The Global Carbon Cycle and the Evolution of Photosynthesis

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ISBN (10): 1-5275-3730-7 ISBN (13): 978-1-5275-3730-9 Dedicated to Professor Simon El'evich Shnoll - my teacher and friend, an outstanding Soviet and Russian biophysicist, one of the founders of the Department of Biophysics of Moscow State University of M. V. Lomonosov, historian of Russian Science and the author of a number of scientific monographs on biophysics and evolution, an author of the concept of cosmophysical factors in random processes and of several books on the history of biological and related Sciences in Russia and the USSR, and a brilliant lecturer and popularizer of science.

His lectures, monographs and oral stories about animate and inanimate nature and their co-evolution evoked my interest in these problems. This monograph is the result of this interest.

CONTENTS

Preface
Introduction
List of Abbreviations
 Chapter One
 Chapter Two
 Chapter Three

Contents

- § 3. Coupling of natural redox carbon and sulfur cycles. The coupling point is thermochemical sulfate reduction occurring in subduction zone.
- § 4. Isotope data on Precambrian carbonates evidence in favor of orogenic cycles' existence.
- § 5. Cycles of the nutrient trace elements in the Phanerozoic ocean confirm the existence of orogenic cycles
- § 6. Geological data are in line with redox carbon cycle model

- § 1 General consideration.
- § 2 What is common and what is the difference between conventional and global photosynthesis?
- § 3. The role of environmental factors in formation of carbon isotope composition of sedimentary organic matter
- § 4. The principal mechanism of formation of carbon isotope composition of the "living matter"

- § 1. Carbon isotope fractionation in heterotrophic organisms and in post-photosynthetic metabolism of photosynthetic organisms
- § 2. The isotopic changes in the transformation of "living matter" into sedimentary organic matter
- §3. Facial carbon isotopic characteristics of sedimentary organic matter
- § 4. Facial carbon isotopic characteristics of sedimentary organic matter in non-oxygenic environment
- § 5 Spatio-temporal facial carbon isotopic characteristics of sedimentary organic matter.

- § 1. Carbon cycle redox model and the periodicity of biodiversity rate on the Earth
- § 2. Carbon cycle redox model and the periodic changes of the climate on the Earth
- § 3. Carbon cycle redox model and the periodicity mass extinction events on the Earth
- § 4. Carbon cycle redox model and petroleum geology problems

 Chapter Seven
 Chapter Eight
Conclusions
References 121
Glossary

PREFACE

Looking back, I can say that writing this book has required knowledge in some specific fields of science. Firstly, the knowledge of the laws of isotope fractionation which I gained as a student and then post-graduate student of the Department "Technology of separation and application of stable isotopes" in the Moscow Institute of Chemical Technology of D. I. Mendeleev (1958 – 1969) under the guidance of Professor Ya. D. Zelvenskii and Professor D. A. Knyazev. Secondly, the knowledge in the field of biochemistry and biophysics which I gained at the Department of Biophysics of Moscow State University, where I listened to the brilliant lectures of two wonderful professors S. E. Shnoll and F. I. Ataullakhanov. I attended the University on my own initiative, just as a listener. Certain knowledge I learned from the fundamental book of S. Z. Roginsky and S. E. Schnoll "Isotopes in Biochemistry" (1963) and the remarkable monograph "Physical and chemical factors of biological evolution" by S.E. Shnoll (1981), which impressed me a lot.

My own research in the field of carbon isotope fractionation in a photosynthetic cell, conducted between 1994 and 2013, also played an important role in the formation of my views on the problems I have touched on in this book. In other words, all my previous life has become a prologue to the writing of this book. The main idea of the book was born when I was in the hospital for a long time and I had a lot of free time to think.

The main findings of the previous period include the discovery of carbon isotope fractionation in photorespiration in plants and photosynthesizing organisms, the opposite signs of isotope effects in CO_2 assimilation and photorespiration, and the oscillatory nature of the above photosynthetic processes.

During the years of my work at the All-Russian Research Geological Oil Institute, I was acquainted with the problems of geology and, in particular, with the problems of Organic Geochemistry and Petroleum Geology. Such a combination of knowledge in different areas made it possible to explore the problems from unusual, non-standard positions and to form the basis of carbon cycle modeling including consideration of photosynthesis as the key element of carbon turnover. I used the observed isotopic links between carbon isotope composition of "living matter", sedimentary organic matter and petroleum as a delicate and powerful tool to study carbon turnover.

