





**Science  
for Everyone**

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и химическая  
эволюция Земли**

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**Origin and Chemical Evolution  
of the Earth**

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"Our planet—two billion\* years  
younger or older—represents  
chemically different bodies."

*V.I. Vernadsky*

## Preface

At present the problem of our planet's origin is still rather obscure. However, the rapid advances in modern science, and the discovery and accumulation of new data in geochemistry, cosmochemistry, geophysics and astrophysics provide new insight into the mysterious problem that has excited many generations—that of the origin of the Earth and other bodies of the Solar System.

The chemical composition of different natural bodies, including the Sun and stars, planets and meteorites, minerals and rocks, natural waters and plants, and soils and atmospheric air, has been studied by many investigators. It has opened up for us a complicated history of the atoms of chemical elements. Chemical elements of Solar System, their isotopic ratios, radioactivity are viewed as historical documents that enable one to reconstruct the preplanetary stage in the development of the matter of the whole System. Much knowledge on the behaviour of chemical elements and their compounds under different thermodynamic conditions and on the composition of celestial bodies—meteorites, the Moon and the Sun—has been acquired. The development of cosmogenic theory and reconstruction of the early history of the Solar System can now be accompanied mainly by the inductive method based on the com-

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\* Billion—million millions or  $10^{12}$  in Great Britain; thousand millions or  $10^9$  in USA,

parison and generalization of only recently obtained empirical cosmochemical data on the composition of meteorites and planets. Moreover, physicochemical approach to the problems of cosmogeny of the Solar System is quite inevitable. Therefore the mechanical features of the Solar System, which received primary consideration in classical cosmogenic hypotheses, should be interpreted in the context of physicochemical processes that occurred in the early history of the Solar System.

We can already assume that the Earth's matter in the past, not long before the formation of planets, was in the form of plasma, and the generation of our planet was connected with the evolution of the substance from the plasma state to the state of formation of chemical compounds, metal phases, and other forms of existence of solid, liquid and gaseous bodies as the temperatures of ancient accumulations of matter were lowered.

In this book the author attempts to describe in popular form some problems of the Earth's origin and its chemical changes over its long geological history on the basis of cosmochemical, geochemical and geophysical data obtained in recent years. The chemical evolution of the Earth is part of the chemical evolution of Space. Modern cosmochemical and geochemical data reveal that the chemical history of the Earth as well as of other bodies of the Solar System is associated not only with preserved stable and nonstable isotopes but also with extinct radioactive isotopes, including the isotopes of transuranium elements.

## Contents

Preface 5

The Distribution of Elements in the  
Solar System and Their Geochemical  
Properties 9

Evidence of the Early History of the  
Solar System 31

The Nature and Chemical Composi-  
tion of Planets 45

Composition and Constitution of the  
Earth 71

The Present and Past Radioactivity  
of the Earth 87

The Birth of Atoms in Space 97

Chemical Evolution of the Protopla-  
netary Material 112

Formation of the Earth's Principal  
Shells 136

Origin and Evolution of the Ocean and Atmosphere	152
Principal Trends in the Chemical Changes in the Earth's Crust and Biosphere	181
The Chemical Evolution of the Earth's Crust	202
Conclusion	223
Bibliography	232

## The Distribution of Elements in the Solar System and Their Geochemical Properties

The origin and development of the Earth are parts of the cosmic history of atoms of chemical elements. Its beginning has not yet been understood to the full and presents the most important problem of astrophysics and cosmochemistry. The chemical composition of our planet resulted from the cosmic evolution of the matter making up the Solar System. In its course certain quantitative proportions of atoms were brought about. In this connection, we should be primarily interested in modern quantitative relationships pertaining to the atoms of chemical elements within the Solar System. These relationships are one of the principal causes having defined the nature and development of a particular body.

The abundance of chemical elements is mainly determined on the basis of the data of the Sun's composition obtained by means of spectral analysis and also from chemical investigations conducted in laboratories on the material from the Earth's crust, meteorites and rocks of the Moon's surface.

At present it is conventional to express cosmic abundance of elements in a particular natural system in terms of atomic relations

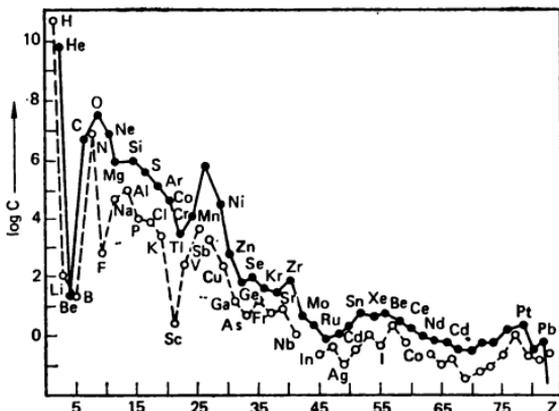


Fig. 1. The relative abundance of atoms of chemical elements in the Solar System versus their ordinal number (Z):

even-numbered elements are denoted by black circles, odd-numbered by light ones

ships. Thus, the quantity of atoms of a chemical element is expressed in relation to silicon. This choice is not accidental because of the difficulty of making silicon volatile. At the same time it is a widespread element.

The relative atom abundance of elements in the Solar System is shown in Fig. 1. The data presented have the attitude to a unity of  $10^6$  silicon atoms and are placed in order of increasing atomic number  $Z$ . The relative abundance shown on the vertical coordinate is expressed in logarithmic values of the atom numbers. Thus, plotted on the graph is the dependence of element abundance on their ordinal number. Distinct regularities in the cosmic abundance of elements are not difficult

to notice. So, it is quite evident that the abundance is characterized by striking differences. For example, beryllium atoms are one million times less than those of oxygen. At the same time, a general pattern of the abundance has a deep-rooted connection with a leading atomic parameter, i.e. the ordinal number or charge ( $Z$ ). So, the following regularities can be distinguished:

the abundance of elements nonuniformly decreases with increase in ordinal number  $Z$ ;

even-numbered elements (having the even-numbered  $Z$ ) are more abundant than the neighbouring odd-numbered ones. In geochemistry and cosmochemistry this regularity is called the Oddo-Harkins rule;

more abundant are the elements mostly containing isotopes with mass number ( $A$ ) which is divisible by four, i.e. a multiple of four.

As the ordinal number of an element is equal to that of protons in its nucleus, and the most stable nuclear structures have the even-numbered combination of nucleons (protons and neutrons), it is easy to arrive at the conclusion that the total abundance of elements in the nature is governed by nuclear properties of their atoms. As can be seen in Fig. 1, the abundance curve of elements has its maximum in the area of iron, then turns downwards and after that of molybdenum ( $Z = 42$ ) it becomes almost horizontal. Most maxima belong to elements where  $A$  of their leading isotopes are multiples of four, namely:

$A=4$	8	12	16	20	24	28	32	36	40
He	—C	O	Ne	Mg	Si	S	Ar	Ca	

Other maxima on the abundance curve are related to the nuclei with neutrons or protons equal to

2, 8, 20, 50, 82 and 126

Named by physicists magic numbers they characterize filled nuclear shells that are typical of the most stable atomic nuclei.

The above facts clearly demonstrate the dependence of the abundance of atoms in the Solar System on their compositions and properties. This is clearly demonstrated by H. Suess and H. Urey: "One can assume that the abundance of elements and their isotopes is determined by nuclear properties and that the substance around us is similar to ash produced by cosmic nuclear fire."

Hydrogen and helium are the most widespread and are the lightest elements of the Solar System. They are readily lost by planets with small masses under all modes of their formation.

If the composition of the Solar System substance is evaluated on the basis of the most common properties of elements, the substance can be divided into two parts: volatile (consisting of gases at normal conditions) and nonvolatile. The first of them includes H, He, CO, CO<sub>2</sub>, CH<sub>4</sub>, O, N and all inert gases, and the second, a great number of chemical elements including main rock- and meteorite-forming ones Si, Fe, Mg, Ca, Al, Na, Ni.

The nonvolatile part of the solar substance is best represented by the most widespread

stony meteorites—chondrites. Figure 2 compares modern data on the abundance of non-volatile elements in the substance of the Sun and ordinary chondrites. These data magnify a basic uniformity in the substances making up

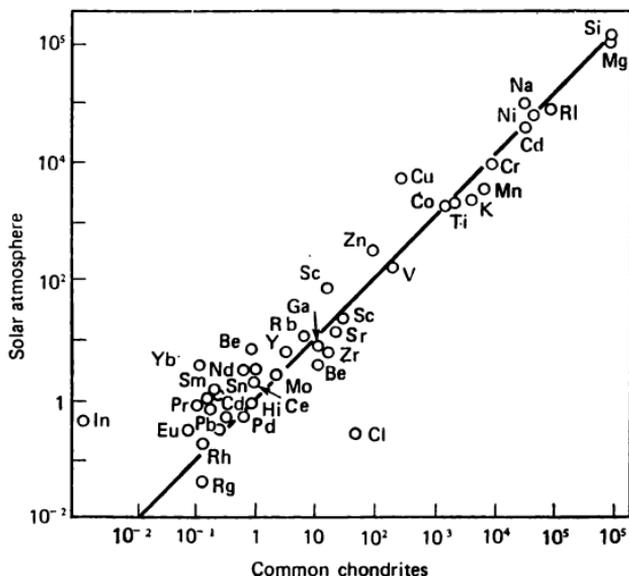


Fig. 2. Metal abundance in common chondritic meteorites and in the Sun (according to J. Wood)

the Sun and meteorites, this being due to the history of the Solar System appearance.

However, the most convincing evidence supporting the genetic uniformity in the whole Solar System substance is found in the isotope composition of chemical elements. Most of stable elements have more than one isotope, their number depends on the even or odd value of  $Z$ . A presence of isotopes is due to the fact

that given the same amount of protons, an atomic nucleus may contain a different number of neutrons. Chemical elements from the middle part of Mendeleev Periodic Table are characterized by the greatest number of isotopes.

Thus, tin consists of 10 and xenon of 9 isotopes. Even-numbered elements contain more isotopes than odd-numbered ones. Elements with the odd-numbered  $Z$  have only one or two stable isotopes. Light ( $Z = 28$ ) and very heavy ( $Z = 81$ ) elements have less isotopes than those from the middle part of the periodic system in the area, where  $Z$  varies from 28 to 81.

