are now being accelerated by an accelerating potential and focused electrostatically.

The mass analyzer separates the ion beams according to their masses. The analyzer can be a curved tube put inside a strong magnetic field, formed by a permanent magnet or an electro-magnet. The magnetic field deflects the ions into circular paths whose radii are proportional to the masses of the ions and their isotopes. The heavier ions are deflected less than the lighter ones. The pole pieces of the magnet are shaped like prisms so that the ions continue on straight paths as they leave the magnetic field.

The ion collector consists of a metallic cup ("Faraday cup") positioned behind a slit plate. The ion beam entering the cup is neutralized by electrons that flow from ground to the collector through a resistor with very high resistance. Dual or triple collectors are now common, making it possible to detect more than one ion beam simultaneously. The voltage difference across the resistor is amplified in low noise amplifiers and measured by very sensitive voltmeters with high internal resistance. The output analog voltage can be fed to a strip chart recorder or be digitalized in analog-to-digital- or voltage-to-frequency converters. The digitalized signal can be fed to digital computers for further processing there.

The switching between sample gas and working gas has been technically improved over the years. The solenoid operated

The presence of ^{17}O must be corrected for. This is done differently for different kinds of collector geometry. Craig (1957) has shown how this is done for an asymmetrical dual collector. The correction factors will be different for a symmetrical dual collector or for a triple collector.

For very precise analysis a number of instrumental correction factors has to be used. This has been treated in great detail by Deines (1970).

When analysing hydrogen isotopes there is not only being produced H_2^+ and HD^+ in the ion source, but also H_3^+ (with the same mass as HD^+). Therefore a H_3^+ correction has to be made.

A problem encountered in mass spectrometers is "memory effect", that is, the influence of previous samples on the current one. Correction schemes have been developed to correct for the memory effect, but a clean mass spectrometer with good vacuum will minimize this effect.

Accuracy and precision

Modern mass spectrometer instrumentation enables a precision better than 0.05 o/oo absolute for C, O, and S isotopes. Errors in the chemical preparation lines limit the precision to 0.1 - 0.2 o/oo absolute. For isotopic analysis of trace elements (like trace carbon and sulfur) larger errors may be expected. For hydrogen isotopes the instrumentation enables a precision of 0.5 to 2 o/oo absolute. A major contribution to this poorer precision is the formation of H_3^+ .

A larger problem than precision is accuracy. The international standards, on which the common delta-scales are based, are in some cases not available any longer, and new

Table 3. CO_2 molecules.

Molecule	Mass
$^{12}\text{C}^{16}\text{O}^{16}\text{O}$	44
$^{13}\text{C}^{16}\text{O}^{16}\text{O}$	45
$^{12}\text{C}^{16}\text{O}^{17}\text{O}$	45
$^{13}\text{C}^{16}\text{O}^{17}\text{O}$	46
$^{12}\text{C}^{16}\text{O}^{18}\text{O}$	46
$^{12}\text{C}^{17}\text{O}^{17}\text{O}$	46
$^{13}\text{C}^{16}\text{O}^{18}\text{O}$	47
$^{13}\text{C}^{17}\text{O}^{17}\text{O}$	47
$^{12}\text{C}^{18}\text{O}^{18}\text{O}$	48
$^{13}\text{C}^{18}\text{O}^{18}\text{O}$	49

standards have in some cases proven to be inhomogeneous. Even if inter-laboratory checks are being done, the accuracy is in most cases worse than the precision of the stable isotope analysis. This is especially true when the isotope ratios of the samples analysed lie far from those of the standards'.

Computer control

With the advent of small and cheap computers more and more functions of the mass spectrometer are being automated.

This of course benefits the mass spec. operator, who can leave the machine on its own after it has been programmed and loaded. Also the mass spec. can be left to run samples overnight, saving a lot of time for the operator. The automatization, however, requires more attention to sample monitoring before and during analysis, and to control and maintenance of the mass spec. so that no precious gas samples are being lost by a "simple-minded" machine.

New micro- and mini-computers and electronic logic building-blocks are now easily obtainable and cheap. Besides, they are fairly easy to program and use. Our own imagination is often the only threshold today for a fully automatic stable isotope laboratory.

FUTURE

I believe that the main problems in stable isotope analysis today don't lie in the instrumentation. As seen earlier the sample preparation errors are larger than the instrumental errors.

Another factor is even more important: "What kind of sample do we want to analyse?" and "what kind of sample did we analyse?". In other words, is the isotope ratio we obtained representative of what we wanted to analyse? Did we have mineralogical or chemical controls of our sample? Was our sample free of contaminants? In our present "macroscopic" stage of stable isotope analysis we ought to consider sampling and problem strategy the most important factor.

Some 40 - 50 years ago geochemists were mainly studying major- and trace element geochemistry of rocks and minerals. While rocks or separated minerals were analysed with the help of X-ray or optical spectrographic techniques, a new dimension was added to the geochemical picture when the electron beam microanalyser (the "micro-probe") could report the chemical composition of mineral spots only a few microns large. Soon elemental zoning on the microscopic scale was reported from minerals, adding useful information to the story on how these minerals formed.

Likewise, the present "whole rock or separated mineral" stage of stable isotope analysis will be added a valuable supplement in the form of the "ion probe microanalyser". So far only a handful of these have been installed throughout the world during the last five years. In the ion probe the sample is being bombarded by a focused plasma (like O_2^+ , N_2^+ , or Ar^+), releasing ions from the bombarded mineral surface. These latter ions are then immediately being focused, led into a mass spectrometer, and analysed. As we understand, the sampling problem and the sample preparation technique problems are being minimized.

The ion probe technique has, however, other problems, like its present problems in analysing the lightest stable isotopes. But given time for improvements the ion probe may prove to be the tool for the next generation of stable isotope analysis.

Selected Litterature

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