In conclusion, I express my special thanks and deep gratitude to the two brilliant scientists, who exerted a huge impact on my scientific activity - Simon El'evich Shnoll and Abir Ubaevich Igamberdiev. I am immensely grateful to all my colleagues who generously shared their knowledge with me. Especially, I am grateful to Prof. A.U. Igamberdiev, an outstanding Russian plant physiologist, the author of many philosophical treatises on harmony of science, music and space. We are linked through long-term friendship and cooperation. He is currently working in Newfoundland University in Canada. His erudition and extensive knowledge in many fields have been very useful and helpful to me. I am much obliged to him for many fruitful discussions and friendly critical notes which have encouraged and motivated me throughout this process.

My sincere gratitude and respect go to Prof. M.V. Dakhnova, a head of the Geochemistry Department at the Oil Research Geological Institute, for our long-term cooperation and fruitful discussions on geological problems and her support. I am also thankful to Associate Professor V.I. Pichouzkin, who showed great interest in my work, and participated in many helpful discussions on different problems.

INTRODUCTION

Numerous studies on the evolution of the biosphere provide compelling arguments in favor of the relationships between the Earth's crust processes and the photosynthesis expansion and evolution. In the background of forward and irreversible evolution, some biosphere events periodically repeat. Paleontological data showed the repeatability of mass extinctions and "explosions of life". The cyclic variations were marked in the rate of biodiversity, in the alternation of "greenhouse" periods, and glaciations in the changes of aerobic and anoxic conditions. The examination of these events in the past makes an effective and solid basis for tracing and predicting the trajectory of life evolution on Earth.

The periodicity also characterizes the chemical evolution of the Earth. Its stone chronicle evidences the active development of the crust, accompanied by mountain building, strong volcanism and magmatism. These periods were invariably replaced by quiet crust development, where weathering has become dominant. Geological data provide evidence for the periodic change of rich and poor sediments in organic matter, for the cyclic sequence of the sedimentary layers, for the repeated sea-level changes, and so on.

The nature of this periodicity is still debatable. The question is, whether these events, differing by nature, are somehow interconnected or entirely independent. The second question, then, is if they are interconnected, what is the cause for this and what is the likely mechanism of the implementation of the mentioned periodicity?

In the study of the natural carbon cycle, the author used the modeling of the physicochemical processes which likely compose the cycle. It is based on the analysis of the observed chemical and isotopic variations of different natural objects in the course of geological time.

The main principle that underlies the analysis is the actualism principle. It claims that physicochemical laws are invariant in time and instead depend on environmental conditions.

The periodicity of most natural processes makes the use of isotopic data very effective because it allows us to study the duration of the process by means of applying isotope effect of pool depletion, or by use of the socalled Rayleigh effect, which establishes a relationship between the isotope composition of the initial substrate, the degree of the extent of pool

Introduction

depletion, and the isotope composition of final product. It makes it possible to study the dynamics of the process. Hence the isotope technique became a very delicate method of studying the natural carbon cycle's processes. Another advantage of using the Rayleigh effect is the potential to amplify often very small, single natural isotope effects due to the multiplication of its magnitude with the increasing depletion of the pool of the initial substrate.

The use of isotopic data allows the author to apply findings obtained in preliminary photosynthesis studies. It was found that carbon isotope effects of photosynthesis are consistent with the effects of CO_2 assimilation and photorespiration having opposite signs. It was also proven that the oscillatory mechanism of photosynthesis functioning, included the alternation of CO_2 assimilation and photorespiration. These findings were found to be key in the interpretation of isotopic shifts in sedimentary organic matter and necessary in finding out the dynamics of carbon turnover.

The mechanism of photosynthesis and the ability of photosynthesizing organisms to self-regulate became a justification in the claim about the spontaneous movement of the carbon cycle toward the ecological compensation point.

Since the isotopic data are of great importance in global carbon cycle modeling, I have devoted "Chapter One" to consider the causes of isotope effects and the basis for their interpretation.

"Chapter Two" describes the essence of the suggested model and its basic features.

"Chapter Three" is devoted to the main arguments that prove the model's statements. They are based on both isotopic and non-isotopic data.

"Chapter Four" considers the stages of carbon isotope composition of sedimentary organic matter formation. It includes the formation of carbon isotope composition on the stage of "living matter" and of postsedimentation transformations.

"Chapter Five" is devoted to the isotopic differences of sedimentary organic carbon. Two cases are possible here. Facial carbon isotopic differences correspond to the case when carbon isotope composition of organic matter of the same age is formed, 1) under different environmental conditions of "living matter" habitats, and 2) under different postsedimentation conditions of the transformation of buried organic matter. The spatiotemporal isotopic differences in organic matter correspond to the other case, when the carbon isotope composition of organic matter is formed, besides the two above reasons, under the modified environmental conditions resulting from the changes in the environment in time. Understanding the difference between these two concepts is very important in the interpretation of isotopic differences of organic matter.