In quite a number of elements having been studied in the material of meteorites, the Moon and the Earth, isotope composition is the same. For example, it proved to be practically alike in C, O, Si, Cl, Fe, Ni, Co, K, Cu, Ga, Ba from the Earth's substance and meteorite material. As for the Sun itself, some of molecular spectra were helpful in determining with moderate accuracy the isotope composition of carbon as a value of  $^{12}\text{C}/^{13}\text{C}$ . These investigations have shown that isotope composition of solar carbon is practically the same as on the Earth. At the same time isotope composition of carbon from other star worlds differs from that of our Solar System.

Thus, modern data on the abundance of elements and their isotopes in the studied cosmic objects and the Earth's material indicate a very close genetic unity of the whole material of the Solar System.

Considering the abundance of elements

and the main forms of their occurrence in the Solar System over a wide temperature range, one can divide the most widespread elements into rock-forming (forming solid bodies), chemically active volatile elements, and inert gases. Table 1 presents data on the abundance

TABLE 1. Relative Abundance of Elements in the Solar System (Si = 10 000)

Element	The Earth's continental crust	Sun	Meteorites	The Earth as a whole
<b>Rock-forming elements</b>				
Si	10 000	10 000	10 000	10 000
Al	3 050	690	850	940
Fe	1 010	2 500	9 000	13 500
Mg	950	7 400	10 000	8 900
Ca	1 030	600	720	330
Na	1 050	910	600	460
K	540	22	32	40
Mn	20	30	93	30
Ti	120	18	23	20
Ni	1	230	490	1 000
P	35	190	127	100
<b>Volatile elements</b>				
H	1 400	$4.8 \cdot 10^8$	55 000	84
O	20 500	440 000	77 000	35 000
N	2	46 000	490	0.2
C	17	170 000	8 200	70
S	3	8 000	5 000	1 000
F	33	25	—	3
Cl	4	21	—	32
<b>Inert gases</b>				
He	—	$3.9 \cdot 10^7$	—	$3.7 \cdot 10^{-7}$
Ne	—	44 000	—	$12 \cdot 10^{-7}$
Ar	—	3 400	—	$5 000 \cdot 10^{-7}$
Kr	—	0.25	—	$0.6 \cdot 10^{-7}$
Xe	—	0.03	—	$0.05 \cdot 10^{-7}$

of chemical elements in the Solar System according to their classification into rock-forming, volatile and inert gases. The bulk of stony bodies of the Solar System: meteorites, the Earth's crust, the Moon rocks and the majority of the planets of the Earth type are made up of rock-forming elements. Volatile elements are typical of the solar material. At a low temperature their atoms form molecular compounds that are also basically volatile and occur in the form of gases at temperature above  $0^{\circ}\text{C}$ , but at temperature between  $-10$  and  $-200^{\circ}\text{C}$  some of them get frozen passing into a solid state. Inert gases do not form chemical compounds with other elements and remain in a gaseous state even at the lowest cosmic temperatures observed with in a Solar System.

The Sun is a gas ball with a temperature equalling 6 000 K on its surface and increasing towards the centre. It is more than a boiling temperature of any material. Therefore, the Sun's material is ionized hot gas. Most of the Sun's mass consists of hydrogen and helium. In this connection the Sun itself can be regarded as a heated hydrogen-helium gas sphere with a small amount of chemical elements.

The differences in composition between the Earth's crust, the Earth, the Sun and meteorites shown in Table 1 demonstrate their formation history, including their fractionation and differentiation of chemical elements. The Earth and meteorites retained a minimum of volatile elements keeping them to a degree commensurate with their chemical activity.

Inert gases are in essence alien to our planet and have the deficiency in meteorites.

So, all the bodies of the Solar System may be thought of as consisting of few elements, their abundance being limited by No. 28 of the periodic system. The whole substance has the same origin. Differences in the composition of individual bodies are due to quite certain properties of elements, their ability to be chemically active, inert or form a gas phase that is easily lost by small planets.

Cosmochemical and geochemical properties of elements influence their behaviour in the planet's shells, meteoritic phases or their distribution among minerals. Elements with similar geochemical properties produce common concentration in certain natural systems.

In forming chemical compounds the outer layer in most of the atoms is constituted by electrons, whose number is a multiple of two. A shell consisting of eight electrons is the most stable one. The formation of natural chemical compounds (minerals) is governed by the type of composition of atoms or ions. Depending on the composition of an outer electron shell one can distinguish four basic types of atoms:

inert gases with eight electrons in the outer layer. To this type belong atoms of inert gases: Ne, Ar, Kr, Xe, as well as He, the latter being distinguished by a rather stable two-electron shell;

atoms easily forming ions similar to the type of inert gases. This second type includes alkali and alkali-earth metals, etc. (Na, K,

Rb, Cs, Mg, Ca, Sr, Ba, Al, Sc). After losing valence electrons these metals acquire the outer eight-electron shell or through acquiring electrons form negatively charged ions  $O^{2-}$ ,  $F^{1-}$ ,  $Cl^{1-}$ ,  $Br^{1-}$ ,  $I^{-}$ ;

atoms forming ions with 18 electrons in the outer shell. These include Cu, Ag, Zn, Ga, In, Hg, Pb, etc. and are characteristic of the so-called second parts of long periods of Mendeleev Periodic Table;

atoms forming ions of the intermediate type between the second and the third types. Losing the electrons of the outer layers they acquire outer 9-17-electrons shells. This type of composition is typical of metals of the iron group, for instance, Fe, Co, Ni.

Atomic volumes, radii of atoms and ions, ionization potentials belong to the most important values governing geochemical properties of elements. We shall only discuss atomic volumes.

These are determined as a ratio of the element's atomic weight to its specific gravity. This value can also be thought of as the volume of one gram-atom of the element in a solid state. Atomic volumes vary as a periodic function of the ordinal number of elements. Atomic volumes are presented in Fig. 3, showing that alkali metals and inert gases have maximum atomic volumes. Minimum values are typical of metals of the iron and platinum group.

Different geochemical classifications of elements were suggested according to their behaviour and occurrence in nature. All of them

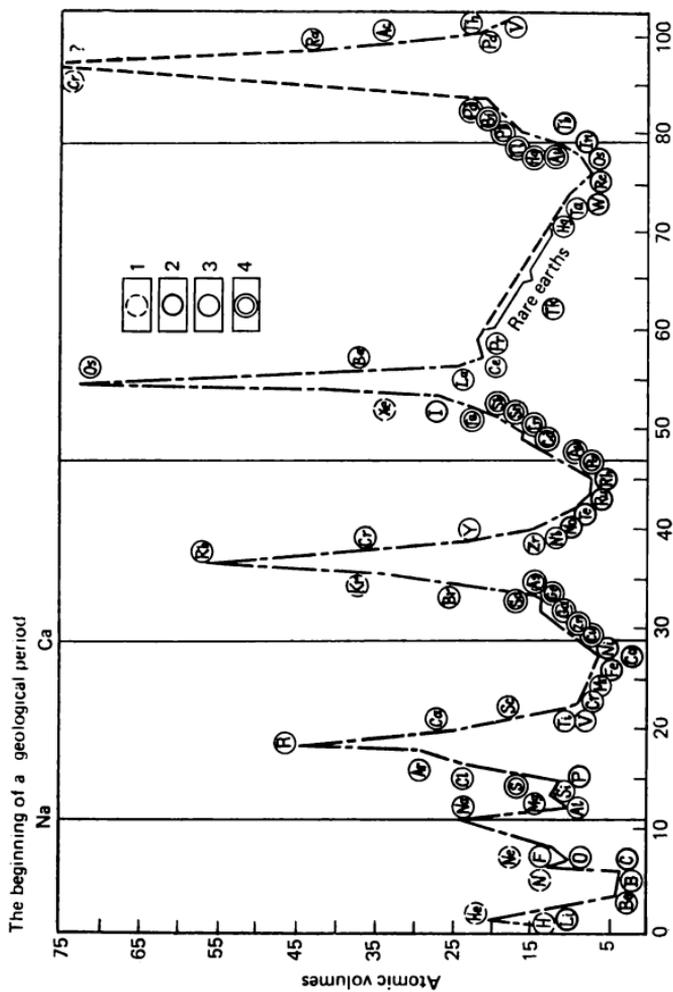


Fig. 3. The curve of atomic volumes of elements:  
 1—atmophile; 2—siderophile; 3—lithophile; 4—chalcophile

are based on the Mendeleev Periodic Table. Taking the elements from this table, V. M. Goldschmidt divided them into four geochemical groups: atmophile, lithophile, chalcophile and siderophile (Table 2). This classification, which had borne the test of time, enjoyed the greatest popularity.

TABLE 2. Geochemical Classification of Elements According to V.M. Goldschmidt

Atmophile	Lithophile	Chalcophile	Siderophile
(H), N, (O)	Li, Na, K, Rb, Cs	(Cu), Ag	Fe, Co, Ni
He, Ne, Ar	Be, Mg, Ca, Sr, Ba	Zn, Cd, Hg	Ru, Rh, Pd
Kr, Xe	B, Al, Sc, Y, La-Lu	Ga, In, Tl	Os, Ir, Pt
	Si, Ti, Zr, Hf, Th	(Ge), (Sn), Pb	Au, Re, Mo
	P, V, Nb, Ta	(As), (Sb), Bi	Ge, Sn, W
	O, Cr, V	S, Se, Te	CC, Cu, Ga
	H, F, Cl, Br, I	(Fe), Mo, (Os)	
	(Fe), Mn, (Zn), (Ga)	(Ru), (Rh), (Pd)	

*Atmophile elements* tend to accumulate in the atmosphere, whence their name. They include all inert gases, as well as hydrogen and nitrogen. These elements have high atomic values and their chemical inertia stems from the stability of the 8-electron outermost shell.

That enables them to be in a free, chemically bound state, in the form of dissipated atoms.

*Lithophile, or oxyphile elements* are concentrated in the Earth's crust (lithosphere) and in the silicate minerals of meteorites. They produce stable compounds with oxygen in the form of oxides, hydroxides, salts of oxygen-containing acids. Their atoms easily form ions with 8 electrons and correspond to the descending paths of the curve of atomic volumes (see Fig. 3). Lithophile elements include the most abundant elements of the Earth's crust and stony meteorites: O, Si, Al, Ca, Mg, Na, K. Iron with its changing geochemical properties behaves as a lithophile (oxyphile) element in an iron-rich medium.