"Chapter Six" describes the application of the suggested model to some periodic events in biosphere, such as the climate in the past, mass extinctions of organisms, the changes in biodiversity rate, irregularity of stratigraphic distribution of rocks rich in organic matter, and of petroleum fields, etc.

"Chapter Seven" is devoted to the spontaneous evolution of the carbon cycle to a steady state as a consequence of photosynthesis evolution under the change of the carbon dioxide to oxygen ratio in the "atmosphere – hydrosphere" system. The hypotheses of the ecological compensation point and the spontaneous evolution of the carbon cycle are also considered here.

The final chapter, "Chapter Eight" is devoted to the applicability of carbon isotope data to the analysis of the main stages of photosynthetic evolution. Four major aromorphosis are described on the basis of the suggested model: 1) photosynthesis origin and emergence of the key photosynthetic enzyme, RuBP carboxylase 2) the origin of photorespiration 3) Krebs cycle origin and formation of the mechanism of postphotosynthetic metabolism; and 4) the emergence of new types of photosynthetic assimilation.

LIST OF ABBREVIATIONS

ATP	adenosine triphosphate
CAM	Crassulacean acid metabolism
Ga	billion years ago
GOE	Great oxidation event
LRV	large ridge volume
OAE	oceanic anoxic event
Ma	million years ago
MCE	mid-Cenomanian Events
NADP(H)	nicotinamide adenine dinucleotide phosphate
PAL	present atmospheric level
PEP	phospoenolpyruvate
PVC	pyruvate dehydrogenase complex
PETM	Paleocene – Eocenec temperature maximum
RuBP	ribulose 1,5-bisphosphate
Rubisco	ribulose 1,5-bisphosphate
	carboxylase/oxygenase complex
S-CIE	Sinemurian carbon isotope excursion
TE	trace elements
TE cycle	trace element cycle
T-OĂE	Toarcrian Anoxic Event
TOC	total organic carbon
SRV	small ridge volume
VPDB	Vienna PeeDee Belemnite

CHAPTER ONE

A BASIC KNOWLEDGE ON ISOTOPE FRACTIONATION

§1. A special role of carbon isotope data in the reconstruction of geological history

The laws of isotope fractionation are the same for different elements regardless of their nature. Among them is carbon, the main element of the biosphere which occupies a particularly special place. It is associated with its ability to form strong carbon chains - branched and non-branched, planar and non-planar rings, and three-dimensional carbon configuration. The carbon structure may include heteroatoms (nitrogen, oxygen, sulfur and is capable of associate functional groups (-OH, -NH₂, -COOH, -SH, etc). Carbon atoms included in the carbon chains and associated with the functional groups behave differently in chemical reactions and related processes of carbon isotope fractionation.

Inorganic oxidized carbon compounds - presented by gaseous and dissolved carbon dioxide, bicarbonate, and carbonate ions - constitute a separate group, which differ from organic ones in their ability to fractionate carbon isotopes. In organic compounds, isotope effects are mainly related to the cleavage of carbon bonds whereas, in the group of inorganic compounds, the changes of the isotopic composition are associated with the chemical exchange reactions. Therefore, carbon atoms in these two groups of compounds carry different isotopic information.

Carbon isotope composition of organic compounds contain the information about the heredity of carbon structures from precursors and about the processes they underwent on the pathway of the transformations. On the contrary, the isotopic composition of inorganic carbon compounds carries the information about the evolution of the "atmosphere – hydrosphere" system where the "carbon dioxide – bicarbonate – carbonate" system ($CO_2 - HCO_3^- - CO_3^-$) exists, until its components are able to participate in the process of chemical exchange and, hence, in isotope exchange.

§ 2. What should one know to use isotopic data effectively? The kinetic and thermodynamic nature of isotope effects

The isotope technique is currently a routine tool for researchers working in the field of geology, paleontology evolution and life sciences. Its effectiveness depends on two factors: Firstly, the accuracy and reliability of measurements, and secondly the level of understanding of the sense of the obtained isotopic information.

At present, the first is mainly provided using a computer in combination with a modern mass spectrometer, which gives high accuracy readings. The second is dependent on the researcher's level of competence, which is not ever adequate to the task. Considering that the following consideration of the global carbon cycle model is mainly based on the interpretation of isotope data, I decided to preface the presentation of the material by the key issues of isotope fractionation theory applied to carbon chemistry. It will help the reader to understand the material more deeply.

The conducted studies allow for the conclusion that isotope effects in chemical reactions play the main role in natural processes. It is known that they are of two types – thermodynamic and kinetic. To interpret isotopic data correctly, it is important to assign the observed isotopic differences to one of these types properly.