*Chalcophile elements* tend to form compounds with sulphur, i.e. behave like copper ions. Their atoms forming ions with 18 electrons occur in the Earth's crust mostly as sulphur minerals, i.e. sulphides occupying mainly the ascending portions of the curve of atomic volumes.

*Siderophile elements* are characterized by a clearly expressed tendency to concentrate together with iron in its natural melts. The atoms of siderophile elements form ions with 9-17-electron patterns. Owing to stable ties between electrons and atoms the latter (for example, gold, platinum, etc.) often occur in native, forming placers. Siderophile elements are represented by atoms of the iron and platinum group. They occupy the minima on the curve of atomic volumes.

However, it should be noted that there are

no sharp boundaries between the geochemical groups described above. We can indicate a number of elements (bracketed in Table 2) with different geochemical properties. They are chalcophile in the presence of sulphur and lithophile in the presence of oxygen. The latter, a typical lithophile element, is present in the molecular form in the Earth's atmosphere, i.e. behaves like an atmophile one, though not without the involvement of other factors, losing close ties in other compounds ( $H_2O$ ,  $CO_2$ ).

The properties of elements shown in the Goldschmidt's geochemical classification are related to the definite electron pattern of their atoms as follows from the above discussion. These properties are also expressed in the mixture of a substance whose molten state is followed by cooling, an example usually being blast furnace melting. The blast furnace is known to be charged with a mixture of different materials: ore, flux, coke. During melting, chemical reactions take place as does the chemical lamination of the materials in a gravity field. The molten metal concentrating siderophile elements flows downwards, lighter sulphides float up with chalcophile elements, and oxides and silicates also float up in the form of slag. Gases, as atmophile elements, volatilize from this system.

The process of differentiation of material in the gravity field due to geochemical properties of elements could basically occur throughout rather a large planet that had passed the stage of a molten state. It has long been sug-

gested that the ancestral planet from which meteorites had originated underwent chemical differentiation that brought about its chemically different parts, i.e. shells.

Three main phases are clearly distinguished in the composition of meteorites: silicate, sulphide (troilite), and metallic (iron-nickel). Their different proportions make up the known meteorites, with the sulphide (troilite) phase being a minor one owing to the relatively restricted cosmic distribution of sulphur (for example, as compared with oxygen, Table 1).

From studying meteorites the scientists have long discovered that the constitution of the deep-seated parts of the Earth closely resembles that of the known meteorites. Thus, the mantle, a huge shell, could be easily identified with stony meteorites, and the inner core, with iron ones. This idea was best expressed in the concept elaborated by V.M. Goldschmidt in 1920-1924.

According to V. M. Goldschmidt, the Earth during the initial stages of its formation was a liquid molten body beginning to cool down gradually. In this process the chemically homogeneous primary Earth underwent the stage of chemical differentiation, thus distributing chemical elements through the zones according to their geochemical properties. So, siderophile elements, in combination with iron, mainly concentrated in the Earth's core, chalcophile elements formed the shell enriched with sulphides, with lithophile ones forming the mantle. Atmophile elements concentrated in the primary atmosphere of the

planet. In other words, the distribution of elements throughout the Earth's shells agrees with their position in Mendeleev Periodic Table.

It is quite evident that the main idea of chemical differentiation of the Earth put forward by V.M. Goldschmidt and supported by many adherents is noted for its logic and simplicity. However, during the last decades there appeared serious doubts as to its truth. It becomes more clear that the process of chemical differentiation of the Earth was not so simple and it was associated with the Earth formation in the remote past. It may be pointed out that geochemical properties of elements basically vary with temperature and pressure predominating in the interior of the Earth. At present there appeared serious arguments in favour of the substantial amount of sulphur in FeS-Fe form that occurs in the Earth's core. Thus, the most remarkable peculiarity of the geochemical distribution of sulphur is its low relative content in the Earth's crust and mantle. It is several orders of magnitude lower than that in the intermediate material of stony meteorites whose composition represents the averaged material of the Solar System free of volatiles. This leads to the conclusion that substantial amounts of sulphur are concentrated in the very core of our planet.

The recent experiments have shown that under conditions of an ordinary atmospheric pressure the lowest temperature at which the FeS-Fe system melts is 988 °C, substantially

below the melting point of pure iron or silicate material. A rise of the melting point of this system with building up pressure is insignificant. Therefore, all other factors being equal, increasing temperature in the interior of the Earth first forms iron melt enriched with sulphur which tends to drain off into the core zone due to its low viscosity and high density.

The basic idea of V. M. Goldschmidt is now transformed in view of the fact that a general geochemical classification of elements is relative and a particular chemical element may change its behaviour according to the differences in chemical and physical conditions.

The volatility of elements and their compounds belongs to their main geochemical properties. As temperature increases, different elements and their most abundant natural compounds pass into a gaseous phase (vapour) in completely different ways. At low temperatures few chemical elements are in a gaseous state, but with a temperature rise their amount progressively grows. A volatility criterion can be put at 1 500 °C. At this temperature basalt, a widespread volcanic rock on Earth, passes into a molten state. The elements and their natural compounds, becoming vapour at this temperature can be called relatively volatile, and those remaining in the melt, non-volatile. According to A. Ringwood, volatile and nonvolatile elements can be subdivided as shown in Table 3.

Taking into account that volatility is a highly important property of elements in nature, directly associated with the formation of

**TABLE 3. Classification of Elements From the Basic Silicate Melt According to Their Relative Volatility Under Reduction Conditions**

Nonvolatile group	Volatile group	
Oxyphylic:		Probable volatile compounds:
Be, B, Mg, Al, Si, P	H, C, N	H <sub>2</sub> O, CO, CO <sub>2</sub> , N <sub>2</sub>
Ca, Sc, Ti, Sr, Y, Zr Nb, Ba, TR, Hf, Ta Th, U	F, Cl, Br, I S, Se	halides hydrides
Siderophile:	Li, Na, K, Rb, Cs	elements
Fe, Co, Ni, Cu, Ag Au	Zn, Cd, Hg, Tl	elements
Mo, Sn (?), W Ru (?), Rh, Pd, Re Cs (?), Ir, Pt	Pb, As, Sb, Bi, Te Ga, Ge, Sn, In	oxides sulphides

planets of the Solar System, V.M. Goldschmidt's geochemical classification can be corrected and, after slight modifications, it can be given in the expanded Mendeleev Periodic Table (Table 4).

According to this classification, which can be called cosmochemical, all elements in the table are subdivided into highly volatile atmophile, volatile lithophile, volatile chalcophile, high-melting lithophile and high-melting siderophile. As compared with the Mendeleev Periodic Table, Table 4 is expanded to show transuranium elements that at present are lacking in the material of the Solar System but might well be present in certain amounts during the early epoch of its formation, Con-

TABLE 4. Cosmochemical Classification of Elements

I	II	III	IV	V	VI	VII	VIII	I	II	III	IV	V	VI	VII	0		
															H He		
Li	Be	B	C									N	O	F	Ne		
Na	Mg	Al	Si	P									S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Ku	105	106	107	108	109	110	111	112	113	114	115	116	117	118
119	120	121															

1
  2
  3
  4
  5

Lanthanides and Actinides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	

1—highly volatile; 2—rather lithophile; 3—volatile chalcophile; 4—high-melting lithophile; 5—high-melting siderophile

vincing proofs indicating their former existence were recently obtained from the data on some of isotope anomalies.

Contradictory cosmochemical properties of certain elements in Table 4 should be pointed out. Thus, carbon, a high-melting element, behaves like siderophile when it goes into a metallic phase where it forms carbides ( $\text{Fe}_3\text{C}$ ). But as gaseous cosmic systems are cooled down, it connects with oxygen to form volatile  $\text{CO}$  and  $\text{CO}_2$ . Therefore, carbon is classed with volatile elements. Sulphur undoubtedly belonging to volatile elements forms volatile  $\text{SO}_2$  and  $\text{H}_2\text{S}$ . However, entering into a chemical connection with iron, it ceases to be

volatile and occurs in the form of troilite FeS that is a typical mineral of meteorites. Cu, Ag, Au are chalcophile elements but they can be partially dissolved in a metallic phase and thus display their siderophile properties. They are considerably less volatile as compared with other chalcophile elements.

As a whole, the cosmochemical classification of elements presented in Table 4 gives a deeper insight into fractionation and differentiation of chemical elements during the formation of the Solar System. Planets and their compositions are closely connected with these processes.

The capability to form minerals as solid atomic structures according to the laws of crystal chemistry is one of the important properties of elements. The mineral is a crystalline constituent of rocks, ores and other aggregates of the inorganic world. The mineral is produced by physicochemical processes that have occurred and are taking place in the shells of the Earth and planets. All the rocks of our planet and the Moon, meteorites and solid shells of planets consist of minerals. Most of the chemical elements constitute the known minerals and an element may be the main constituent of a mineral and appear in its chemical formula, for example, Si, O, Ca, F, Zn, S in  $\text{SiO}_2$ ,  $\text{CaF}_2$ ,  $\text{ZnS}$ . It may also be present in the form of an admixture. Chemical analysis of natural minerals in many cases reveals that their composition does not correspond to the ideal formula, this being explained by a specific amount of admixtures. Elements are

often present in the form of the so-called isomorphous admixtures replacing atoms and ions in the mineral's structure as far as their sizes are similar to each other. The number of minerals known in nature is limited: there are about 5 000 minerals known in the Earth's crust, and only 140 in meteorites. This limited number of minerals as compared with an infinite number of chemical compounds obtained in laboratory is caused by different reasons, the main one being the abundance of elements capable of making up minerals, physico-chemical conditions of the formation of minerals themselves and proper chemical (crystallochemical) properties of the elements. Generally, in the Earth's and Moon's crusts and in meteorites the following rule is derived: the more abundant is an element, more minerals are formed.

Any mineral as a type of atomic structure can be stable at a given temperature (T) and pressure (P). The melting points of minerals increase as pressure builds up. A mineral with the given composition under pressure can change its physical properties through rearranging the atoms (ions) inside the structure and attaining another crystalline structure. This change in the inner structure of one and the same substance is called polymorphism. Certain kinds of polymorphic states are usually known as polymorphic modifications. For instance, a hard carbon may occur in two polymorphic modifications—cubic diamond and hexagonal graphite.