A vivid illustration of the above was a sharp discussion in literature on the nature of the carbon isotopic variations in the "living matter" that was held in the eighties and nineties of the last century. As will be shown later, the question is relevant to the isotopic differences in organic matter as well. Therefore, we will look into the question more thoroughly.

In his monograph, Galimov (1973) put forward an idea about equilibrium-like carbon isotope distribution in living organisms. In his subsequent works he has developed this idea suggesting a "microscopic" reversibility in enzymatic reactions (Galimov, 1985). He and his colleague (Galimov, Polyakov, 1991) insisted that thermodynamic distribution was characteristic of any carbon components of the "living matter" and could be used as a criterion of biogenic or abiogenic origin in organic compounds (Galimov, 1993).

This idea was supported first by Schmidt (2003), who suggested that equilibrium in living systems may be achieved in cyclic metabolic processes. However, later he publicly acknowledged the failure of the thermodynamic concept (Schmidt et al., 2015). Most researchers argued that carbon isotope distribution in living organisms are of kinetic nature (Ivlev, Shnoll, 1976; O'Leary, Yapp, 1978; Monson, Hayes, 1982; Varshavskii, 1988; Buchachenko, 2003, 2007). Although no one denied

that at some points (atom position in the molecule) on the reversible steps of enzymatic transformations the equilibrium isotope effect can arise, but this cannot lead to the equilibrium isotope distribution of the whole molecule.

The discussion ended when new experimental data proved definitively the kinetic nature of carbon isotope distribution in "living matter".

§ 3. Thermodynamic isotope effect

A prerequisite for the emergence of thermodynamic isotope effects is the reversibility of chemical reactions. In unidirectional irreversible reactions, including cyclic ones, thermodynamic isotope effects do not occur. If the time is sufficient to achieve the equilibrium, thermodynamic isotope effects are characterized by a constant. Their value doesn't depend on the pathway or the mechanism of the reaction and is determined only by the properties of the exchanging molecules.

For the arbitrary reaction of chemical isotope exchange between the molecules AX_n and BX_m :

$$m AX_n + n BX_m^* \Leftrightarrow m AX_n^* + n BX_m$$
 (I.1)

under thermodynamic isotope effect is usually understood as the ratio of isotopic concentration in exchanging molecules, called thermodynamic isotope fractionation factor α :

$$\alpha = \frac{(X^*/X)_{AX_n}}{(X^*/X)_{BX_m}} = 1 + (\delta X_{AX_n} - \delta X_{BX_m}) \cdot 10^3$$
(I.2)

Here, $(X^*/X)_{AXn}$ and $(X^*/X)_{BXm}$ are the ratios of isotopic concentration of atom X in the molecules X_{AXn} and X_{BXm} . δX_{AXn} and δX_{BXm} are the isotope composition of X in the above compounds measured by mass-spectrometer.

From the other side, α is linked to the equilibrium constant of the above reaction by the expression:

$$K_{AX_n/BX_m} = \alpha^{nm} \tag{I.3}$$

In statistical thermodynamics it is proven that the equilibrium constant in the chemical reaction of isotope exchange can be expressed by means of a statistical sum that characterizes the distribution of the molecules in the corresponding energy levels. Isotopic substitution affects the distribution.

Chapter One

$$_{K_{AX_{n}/BX_{m}}} = \frac{\mathcal{Q}_{AX_{n}}^{m} \cdot \mathcal{Q}_{BX_{m}}^{n}}{\mathcal{Q}_{AX_{n}}^{m} \cdot \mathcal{Q}_{BX_{m}}^{n}} = \left(\frac{\mathcal{Q}_{AX_{n}}}{\mathcal{Q}_{AX_{n}}}\right)^{m} / \left(\frac{\mathcal{Q}_{BX_{m}}}{\mathcal{Q}_{BX_{m}}}\right)^{n}$$
(I.5)

Here $Q_{AXn}, Q_{BXm}, Q_{AX_n^*}, Q_{BX_m^*}$ are the statistical sums for the molecules AX_n , BX_m and its isotopic species are denoted by an asterisk.

If the molecules are in a highly excited state (at high temperatures), the statistical sum Q (energy distribution function) is based on the independence of the degrees of freedom of movement which can be represented in the form of independent contributions of translational, rotational, and vibration energy per unit volume:

$$Q = \frac{Q_{transl}Q_{rot}Q_{vibr}}{V}$$
(I.6)

1

Presenting each of the contributions and substituting (I.6), as shown in (Roginskii, 1956), the statistical sum can be represented as follows:

$$Q = \frac{(2\pi MkT)^{3/2}}{h^3} \cdot \frac{g_{el}g_{nucl}}{s} \cdot \frac{8\pi^2 (8\pi^2 ABC)^{1/2}}{h^3} \cdot \prod \frac{\exp(-\frac{hv_i}{kT})}{1 - \exp(-\frac{hv_i}{kT})}$$
(1.7)

Here M is a mass of the molecules, A, B and C are the principal moments of inertia, v_I is a vibration frequency, g_{el} is a factor of degeneration of the ground state, g_{nucl} is a degeneracy factor taking into account the orientation of the nuclear spins, s is a symmetry number for rotational levels.