Data on polymorphic transformations of

the compounds that were formed from the most widespread elements (O, Si, Fe, Mg, S) are particularly important for the understanding of the nature of the interior of the Earth. The compounds of these elements form minerals with different properties and various polymorphic modifications, the most important of them being  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$ ,  $\text{FeSiO}_3$ . These minerals at normal atmospheric pressure will have the following density ( $\text{g/cm}^3$ ):

$\text{SiO}_2$	Quartz	2.533
$\text{FeO}$	Wüstite	5.745
$\text{MgO}$	Periclase	3.58
$\text{Mg}_2\text{SiO}_4$	Forsterite	3.21
$\text{MgSiO}_3$	Enstatite	3.1
$\text{FeSiO}_3$	Hypersthene	3.40

However, as pressure increases, so does the density of minerals because they pass into denser polymorphic modifications. So, quartz can pass into its denser modification, i.e. stishovite with the density of  $4.25 \text{ g/cm}^3$ . Similar changes also occur in other minerals.

Thus, data on the occurrence and distribution of elements within the bodies of the Solar System unambiguously indicate that their destiny depends on a number of specific properties of atoms. Total occurrence of atoms is caused by the properties of their nuclei and the way of their formation. The elements distribution in planetary shells and generally in different cosmic systems is found to be related to the structure of electron shell of their atoms, i.e. the position in Mendeleev Periodic Table.

## Evidence of the Early History of the Solar System

Until recently, before the first stony material had been retrieved from the Moon's surface, meteorites constituted the unique cosmic extraterrestrial material accessible to quantitative laboratory investigations. The composition, constitution, inner texture, radioactivity, age and physical properties of meteorites are undergoing the most detailed investigation. The majority of them proved to be very old, the fact being of basic importance for the knowledge of the history of the Solar System.

The age of meteorites according to radiological data is the time that has passed since their crystallization into solid bodies. Interesting results were obtained as regards the age of meteorites. The modern methods of nuclear chronology based on radioactive decay of uranium, thorium, rubidium ( $^{87}\text{Rb}$ ) and potassium ( $^{40}\text{K}$ ) have shown that most of the meteorites belonging to different classes are of a similar age (4.5-4.6 billion years), which is similar to the modern age dating for the Earth and the Moon. Some of the classes of meteorites, despite their antiquity, changed but slightly and so their chemical and mineralogical compositions bear the signs of events that had occurred during the formation of the Solar System or soon after it.

A surprising age similarity of meteorites and our planet suggests that the formation of

the Earth as a differentiated planet and that of meteorites (or larger bodies like asteroids originally enclosing these meteorites) date back to an ancient epoch in the history of the Solar System. Hence one can also suppose that the birth of planets of the Solar System was a coeval (synchronous) event; to put it more precisely, the planets were formed within a relatively narrow time interval.

The meteorites falling on the Earth's surface out of cosmic space are divided into stony, stony-iron, and iron meteorites. They can be classified as follows:

Stony	{ Chondrites Achondrites
Stony-iron	{ Mesosiderites Pallasites
Iron	{ Hexahedrites Octahedrites Ataxites

Stony meteorites falling on the Earth's surface (Fig. 4) are more abundant. The most widespread among them are chondrites, meteorites, named so because of their specific chondritic structure. Silicate minerals are leading components of all stony meteorites. Iron meteorites, falling more rarely, represent a natural native alloy of iron and nickel. Stony-iron meteorites are made up of commensurable parts of nickelous iron and silicate material.

Table 5 presents an average chemical composition of meteorites of different classes. Only O, Si, Fe, Mg, Ca, Ni, S account for over 90 per cent of the mass of any meteorite. There-

fore, the combinations of these elements in the form of certain solid chemical compounds

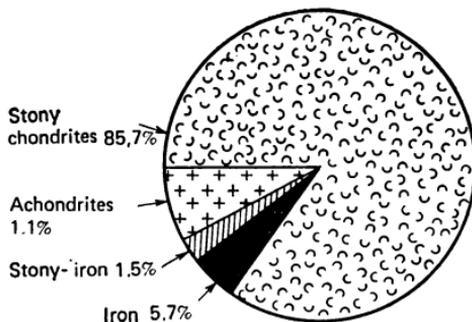


Fig. 4. The relative frequency of the fall of meteorites of different classes (according to J. Wood)

(minerals) are mainly responsible for the chemical nature of meteorites.

TABLE 5. Average Chemical Composition of Different Classes of Meteorites, wt. %

Element	Class of meteorites			Element	Class of meteorites		
	Iron	Stony-iron (pallasite)	Stony		Iron	Stony-iron (pallasite)	Stony
Fe	90.85	55.33	15.5	Ca	0.02	—	1.80
Ni	8.5	5.43	1.10	Si	0.01	8.06	21.00
Co	0.60	0.30	0.08	Na	—	—	0.80
Cu	0.02	—	0.01	K	—	—	0.07
P	0.17	—	0.10	Al	—	—	1.56
S	0.04	—	1.82	Mn	0.05	—	0.16
	0.5						
C	0.03	—	0.16	Cr	0.01	—	0.40
O	—	18.55	41.0	Ti	—	—	0.12
Mg	0.03	12.33	14.3				

Meteorites are found to contain 140 minerals, most of them similar to the crustal minerals on Earth. The most widespread minerals are olivine, pyroxene and native iron. Olivine is a solid solution of fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and forsterite ( $\text{Mg}_2\text{SiO}_4$ ) in different proportions, pyroxene is a solution of ferrosilite ( $\text{FeSiO}_3$ ) and enstatite ( $\text{MgSiO}_3$ ). Iron occurs in two polymorphic modifications Fe- $\alpha$  (kamacite) and Fe- $\gamma$  (taenite), constituting the majority of iron meteorites. Troilite ( $\text{FeS}$ ) belongs to typical meteoritic minerals. Other minerals common for the Earth's crust and meteorites occur in small quantities. Besides, meteorites contain minerals that are unknown in terrestrial conditions:

Moissanite	SiC	Daubreelite	$\text{FeCr}_2\text{S}_4$
Cohenite	$\text{Fe}_3\text{C}$	Niningerite	(Fe, Mg, Mn, Co)S
Osbornite	TiN	Whitlockite	$\text{Na}_2\text{Ca}_3(\text{PO}_4)_2\text{O}$
Sinoite	$\text{Si}_2\text{N}_2\text{O}$	Ureyite	$\text{NaCrSi}_2\text{O}_6$
Oldhamite	CaS		

We shall briefly describe the main classes of meteorites and the changes in their chemical composition.

*Chondritic meteorites* belong to the most primitive class of meteorites. Other meteorites are the products of much more complicated processes of chemical separation of the material. The mineral composition of chondritic meteorites is generally rather simple and uniform. Chondrites are mostly composed of olivine and pyroxene with a small admixture of nickelous iron, plagioclase and troilite. The mineral composition of a typical chondrite

is presented in Fig. 5. An exception are carbonaceous chondrites that mostly consist of hydrated silicates.

Structurally, chondritic meteorites are characterized by a combination of fine-grained spherical formations—chondrules. The term “chondrites” was proposed by the German mineralogist G. Rose in 1864. Chondrules are spherical formations of different sizes, from fractions of a millimetre to several millimetres in diameter. They consist of olivine, rhombic pyroxene and other silicates with different degrees of crystallization. The rest of the fine-grained mass of the chondrites is a mixture of olivine and pyroxene with nickelous iron, troilite and plagioclase. Sometimes glass can be found here. The structure of a chondritic meteorite is given in Fig. 6.

It is conventional to divide chondritic meteorites into:

Enstatite chondrites	group E
Common chondrites	{ group H
	{ group L
	{ group LL
Carbonaceous chondrites	{ type C1
	{ type C2
	{ type C3

Enstatite chondrites are mainly composed of enstatite and native metallic iron. Common chondrites are distinguished by their mineral compositions and iron content. Depending on the latter, H. Urey and H. Craig single out two main groups of common chondrites: group H with high iron content, and group L

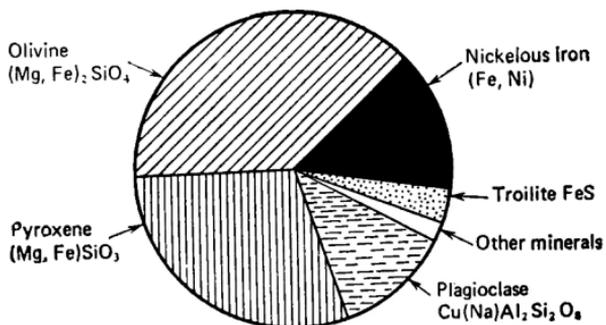


Fig. 5. Mineral composition of a typical chondrite. The areas on the diagram are proportional to weight percent of minerals content

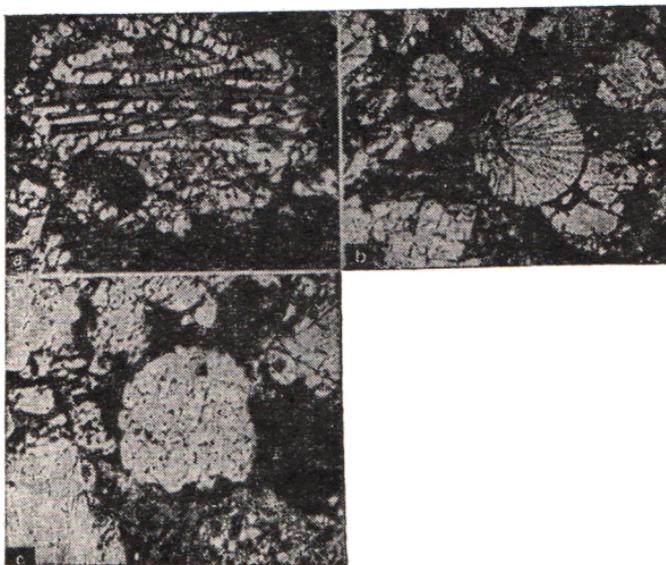


Fig. 6. Microstructure of a chondritic meteorite

with relatively low iron content. Group H on the average has a gross content of iron about 28 per cent, and group L, 22 per cent. All the studied chondrites tend to be in one or other group. In recent years group LL with the lowest iron content has also been distinguished. All its iron in an oxidized form is part of silicates.