The above function also takes into account the orientation of nuclear spins and the degeneracy of rotational levels (the symmetry number). The calculations using equation (I.7) can be significantly simplified if we apply Teller – Redlich's rule (Redlich, 1935). Then for the molecule AX_n the ratio of statistical sums for isotopic forms may be written as follows:

$$\frac{Q_{AX_n^*}}{Q_{AX_n}} = \frac{s}{s^*} \prod_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}$$
(I.8)

for the molecule BX_m the same ratio has the similar form:

$$\frac{Q_{BX_m^*}}{Q_{BX_m}} = \frac{s}{s^*} \prod_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}$$
(1.9)

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In the expressions (I.8) and (I.9)

$$u_i = \frac{hv_i}{kT} \tag{I.10}$$

u_i is a reduced frequency

Using expression (I.10) the expression (I.5) can be written

$$K = \left(\frac{s}{s}\right)_{AX_{n}}^{m} \cdot \left(\frac{s}{s}\right)_{BX_{m}}^{n} + \left\{\frac{\prod_{i=1}^{3N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}\right\}_{AX_{n}}^{m} + \left\{\frac{\prod_{i=1}^{3N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,1})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,2})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,2})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,2})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,2})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,2})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left\{\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left(\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,1}} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left(\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,2}} \frac{1 - \exp(-u_{i,2})}{1 - \exp(-u_{i,2})}\right\}_{BX_{m}}^{n} + \left(\frac{1}{2}\sum_{i=1}^{N-6} \frac{u_{i,2}}{u_{i,2}}$$

Varshavskii and Vaisberg (1957) have suggested removing symmetry numbers which characterize equiprobable isotope distribution. Then in the nominator and denominator of expression (I.11), only the multipliers characterizing non-equiprobable isotope distribution were left:

$$\beta_{AX_n} = \prod_{i=1}^{3N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}$$
(I.12)

$$\beta_{BX_m} = \prod_{i}^{3N-6} \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}$$
(I.13)

They called them β -factors. Considering expressions (I.12) and (I.13), thermodynamic isotope fractionation factor α is equal:

$$\alpha = \frac{\beta_{AX_n}}{\beta_{BX_m}} \tag{I.14}$$

It is obvious that β - factor is a thermodynamic function, characterizing the ability of each individual compound to attach a heavy isotope (marked with an asterisk). This ability is determined by the distribution of energy levels which are unique to each of the exchanging molecules. Note that the thermodynamic factor of isotope fractionation depends on a temperature, which is included in the expression (I.10) for the reduced frequency u_i .

Let's consider an example of the thermodynamic isotope effect carbon dioxide – bicarbonate– carbonate system in nature:

$$CO_2(gas) + H_2O \leftrightarrow CO_2(dissolved) \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^{-} \leftrightarrow CO_3^{-2}$$
 (I.15)

Chemical isotope exchange of oxygen and carbon in this system takes place through the reversible reactions of hydration/dehydration and electrolytic dissociation.

The initial steps of the chain (I.15) are:

$$\begin{array}{c} K_P \\ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \end{array}$$

Oxygen isotope effect for this reaction may be expressed as the ratio of isotopic equilibrium constants:

$$\frac{k_p^{18}}{k_p^{16}} = \frac{[H_2 C^{18} O_3]}{[H_2^{18} O] \cdot [C^{18} O_2]} \cdot \frac{[H_2^{16} O] \cdot [C^{16} O_2]}{[H_2 C^{16} O_3]}$$
(I.16)

This ratio in turn can be written as a product of factors, each of which corresponds to the three reactions of isotope exchange shown below.