Carbonaceous chondrites are rare but they represent a particularly interesting case because of their hydrated minerals, the products of interaction between silicates and water, and also organic compounds. Carbonaceous chondrites are divided into three types: C1, C2, and C3. Type C1 occupies a special place, having the lowest density ( $2.2 \text{ g/cm}^3$ ), and being composed of amorphous hydrated silicates, having much sulphur in form of water-soluble sulphates most enriched with gas. According to the atomic ratios and amount of volatiles the chemical composition of the C1 carbonaceous chondrites is most close to that of the Sun. There are serious grounds to believe that these chondrites are the least differentiated and fractionated material of the Solar System, most similar to the protoplanetary material from which planets and asteroids have been formed. This conclusion is supported by the unusual similarity of atomic ratios in carbonaceous chondrites and the Sun's material. This can be seen in Fig. 7 illustrating the atomic abundance of a number of chemical elements on the Sun and in carbonaceous chondrites.

The most characteristic feature of the change

in chemical composition of chondrites is a transfer from the maximum oxidation in carbonaceous chondrites to the complete reduction of iron in enstatite chondrites. This regularity was noted by G. Prior who formulated the following rule: as metallic nickelous iron content in chondritic meteorites decreases, their magnesium silicates become richer in nickel and iron.

Chondritic meteorites display the wide variety of an oxidizing state (Fig. 8). This points out the fact that reduction-oxidation conditions during the formation of chondritic parental bodies (asteroids) varied widely through the Solar System. Common L-chondrites contain much of the oxidized iron, and all silicon, calcium, chromium and most of phosphorus are combined with oxygen. When reduction becomes more intense (as in H-chondrites), most of phosphorus occurs in the form of the mineral schreibersite  $(\text{Fe, Ni, Co})_3\text{P}$ . And calcium occurs in the form of oldhamite  $(\text{CaS})$ , phosphorus, in the form of schreibersite, and chromium, daubreelite  $(\text{FeCr}_2\text{S}_4)$  at higher stages of reduction, as in the enstatite chondrites. Even their silicates are partially reduced to elementary silicon being part of the nickel-iron phase. A regular change of the chondritic meteorites in the oxidized state undoubtedly indicates that their formation was associated with reduction-oxidation reactions of the primary protoplanetary cloud.

As the reactions of this type in the material having a solar composition depend on temper-

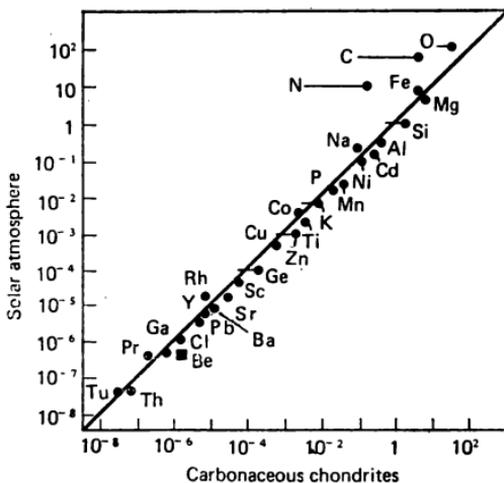


Fig. 7. The comparison between atomic abundance of elements in the Sun and in carbonaceous chondrites. The limits of deviations in contents are indicated with horizontal lines

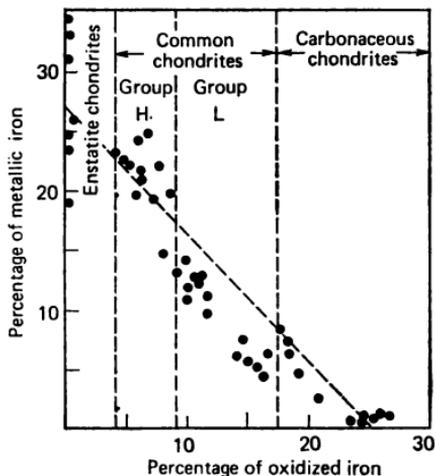


Fig. 8. The ratio between the oxidized and metallic iron in the chondritic meteorites (according to A. Ringwood)

ature, it can be concluded that the temperature conditions differ in different parts of the protoplanetary cloud (nebula), from which parental bodies of chondritic meteorites had appeared. Thus, at higher temperatures iron is reduced and at lower temperatures, it is oxidized and converted into oxides and silicates.

The mean density of chondrites varies depending on the oxidation state. The C1 type carbonaceous chondrites are the lightest, most oxidized and have a density of about  $2 \text{ g/cm}^3$ . The most reduced are the enstatite chondrites, their density being about  $3.5 \text{ g/cm}^3$ . An increase of metallic iron is the deciding factor in increasing the density.

The origin of the chondritic meteorites is associated with that of their characteristic chondritic structure. Most investigators of meteorites believe that chondrules were formerly the solidified and crystallized drops of melt.

*Achondrites* belong to a group of stony meteorites with a crystalline structure (that is lacking in chondrules). Many of these are similar to terrestrial and lunar rocks. Eucrites and howardites, most similar to terrestrial rocks, are composed of pyroxene and anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ). Mineralogically and texturally, eucrites are close to the basic gabbroid rocks of the Earth's crust but differ from them by an increased proportion of a dark-coloured mineral (pyroxene). On the whole textural peculiarities and mineralogical composition of most of the achondrites indicate that they original-

ly crystallized from magma in the same way as did terrestrial igneous rocks. All the achondrites are divided into rich and poor in calcium. The achondrites rich in calcium are composed of plagioclase and have another name—basaltic achondrites.

As it was already noted, *stony-iron meteorites* are made up of nickel-iron and silicate material, and approximately equal quantities of nickelous iron and silicates compose mesosiderites. The silicates are mostly composed of pyroxene and plagioclase, pyroxene being sharply dominant. The nickelous iron in grains of different sizes is nonuniformly distributed through the whole meteorite. Pallasites belong to a nickel-iron mass in which silicate minerals occur as inclusions. There are sporadic small inclusions of troilite and schreibersite in the nickelous iron. A silicate part mainly consists of olivine in the form of angular and rounded grains. Generally the pallasites are more close to the iron meteorites. Their metallic part contains structures similar to that of the iron meteorites.

*Iron meteorites* are enriched with siderophile elements and are almost entirely devoid of lithophile elements. Depending on the structure and nickel content they are subdivided into separate groups: hexahedrites (4-6%), octahedrites (6-14%), ataxites (exceeding 12%).

Besides iron, nickel and cobalt, the iron meteorites include small amounts of phosphorus, copper, sulphur, carbon in the form of inclusions of schreibersite, troilite, cohenite and graphite. Sometimes iron meteorites contain

silicate inclusions of enstatite and olivine, very poor in iron. The nickel content in some parts of the iron meteorites ranges from 5 to 62 per cent. As shown by G. Lowering, this is caused by differentiation during crystallization of a homogeneous nickel-iron melt that has formed the core of the original meteoritic body of asteroid sizes. About 80 per cent of all known iron meteorites belong to the class of octahedrites. Upon pickling their polished surface with a dilute acid special patterns develop the so-called Widmanstätten structures made up of stripes intersecting each other at certain angles. The stripes are formed by a system of plates of the alloy with a low nickel content (kamacite). The system lies parallel to four planes of the faces of octahedron and consequently iron meteorites of a similar texture are called octahedrites. It has been possible to produce these small structures artificially through a very slow cooling of nickel-iron melts. A study of physicochemical equilibria of nickel-iron melts has shown that these structures and the composition of iron meteorites could appear upon slow cooling to 300 °C and at a pressure of  $10^5$  atm. This undoubtedly indicates that iron meteorites were formed in integral parts of the cosmic body of a planetary size.

Precise evaluation of nickel, gallium, and germanium contents in iron meteorites made by H. Brown and J. Wasson helped distinctly divide meteorites into certain groups. It has been possible to distinguish 16 groups of iron meteorites in which the distribution of nickel,

gallium, germanium and other microelements, and principally that of their ratios have certain regularities. These data indicate that the material of iron meteorites has been formed in different conditions: at different temperatures, pressures and even under different conditions of heating and cooling. This could by no means occur in the interior of a single planet.

The above data on the composition and texture of the known meteorites shed some light on their origin. As long ago as the beginning of the 19th century A. Stoikovich and W. Olbers independently of one another advanced a hypothesis that all the meteorites were the fragments of the planet that had disintegrated in the old days. However, at present we can conclude that the problem is not so simple. According to the present-day data meteorites are the fragments of bodies of asteroid size but belong to different types. Thus, achondrites, stony-iron, and iron meteorites make it possible to reconstruct a common appearance of their parental bodies subjected to melting and differentiation and to study the processes of fractionation in detail. In other words, the above chemically distinct meteorites can be in fact regarded as the products of decay of an asteroid that has undergone chemical differentiation resulting in the outer silicate shell (howardites, eucrites), the inner shell (mostly achondrites at the top and partially mesosiderites at the bottom) and metallic nucleus (iron meteorites and partially palacites).

On the other hand, chondritic meteorites

apparently originated from many small asteroids that had not been subjected to chemical differentiation. At the same time these asteroids had small masses and therefore the pressure in their central parts could not break the chondritic texture. In this case chondritic meteorites of H and L groups resulted from the bodies of different initial compositions in respect to iron content.

All briefly described data on meteorites allow one to reach certain conclusions that are important for an understanding of the origin of the Earth and small bodies of the Solar System. Rather similar age of the Earth and meteorites of different types indicates that the formation of solid bodies in the Solar System was mainly a synchronous process. If we assume that achondrites, stony-iron and iron meteorites are fragments of chemically differentiated planets, the coincidence of the age of these meteorites and chondrites will suggest a relatively rapid process of chemical differentiation of parental planets (asteroids).

Carbonaceous chondrites of the C1 type are the most primitive meteorites and the similarity between their atomic ratios and those of the solar material allows one to make a suggestion that they belong to the least differentiated material of the Solar System that is most similar to the protoplanetary material from which planets and asteroids had been formed.

The chemical composition of chondrites provides a wide range of their oxidation states from maximally completely oxidized iron in

carbonaceous chondrites to completely reduced iron in enstatite chondrites which indicates chemical processes of a redox character in different parts of the Solar System during its formation.

## The Nature and Chemical Composition of Planets

Our knowledge of the composition of planets is rather limited. For the time being it was based on the indirect data, predominantly on the mass, average density, size, reflectance, and distances from the Sun. Space flights provided us with more detailed information on the nature of the upper layers of Venus, Mars and Mercury. Lunar material, whose composition proved to be similar to that of some igneous rocks on Earth, was brought to the Earth's laboratories. Despite outstanding achievements in the field of introducing modern technique in the near-Sun space, the data resulting from space flights have been obtained only on the nature of the planet's surface. However, their inner structure and composition are very little known to us. Nevertheless, the main data on mechanical properties of planets on the whole reveal their composition.

All the planets of the Solar System are divided into inner, or the planets of a terrestrial type, and outer, or the planets of a Jupiter type. The inner planets include those that are located at a short distance from the Sun: the

Moon, Mercury, Venus, the Earth, Mars, and the distant planets, Jupiter, Saturn, Uranus, Neptune, and Pluto, belong to the outer planets. The inner planets are mainly solid stony bodies. Asteroids and satellites of planets are similar to them in their nature.

Table 6 presents the most important characteristics of planets as compared with those of the Earth.

TABLE 6. Planetary Characteristics in Comparison with Earth

Planet	Mass	Radius	Mean density, g/cm <sup>3</sup>	Mean density on the zero pressure	Escape velocity, km/s	Albedo
<b>Inner planets</b>						
Moon	0.0123	0.273	3.34	3.31	2.38	0.067
Mercury	0.0558	0.382	5.42	5.3	4.3	0.056
Venus	0.8150	0.949	5.25	4.4	10.3	0.76
Earth	1.0000	1.000	5.52	4.4	11.2	0.36
Mars	0.1074	0.532	3.94	3.9	5.0	0.16
<b>Minor planets</b>						
Asteroids	~0.00066	~0.11	3.5-2.0	3.5-2.0	—	—
<b>Outer planets</b>						
Jupiter	317.9	11.27	1.314	—	59.5	0.67
Saturn	95.15	9.44	0.69	—	35.6	0.69
Uranus	14.54	4.10	1.19	—	21.2	0.93
Neptune	17.23	3.88	1.66	—	23.6	0.84
Pluto	0.0023	(0.24)	1	—	(1.1)	0.49

The density is an essential value that defines the composition of planets. The average

density of planets results from dividing their mass by volume  $d = M/V$ . It is obvious that it varies widely. On the one hand, we can indicate the planets of a terrestrial type with a high density within 3.35-5.52 g/cm<sup>3</sup> that are mostly composed of the solid material, on the other, outer planets are distinguished by their low density (1.35-0.71 g/cm<sup>3</sup>), which mainly suggests their gaseous composition. Indeed, Jupiter and the planets that are close to it, according to theoretical data, are mostly made up of gases, among which hydrogen, as the most widespread cosmic element, occupies the first place.

A comparison of the planets of a terrestrial group between each other and with our planet on the whole is very important in understanding the chemical nature of the globe. Therefore we shall briefly discuss the characteristic features of the inner planets and the Moon.

*Mercury*, the nearest planet to the Sun, has the highest density. According to its size Mercury occupies the thirteenth place in the Solar System, giving way to Jupiter's satellites—Callisto and Ganymede, Saturn's satellite—Titan, and Neptune's satellite—Triton. Until very recently the orbital period of Mercury around the Sun was considered to be equal to the period of its rotation around the axis. However, the newly obtained data reveal that the latter is 1.5 times smaller than its orbital period. The temperature on the illuminated side of Mercury reaches 625 K, and on the dark, non-illuminated part it is probably

only 10-20 K. Most gases must freeze on the non-illuminated side, and on the illuminated, hot side the molecules of common gases must acquire heat velocities exceeding volatilization velocities from the surface. Therefore Mercury is practically devoid of atmosphere. It is possible that it has some argon atmosphere as a product of decay of radioactive  $^{40}\text{K}$  concentrated in the solid body of the planet.

*Venus* is most similar to the Earth in sizes and density. It possesses the most thick, dense and warm atmosphere of all the planets of a terrestrial group. According to the data of Soviet *Venera* interplanetary stations, 97 per cent of the planet's atmosphere consist of carbon dioxide. Hydrogen and water are also present. The atmosphere's temperature near a solid surface reaches  $747 \pm 20$  K and the pressure is 90 atm. Abundance of carbon dioxide may be explained by decomposition of carbonates at high temperatures according to the



equation which in the condition of Venus is shifted to the right (in modern conditions of the Earth it is shifted to the left). The decomposition of other carbonates occurs in a similar way to form carbon dioxide. Free oxygen on the planet Venus results from water decomposition due to solar radiation. Hydrogen, another decomposition product, is easily lost by the upper layers of the atmosphere. This caused a slow secular loss of water on Venus and the planet was slowly drying up. Practically all the water in the atmosphere is in a vaporous

state at high temperatures of the surface. The presence of a light water vapour determines a high reflectance of the planet that reflects 76 per cent of the sunlight falling on it.

A solid surface of Venus is covered with the rocks being similar to terrestrial ones of a basalt type and granodiorites according to radiometric evidence.

*The Earth* is the largest of all inner planets. At the same time it has a large satellite, the Moon, whose mass accounts for 1/81 part of the Earth's mass. The nitrogen-oxygen atmosphere of the Earth differs in its composition from those of other planets and is a result of the evolution of life. Most of the atmospheric argon of the Earth has a radioactive origin owing to decay of  $^{40}\text{K}$  both in the crust and the interior of the planet.

*The Moon* proved to be the first planet, whose material was brought to the Earth laboratories and studied by all modern physico-chemical methods. The surface of the Earth's satellite is composed of relatively light patches, formed by mountain systems and uplands, and of dark areas, the so-called maria. The names of lunar objects were proposed by the Polish astronomer (Johannes Hevelius) and the Italian astronomer (J. Riccioli). The largest maria were named the Mare Imbrium, the Mare Serenitatis, the Mare Fecunditatis, the Mare Nectarus, the Mare Tranquillitatis, the Oceanus Procellarum. The whole of the Moon's surface is covered with a great number of funnels of different sizes, the largest being called lunar cirques. Lunar cir-

ques are called after outstanding scientists and cultural workers. The entire surface of the Moon is composed of igneous rocks and the products of their disintegration, the uplands, of mostly anorthosites that are characterized by the following mineral composition (in per cent):

Orthoclase	$\text{KAlSi}_3\text{O}_8$	0.35-0.47
Plagioclase	$\text{Ca(Na)Al}_2\text{Si}_2\text{O}_8$	71.6-74.8
Diopside	$\text{CaMg(SiO}_3)_2$	2.44-4.8
Hypersthene	$\text{FeSiO}_3$	8.7-16.3
Olivine	$(\text{Mg, Fe})_2\text{SiO}_4$	5.3-10.0
Ilmenite	$\text{CaTiO}_3$	0.4-0.8
Apatite	$\text{Ca}_3(\text{PO}_4)_3\text{Cl}$	0.07-0.11

Lunar maria are wide depressions filled with dark basalts, fine-grained volcanic rocks. Lunar basalts differ from terrestrial ones by an enhanced iron and titanium content and a decreased sodium and potassium content. The chemical composition of typical rocks of the Moon is shown in Table 7.

In respect to other chemical elements all lunar rocks are distinguished by a high concentration of high-melting lithophile elements and a decreased concentration of volatile chalcophile elements. Heavy chalcophile metals (Hg, Tl, Pb, Bi) are sharply contrasting, their concentration in lunar rocks being two orders of magnitude lower than that in the similar rocks of the Earth.

On the whole the chemical composition of rocks of the lunar crust is most similar to that of eucrites, feldspathic achondrites enriched with calcium. All lunar rocks are exceptionally dry.

The age of lunar rocks proved to be very old: old anorthosites are dated at 4.5-4.0 billion years and younger lunar basalts at 3.6-3.3 billion years. This indicates that

TABLE 7. Chemical Composition of Lunar Rocks

Oxide	Terra rocks		Basalts of lunar maria		
	Anorthosite Apollo-15	Anorthosite Moon-20	Mare Tran- quilli- tatis	Mare Fecun- ditatis	Basalts of the Pacific Ocean
Si <sub>2</sub> O <sub>2</sub>	44.1	44.2	40.5	42.95	48.44
TiO <sub>2</sub>	—	0.52	11.4	5.5	1.26
Al <sub>2</sub> O <sub>3</sub>	35.5	19.1	9.7	13.88	15.85
FeO	0.2	6.91	19.0	20.17	8.78
MnO	—	0.12	0.21	0.20	0.21
MgO	0.1	13.37	8.0	6.05	6.39
CaO	19.7	13.3	9.6	10.8	12.15
Na <sub>2</sub> O	0.35	0.48	0.53	0.23	2.57
K <sub>2</sub> O	—	0.47	0.16	0.16	0.46
P <sub>2</sub> O <sub>5</sub>	—	0.12	0.13	0.14	0.13
Cr <sub>2</sub> O <sub>3</sub>	—	—	0.29	—	—

deep-seated processes of igneous activity of the Moon had been completed very long ago.

According to the present-day data the Moon is a spherical body composed of silicate material. It comprises the crust 20 to 30 km thick, the mantle reaching 1 000 km and a compressed silicate core deeper than 1 000 km. The radius of the lunar core is 700 km.

The study of the Moon revealed many mysteries, and at present the problem of its evolution has become much more complicated.

Now we can only say that the material of the Moon was formed under different thermodynamic conditions as compared with that of the Earth and chondritic meteorites. These conditions corresponded to higher temperatures that favoured the formation of solid phases of high-melting lithophile elements and prevented volatile elements from entering into their composition.

Of all inner planets, *Mars* is the most distant from the Sun and has the lowest density. The studies made by Mariner, Viking, Mars-1, 2, 3 space vehicles have revealed that the planet's surface is covered with numerous craters and in this respect is similar to the Moon's surface. There is a vast area Hellas on Mars that is almost devoid of craters. Three types of the Mars' surface are observed: light "terra" areas, yellow "marine" and snow-white polar caps. Most of the planet's surface has an orange colour, which according to optical and radio astronomy data indicates a fine-grained character of crushed silicate rocks, covered with a film of iron oxides.

The atmospheric pressure at the surface of Mars does not exceed 6 mm Hg, i.e. two orders of magnitude less than that on Earth. Carbon dioxide (probably exceeding 50%) is the main component of the atmosphere of Mars. The admixtures of nitric oxides are found. The oxygen and ozone contents are negligibly small. The planet's atmosphere contains vapours as well as aerosols associated with "dust storms". The temperature on the surface of Mars varies with latitude and at the boundary of polar

caps it lowers down to 140-150 K. Carbon dioxide must freeze at such temperatures. It can be assumed that polar caps of Mars consist of frozen carbon dioxide. The thickness of its layer may attain several metres. In polar areas a considerable amount of water vapour must freeze which can cause the formation of glaciers.