$$\frac{1}{2}C^{18}O_{2} + H_{2}^{16}O \leftrightarrow \frac{1}{2}C^{16}O_{2} + H_{2}^{18}O$$

$$K_{1,is.ex} = \frac{[C^{16}O_{2}]^{\frac{1}{2}}}{[C^{18}O_{2}]^{\frac{1}{2}}} \cdot \frac{[H_{2}^{18}O]}{[H_{2}^{16}O]}$$

$$H_{2}^{16}O + \frac{1}{3}H_{2}C^{18}O_{3} \leftrightarrow H_{2}^{18}O + \frac{1}{3}H_{2}C^{16}O_{3}$$
(I.17)

$$K_{2,is.ex..} = \frac{[H_2^{\ 16}O]}{[H_2^{\ 18}O]} \cdot \frac{[H_2C^{\ 18}O_3]^{\frac{1}{3}}}{[H_2C^{\ 16}O_3]^{\frac{1}{3}}}$$
(I.18)

$$\frac{1}{2}C^{18}O_2 + \frac{1}{3}H_2C^{16}O_3 \leftrightarrow \frac{1}{2}C^{16}O_2 + \frac{1}{3}H_2C^{18}O_3$$
(I.19)

$$K_{3,is.ex..} = \frac{[C^{16}O_2]^{\frac{1}{2}}}{[C^{18}O_2]^{\frac{1}{2}}} \cdot \frac{[H_2C^{18}O_3]^{\frac{1}{3}}}{[H_2C^{16}O_3]^{\frac{1}{3}}}$$

It easy to see, that $\frac{K_p^{18}}{K_p^{16}} = K_{1,is.ex.} \cdot K_{2,is.ex.} \cdot K_{3,is.ex.}$ (I.20)

Thus, to calculate the equilibrium isotope effect of the overall reaction, it is necessary to define the thermodynamic isotope effect at each stage.

Thermodynamic carbon isotope effect in the above reaction is expressed as follows:

$$\frac{K_p^{13}}{K_p^{12}} = \frac{[H_2^{13}CO_3]}{[H_2O] \cdot [^{13}CO_2]} \cdot \frac{[H_2O] \cdot [^{12}CO_2]}{[H_2^{12}CO_3]} = \frac{[H_2^{13}CO_3]}{[H_2^{12}CO_3]} \cdot \frac{[^{12}CO_2]}{[^{13}CO_2]} \quad (I.21)$$
then
$$\frac{K_p^{13}}{K_p^{12}} = \frac{[^{13}CO_2]}{[^{12}CO_2]} \cdot \frac{[H_2^{12}CO_3]}{[H_2^{13}CO_3]} \quad (I.22)$$

The natural isotope exchange equilibriums on oxygen and carbon are established almost instantly as the time of equilibrium achievement is much less than the geological time. This is confirmed by the proximity of the isotopic differences in oxygen and carbon, measured experimentally and calculated theoretically (Table I.1). From Table I.1 it can be seen that the theoretical values of the thermodynamic coefficients of isotope fractionation correspond well enough to the experimental findings. In cases where it is difficult to get experimental values with good enough accuracy, the thermodynamic isotope fractionation coefficients can be evaluated theoretically.

Chemical isotope exchange	T ⁰	α_{exp} ,		α_{theor}	Reference
reactions	С	· •	Reference		
$\frac{1}{2}C^{18}O_2 + H_2^{16}O \leftrightarrow \frac{1}{2}C^{16}O_2 + H_2^{18}O$	25	1,042	Dole, Slobad	1,04 7	Webster et al. (1935)
			(1940)		
$\frac{1}{2}C^{18}O = +H^{16}O \leftrightarrow \frac{1}{2}C^{18}O =$	25	1,036	Urey,	1,04	Urey et
$\frac{1}{3}$ U_3 H_2 U_3 $\frac{1}{3}$ U_3			Greiff	7	al.(1951)
			(1935)		
$^{13}CQ + H^{12}CQ \leftrightarrow C^{12}Q + H^{13}CQ$	25	1,012	Seminikhi	1,	Stranks,
2 3 2 3			n et al	019	Harris
			(1960)		(1953)
$^{13}CQ + ^{12}CQ^{=} \leftrightarrow C^{12}Q_{2} + ^{13}CQ^{=}$	25	1,012	Thode et	1,	Thode et
			al. (1965)	013	al.(1965)
$^{13}CO + H_{2}O \leftrightarrow ^{13}CO + H_{2}O$	25	1,008	Abelson,	1,00	Thode et
$CO_2 + II_2O + CO_2 + II_2O$		3	Hoering	77	al.(1965)
			(1960)		

Table I.1. The comparison of experimental and theoretical values of equilibrium isotope effects in carbon dioxide – carbonate system.

An example of the application of theoretical evaluation of thermodynamic oxygen isotope fractionation coefficients was given in the work of Urey et al. (1951). The method was used for the determination of paleotemperatures. For this purpose, the temperature dependence of α in equilibrium isotope exchange of oxygen between H₂O and carbonates was calculated.