In 1969 on the basis of properties of the material of the Earth's mantle and a very precise evaluation of the radius and mass of Mars according to the data of Mariner-4 space vehicle, A. Binder studied theoretically the inner structure of Mars. Theoretical modelling has revealed that probably Mars has an inner iron core, the radius being of the order of 790-950 km. The composition of the shell, i.e. the mantle of Mars, should not essentially differ from that of the Earth's mantle. The temperature inside Mars should be from 800 to 1 500 °C, i.e. considerably lower than in the interior of the Earth.

Mars has two small satellites: Phobos and Deimos. They move along the orbits almost coinciding with the plane of the planet's equator (Phobos at a distance of 9 400 km and Deimos, 23 500 km). Both satellites are of irregular shape and have a low albedo that is similar to that of carbonaceous chondrites and basalts. The satellites are covered with funnels of an impact origin. The biggest funnel on Phobos is 5 km in diameter. Generally the entire surface of satellites of Mars is characterized by a high density of funnels. This may indicate that the satellites are very old and have a great history.

In 1948 the English astronomer W. Ramsay hypothesized that all the inner planets have a similar composition and the difference in their average densities is governed by different compression ratios of the material affected by high pressures, proportional to the planet masses. In particular, the existence of the Earth's core was due to the phase transition of the silicate material to the metallic state caused by a high pressure. However, if the inner planets had had a similar chemical composition, and the compaction in central parts had been determined by the mass of the planet itself, we would have observed a successive increase of density in the successive sequence of the planet mass increase (Mercury, Mars, Venus, Earth). In reality as can be seen in Table 6, the small Mercury has a higher density as compared with the more massive Mars or Venus. Therefore it can be concluded that inner planets have different chemical compositions.

While evaluating their compositions the value of average densities calculated for the zero pressure in the centre of planets is of great interest. The difference in the compositions is determined by different ratios between silicate (the density is  $3.3 \text{ g/cm}^3$ ) and metallic nickel-iron material (the density is  $7.23 \text{ g/cm}^3$ ). The development of these concepts in recent years has been favoured. At the same time the distribution of metallic and silicate parts inside the planets remains the subject under discussion: do they exist together and are uniformly distributed within the entire volume of

each of the planets or do they coexist separately—metallic phase in the form of inner core, and a silicate one, in the form of shell, i.e. the mantle of different thicknesses?

Considering all the data available in the field of geophysics, geochemistry, and cosmochemistry it seems quite probable that there are central metallic cores inside the planets of a terrestrial type. Such a conclusion better

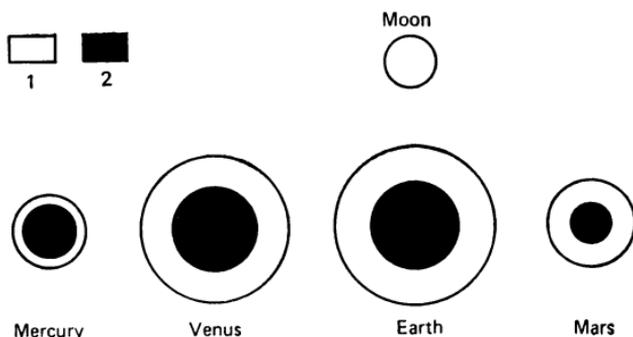


Fig. 9. The composition of inner planets with different ratios of silicate (1) and metallic (2) material

corresponds to all that is known and is supported by such meteorites as iron, stony-iron, and achondrites.

If we advance the working hypothesis, the most probable one, that a metallic phase formed the inner cores of all the planets, it is easy to imagine the main values of these cores. According to calculations made by R. Reynolds and A. Summers, the radii of inner cores amount to 0.8 of the outer radius of Mercury, 0.53 of that of Venus, 0.55 of that of the Earth, 0.4 of that of Mars. Figure 9 presents a

comparison between the inner constitution and composition of the planets of a terrestrial group.

It follows that the different densities of the inner planets are mostly determined by the difference in their chemical composition. More denser planets contain more iron, less denser ones contain less iron. But in all probability the difference in composition not only comprises the main chemical elements (O, Si, Fe, Mg, Ni, Ca) but refers to all the elements of the Mendeleev Periodic Table. In any case the data on the distribution of rare elements in meteorites of different classes, obtained in the last few years, support such an assumption.

Noteworthy is a spatial trend in the composition of inner planets: the proportion of metallic iron in the planets that are most close to the Sun is higher than in those that are more distant. This is very well seen in Fig. 9, when we compare Mercury that is near the Sun and Mars that is away from it. Apparently in this case there is an important cosmochemical trend, which should be explained by any theory of the Solar System evolution.

*Asteroids* are small solid bodies of the Solar System, most of which move in the so-called asteroidal belt between the orbits of Mars and Jupiter. The masses of asteroids are within wide ranges and are inferred from indirect data. Most of asteroids with masses from  $10^{15}$  to  $10^{23}$  g are of irregular shapes. Actually they are blocks of cosmic rocks with the periods of proper rotation of 8 to 9 hours, which are similar to the periods of rotation of large plan-

ets. Only the largest asteroids exhibit the form close to a spherical one. Large asteroids include Ceres, Pallas, Vesta, their diameters being 1003, 608, and 538 km, respectively. The comparison between the sizes of these asteroids and those of the Moon is given in Fig. 10. At present there are 112 asteroids with the

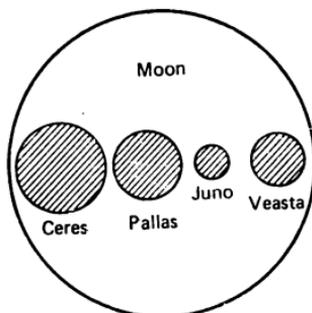


Fig. 10. The comparison between the sizes of large asteroids and the Moon

diameter exceeding 100 km in the Solar System. The total number of well-known asteroids exceeds 2 000.

The reflectance of asteroids indicates their lithology. E.L. Krinov has established that the albedo of asteroids and the known meteorites mainly coincide. In recent years the albedo of asteroids in the different parts of the spectrum was studied in detail by T. MacCord, S. Chapman and D. Morrison. We shall discuss here only the main results of these studies.

Depending on the albedo the studied asteroids are divided into two large groups: dark, or C-asteroids, and relatively light, or S-asteroids. The former are characterized by a rather

low albedo of less than 0.05, and the latter, of more than 0.1. According to the spectral reflectance group C is close to carbonaceous chondrites, and group S, to stony-iron meteorites and common chondrites. Therefore all mineral, chemical and structural peculiarities of meteorites can be basically applied to asteroids. In general the latest photometric measurements have shown the unity of the material of meteorites and that of asteroids. The main groups of asteroids, according to photometric measurements, are distinguished rather clearly.

The most essential result of studying asteroids is that the composition of asteroids differs in different parts of the asteroidal belt (Fig. 11). The bodies that are similar to common chondrites occur in the inner part of the asteroidal belt, but as the distance from the Sun increases within 2.5-3.2 AU\*, their number decreases and the number of asteroids of the type of carbonaceous chondrites increases. The latter dominate in the centre and marginal parts of the asteroidal belt. Thus, a definite cosmochemical trend is observed: the composition of asteroids depends on the heliocentric distance.

Asteroid Vesta has a special place in elucidating the genetic ties between other meteorites and asteroids. According to photometric measurements, Vesta is the only asteroid out of 100 studied ones, whose surface is similar

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\* Astronomical unit (AU) is a modern distance from the Earth to the Sun (149.5 mln km).

to that of basaltic (enriched with calcium) achondrites. It can be assumed that actually Vesta is a chemically differentiated asteroid with achondritic crust and the interior composed of stony-iron masses. The modern study of asteroids reveals that they are the most actual sources of meteorites. Chondritic meteorites can be the fragments of non-differentiated

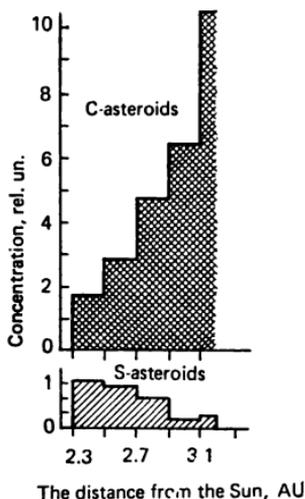


Fig. 11. The concentration of asteroidal bodies with diameter exceeding 50 km. The outer ring of asteroids has mostly dark C-asteroids, and the inner margin has mostly light S-asteroids

asteroids, and the asteroids of the Vesta type, the source of achondrites, stony-iron and iron meteorites.

The belt of asteroids is an area of continuous mechanical decay and disintegration of solid bodies as a result of encounters. Carbo-

naceous-chondritic bodies predominate in the asteroidal belt. A relative rarity of carbonaceous chondrites on the Earth's surface is attributed to the fact that the corresponding material rarely occurs on our planet.

The total mass of the material concentrated in the asteroidal belt is approximately estimated at  $4.5 \times 10^{24}$  g, that makes up 1/20 of the Moon's mass or 1/1 500 of the Earth's mass. The asteroids taken together would form a body 1 400 km in diameter. At present the main mass is concentrated in the largest asteroids, so Ceres alone accounts for 1/3 of the total mass.

The outer planets of the Solar System differ markedly from the inner planets of the terrestrial group in composition, constitution and sizes (see Table 6). They have a low density (0.7-1.7 g/cm<sup>3</sup>) that is determined by the main gaseous composition. Hydrogen and helium are the leading elements in gaseous covers. All the planets without exception have satellites of rather peculiar properties.

*Jupiter* is the largest planet of the Solar System. Its mass exceeds 318 times that of the Earth and 2.3 times that of other planets, taken together. On the basis of recent astrophysical measurements different models of a general constitution of Jupiter were proposed. All of them have common features and admit stratified (shell-type) constitution of the planet that is generally of a solar composition. It is not difficult to imagine that the entire mass of Jupiter is a cooled solar substance. In this case heavy elements are concentrated

in the central areas and the light ones form vast outer shells. According to one of the probable models, Jupiter is made up of the central core with the mass of 40 terrestrial masses composed of a solid material in the compacted state. A vast zone is located above the core mainly consisting of hydrogen. The inner part of this zone, from the centre of the planet up to 40 000 km, is under pressure of 3 million atm and at a temperature of 10 000 K. In this part hydrogen forms the liquid of high electric conduction. Electric currents that appear in this medium cause an extensive magnetic field of Jupiter as inferred from the measurement made by the Pioneer-10 space station.