§ 4. Kinetic isotope effect

In contrast to the thermodynamic, kinetic isotope effect depends on the pathway and mechanism of the transformation. The algorithm for the calculation of kinetic isotope effect is similar to that of the thermodynamic one. In both cases the equilibrium is assumed. In the case of thermodynamics, the characteristics of all substances involved in the reaction are considered known. This provides relatively good results. In the case of kinetics, the equilibrium between substrates and the so-called activated complex, whose characteristics are commonly unknown, is considered, and the use of the assumptions, instead of experimental values, can sometimes significantly reduce the accuracy. Therefore, theoretical estimates of the kinetic isotope effect are only qualitative Fortunately relatively correct results are obtained in the case where the rate limiting stage of the reaction is a bond cleavage. This corresponds to the case when the activated state is formed at the saddle of potential energy surface where fairly reasonable suggestions on activation complex can be done. The cleavage of C-C bond in organic compounds is the most common case of the kinetic isotope effect manifestation in nature. It occurs in enzymatic reactions at the degradation of the organic matter molecules in sediments. Often it occurs at the point of the attachment of functional groups.

There are many books devoted to the theoretical description of the kinetic isotope effect (Roginsky, 1956; Roginsky, Shnoll 1963; Melander, 1960; Melander, Saunders, 1983). We shall mention only those aspects that will help the reader to understand how to estimate kinetic isotope effects and how to interpret them.

In the framework of the theory of absolute rates of reactions (Glesston et al., 1948), the transformation of initial substances A and B into products occurs through the state of the activated complex M^{\otimes} with which they are in equilibrium. Then for the chemical reaction:

$$A + B \Leftrightarrow M^{\otimes} + N \rightarrow \text{products}$$
 (I.23)

Its rate is described as:

$$v = v_L^{\otimes} \left[M^{\otimes} \right] \tag{I.24}$$

Here v_L^{\otimes} is the decay frequency of the activated complex, $[M^{\bigotimes}]$ the concentration of the activated complex. The rate constant of a chemical reaction can be expressed through the equilibrium constant as

$$k = V_L^{\otimes} K^{\otimes} \tag{I.25}$$

Here K^{\otimes} is expressed as:

$$K^{\otimes} = \frac{\left[M^{\otimes}\right]N}{\left[A\right]\left[B\right]} \cdot \frac{f_{M}^{\otimes}f_{N}}{f_{A}f_{B}}$$
(I.26)

The first term is the ratio of the concentrations of the reaction products and initial substrates, the second is the similar ratio for the activation coefficients.

Chapter One

As shown before, methods of statistical thermodynamics allow for the submission of K^{\otimes} via statistical sums describing the distribution of the molecules on possible energy levels:

$$K^{\otimes} = \frac{\prod \mathcal{Q}_{npodykmos}^{\otimes}}{\prod \mathcal{Q}_{ucxodseugecms}} \exp(-\frac{E_A}{RT})$$
(I.27)

Here Qs are the statistical sums of participants of the reaction which are in equilibrium. E_A is a classical activation energy which represents the difference between the initial energy of the products in the state of activation equilibrium, and that of the reactants. Energies are measured from the potential energy surface. R is the universal gas constant, T is the absolute temperature.

If the molecules are not in a highly excited state (at high temperatures), the statistical sum Q - according to the principle of the independence of the degrees of freedom of translational, rotational, and vibration movement - can be represented in the form of independent contributions per unit volume.

As shown by Melander and Saunders (1980), the statistical sum, as in classical thermodynamics, can be represented like:

$$Q = \frac{(2\pi MkT)^{3/2}}{h^3} \cdot \frac{g_{33}g_{30}}{s} \cdot \frac{8\pi^2 (8\pi^2 ABC)^{1/2}}{h^3} \cdot \prod \frac{\exp(-\frac{hv_i}{kT})}{1 - \exp(-\frac{hv_i}{kT})}$$
(I.28)

All symbols have the same meaning as in equation (I.7).

Isotope effect in the reaction is interpreted as the ratio of the rate constants of the reactions of the isotopic forms (Melander,1964; Melander and Saunders, 1980). Denoting them by the indices 1 and 2, the coefficient of kinetic isotopic fractionation can be recorded as:

$$\alpha = \frac{k_1}{k_2} \tag{1.29}$$

Then considering expressions (I.26) and (I.28) and using the reduced $u_i = \frac{hv_i}{kT}$ frequency, the expression (I. 29) can be represented as (1.30):

$$\alpha = \left(\frac{M_{1}^{\otimes}}{M_{2}^{\otimes}} \cdot \frac{M_{2}}{M_{1}}\right)^{3/2} \left(\frac{A_{1}^{\otimes} B_{1}^{\otimes} C_{1}^{\otimes}}{A_{2}^{\otimes} B_{2}^{\otimes} C_{2}^{\otimes}} \cdot \frac{A_{2} B_{2} C_{2}}{A_{1} B_{1} C_{2}}\right)^{1/2} \prod^{3N^{\circ}-7} \left\{\frac{\exp(1/2u_{i,2}^{\otimes})}{\exp(1/2u_{i,1}^{\otimes})} \cdot \frac{1 - \exp(-u_{i,2}^{\otimes})}{1 - \exp(-u_{i,1}^{\otimes})}\right\} \times (I.30)$$

$$\times \prod^{3N-6} \left\{\frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \cdot \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}\right\}$$

Since the expression (I. 30) includes the ratio of the values independent of isotope substitution (which are present in (I.26) and (I. 27) and include E_A and activation coefficients f_i) they should be reduced. Using the expression Teller-Redlich rule (Redlich, 1935), one can obtain (I.31):

$$\alpha = \frac{v_{L,1}^{\otimes}}{v_{L,2}^{\otimes}} \cdot \prod_{u_{i,2}^{\otimes}}^{3N^{\circ}-7} \{ \frac{u_{i,1}^{\otimes}}{u_{i,2}^{\otimes}} \frac{\exp(l/2u_{i,1}^{\otimes})}{\exp(l/2u_{i,1}^{\otimes})} \cdot \frac{1 - \exp(-u_{i,2}^{\otimes})}{1 - \exp(-u_{i,1}^{\otimes})} \} \cdot \prod_{i=1}^{3N^{\circ}-6} \{ \frac{\exp(l/2u_{i,1})}{\exp(l/2u_{i,2})} \cdot \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})} \} (I.31)$$

The factor $\frac{v_{L,1}^{\otimes}}{v_{L,2}^{\otimes}}$ takes into account the isotopic frequencies related to

the motion of the system along the reaction coordinate. This frequency is excluded from the ratio of statistical sums for the activated complex, the second factor in the expression (I.30). The remaining factors represent the ratio of the statistical sums for the activation complex (without the frequency along the reaction coordinate) and the ratio of the statistical sums for the reactants.

For the most important and common case when the reaction rate is limited by the bond cleavage, the expression (I.10) can be significantly simplified. The contributions of the frequencies for the activated complex and the reacting substrates are reduced, corresponding, with the exception of one, to the frequency related to the motion along the reaction coordinate. In this case, the expression (I. 31) takes the form:

$$\alpha = \frac{v_{L,1}^{\otimes}}{v_{L,2}^{\otimes}} \cdot \frac{u_{i,2}}{u_{i,1}} \frac{\exp(1/2u_{i,1})}{\exp(1/2u_{i,2})} \frac{1 - \exp(-u_{i,1})}{1 - \exp(-u_{i,2})}$$
(I.32)

From the expression (I.32) describing the decay of a diatomic molecule, it is easy to understand why the reaction products during the bond cleavage are always enriched with a "light" isotope.

In fact, the first factor in the expression (I.31) is defined as the square root of the ratio of the reduced masses of molecule:

$$\frac{v_{L,1}^{\otimes}}{v_{L,2}^{\otimes}} = \sqrt{\frac{\mu_2}{\mu_1}} , \qquad (I.33)$$

Here μ_i is the reduced mass, which is expressed through the masses of atoms (or fragments) of the molecule m_1 and m_2 that form a bond, according to the expression:

$$\mu_i = \sqrt{\frac{1}{m_{i,1}} + \frac{1}{m_{i,2}}} \tag{1.34}$$

If we assume that index 1 in the expression (I.30) refers to a light isotope, and that index 2 refers to a heavy isotope, it is easy to show that the above multiplier is always greater than 1. Then the remaining part of the expression (I. 31) can be converted to the form

$$\frac{u_{i,2}}{u_{i,1}} \cdot \frac{sh\frac{u_{i,1}}{2}}{sh\frac{u_{i,2}}{2}}$$
(I.35)

Here the first multiplier is always less than 1, while the second one is always more than 1, but their product is greater than 1. Indeed, the ratio of the reduced frequencies is always less than the ratio of the hyperbolic sinuses of these frequencies. Hence the second part of the expression (I. 31) is also greater than 1. It allows for the conclusion that kinetic isotope effect α , in cases where reaction rate is limited by the bond cleavage, is always greater than 1.

A more visual representation can be seen in Fig I.1, which shows the profile of potential energy along the reaction coordinate for the case being studied.

The kinetic isotope effect is determined by the difference between the zero-energies, approximated by the reduced isotopic vibrations of the broken bond in the activation complex and in the substrate. In the activation complex the difference between zero-energy levels in isotopic and non-isotopic species is negligible (see Fig I.1), since the reduced frequencies of the broken bonds in both cases are close to zero. Therefore,