The outer shell 70 thousand kilometers thick consists mostly of liquid hydrogen in the molecular form  $H_2$ . The gaseous shell, Jupiter's atmosphere proper, comprising mainly molecular hydrogen, helium, methane ( $CH_4$ ), ammonia ( $NH_3$ ) stretches above it for 1 000 kilometres. The temperature of outer layers varies between 140 and 150 K. According to G. Lewis, the planet's atmosphere is characterized by the following indications: in the hydrogen-helium medium at a certain level there appear the droplets of aqua ammonia above which there is a layer of small particles of ice. Above the latter there is hydrogen combined with ammonia. In this case small particles of ammonium hydrosulphide ( $NH_4SH$ ) are formed. The highest cloudy layer forming a visible surface of Jupiter consists of small particles of solid ammonia. The coloured orange-yellow surface of the planet

can be related to the photochemistry of the layers of ammonium hydrosulphide and the particles associated with it. The atmosphere of Jupiter is in convective motion.

Jupiter, together with its 14 satellites, forms an original planetary system that resembles the Solar System in miniature. The largest four satellites were discovered by G. Galilei as far back as the 17th century and were named Galilei's satellites ever since. They include Io, Europa, Ganymede, and Callisto. The studies of the Jupiter system were most thoroughly made by Voyager-1, 2 space vehicles in 1979. According to the recent data Galilei's satellites of Jupiter are characterized by the following values (Table 8).

TABLE 8. Characteristic of Galilei's Satellites of Jupiter

Satellite	Distance from Jupiter, $10^2$ km	Radius, km	Average density, $g/cm^3$
Io	422	$1\ 840 \pm 30$	$3.41 \pm 0.19$
Europa	671	$1\ 552 \pm 20$	$3.06 \pm 0.15$
Ganymede	1 070	$2\ 650 \pm 25$	$1.90 \pm 0.06$
Callisto	1 880	$2\ 420 \pm 20$	$1.81 \pm 0.06$

It is quite evident that the average density of satellites depends on the distance from Jupiter. The nearest satellites have a higher average density as compared with the remote satellites. This peculiarity in miniature repeats the same trend that is observed for inner planets depending on the heliocentric distance.

However, the composition of Galilei's satellites is mainly determined by a different proportion of stony-silicate material and water ice. The satellites of a decreased density can also contain condensed ammonia and water that form an eutectic mixture at a temperature of 173 K. Models of inner constitution of Galilei's satellites are presented in Fig. 12.

Io is the most outstanding satellite of Jupiter and is mostly composed of solid stony material. Its surface is characterized by a combination of red, orange, yellow, and white

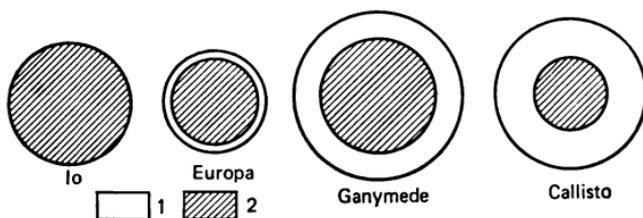


Fig. 12. The composition of Galilei's satellites of Jupiter with a different relation between glacial (1) and stony (2) material

colours. This colouring is mainly due to sulphur at different temperatures. Io is marked by a rather intense volcanic activity. Sulphur dioxide ( $\text{SO}_2$ ) is an agent of volcanism, the lava being presented by a brimstone. There is a number of acting volcanoes on the surface, the largest of which is called Prometheus. It is assumed that intense volcanism on Io is caused by a tidal influence of Jupiter.

Europa is a spherical body, mostly composed of stony material. The surface is covered with a glacial cover 100 km thick. A white surface is covered with a net of dark and, more rarely, light bands. Their origin remains unknown. Impact craters are very scarce, which indicates a relatively young age of the surface. Europa, in all probability, is a dynamically active body. Its surface is covered with a thick glacial crust that apparently floats on the ocean of liquid water. Internal heat is sufficient to cause crushing and displacement of glacial crust. Dark and light bands probably indicate the outlets of heat, i.e. inner activity of the planet as a whole.

Ganymede is the largest Jupiter's satellite. Its density ( $1.9 \text{ g/cm}^3$ ) suggests that it is half composed of stony material, half of ice. The surface is covered with ice with numerous funnels of impact origin. There are uplands and trench-like valleys. The bending chains of hills are about 10 km wide and extend up to 50 km. Generally all the indications of dynamic activity of the glacial crust are observed on Ganymede.

Callisto is the last of Galilei's satellites. The portion of the glacial material is the highest. It is covered with numerous traces of meteorite impacts, whose density is exceptionally high. Unlike the Moon and Mercury, on Callisto there are no craters whose diameter exceeds 150 km. The depth of the craters themselves is much smaller. Ice possesses plastic properties and does not provide the development of contrasting forms of the relief thus

causing the absence of mountains on Callisto. On the whole, Callisto is a dead frozen planet.

The main satellites of Jupiter described are closely related to the central planet that is probably of genetic significance. The rest of Jupiter's satellites have been so far studied very poorly because of their small sizes and a long distance. In all likelihood, they are composed of stony-silicate material and are similar to the asteroids or satellites of Mars.

*Saturn* is the second planet in size after Jupiter. Because of its remoteness it is studied worse than Jupiter. A relatively low average density ( $0.7 \text{ g/cm}^3$ ) decidedly indicates its mainly gaseous composition. A rapid rotation of the planet with a 10-hour period results in strong compression. Thus a polar semi-axis is  $1/10$  shorter than an equatorial one. Gravity field and visible compression of Saturn suggest that its upper shells are lighter and the central ones are heavier than those of Jupiter. The constitution of the planet may be similar to that of Jupiter. However, due to a small mass the pressure in the interior of Saturn grows slower and the layer of metallic hydrogen begins at the depth approximately equal to one-half the radius of the planet. One of the models of Saturn's inner constitution is given in Fig. 13. There is a somewhat greater amount of methane in the upper layers of Saturn or its atmosphere and a somewhat smaller amount of ammonia as compared with Jupiter's atmosphere.

Saturn on the equatorial plane is surround-

ed by a thin ring creating its colourful and unique appearance. The ring is divided into several separate rings, whose origin has not yet been exactly established.

Together with its satellites Saturn forms an individual planetary system. At present

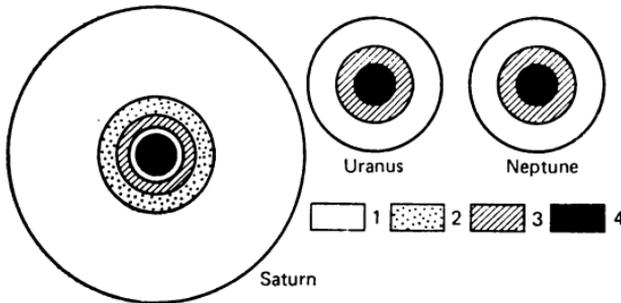


Fig. 13. The inner constitution of Saturn, Uranus and Neptune

17 satellites were discovered, the two being discovered by means of telephotographs Voyager-1, 2. In the direction from Saturn the satellites bear the following names: Ianus, Mimas, Enceladus, Tethys, Dione, Rhea, Titan, Hyperion, Iapetus, Phoebe. The largest Titan has the radius of 2 900 km.

Because of great remoteness the satellites of Saturn are studied worse than those of Jupiter. The average density of the largest Titan is estimated at  $1.34 \text{ g/cm}^3$ , which shows a great role of ice in its composition. According to the most probable model in the central part of Titan there is a stony core surrounded by the mantle made up of the mixture of ice and

particles of silicate rocks. The mantle is covered with a peculiar mixture of water with dissolved ammonia. Titan's "crust" is a mixture of ice and methane. Unlike commensurable satellites of Jupiter, Titan has a noticeable atmosphere composed of nitrogen with the admixture of methane and hydrogen.

The data on other satellites of Saturn are very scarce. Dione and Rhea are characterized by a high albedo (0.6). The density of Dione is  $1.4 \pm 0.6 \text{ g/cm}^3$ . The density of Mimas, Enceladus and Tethys is close to unity. All this suggests the probability of Saturn's satellites being mainly constructed of ice.

*Uranus and Neptune.* Relatively high densities of these planets, 1.6 and 1.7  $\text{g/cm}^3$ , respectively, in comparison with other outer planets allow one to consider that they contain an increased proportion of heavier substances than hydrogen and helium. A number of models of these planets with different combinations of chemical elements have been proposed (see Fig. 13). According to the models constructed by D. Hunten, the planets have cores approximately 16 000 km in diameter, surrounded by the mantles composed of ice. Above them there are vast gaseous covers consisting mostly of molecular hydrogen. The upper layers of Uranus contain methane that may form a cloudy cover. There is also methane in the atmosphere of Neptune. However, ammonia has not been discovered in the planets as it freezes out at low temperatures (about minus 180 °C). In a solid state it could settle out in the lower horizons having formed a correspond-

ing layer. A relative deficit of hydrogen and helium on Uranus and Neptune was probably associated with the leakage of helium and molecules of hydrogen beyond the Solar System as the Sun's attraction at such far distances was essentially reduced, thus causing the loss of light atoms.

Uranus and Neptune have a number of satellites and form individual space planetary systems. Uranus is known to have five satellites (Miranda, Ariel, Umbriel, Titania, Oberon), Neptune has two satellites (Triton, Nereid). The data on the satellites of these planets are exceptionally scarce. According to photometric measurements made by D. Cruikshank (1980), all the satellites of Uranus have a reflecting surface, differing from those covered with water ice. Their albedo is within 0.2-0.5. Titania is the largest satellite, its radius being 800-500 km.

Of the two Neptune's satellites a huge Triton (the radius is 3 000 km) has a retrograde motion, and a small satellite Nereid (the radius is approximately 250 km), has a direct motion. Their origin is not yet known with assurance.

*Pluto* is the most distant planet. The data on its origin and constitution were only recently obtained. Due to the measurement of its albedo by means of a powerful telescope of the observatory located on the Hawaiian Islands it was possible to establish that the planet's surface is solid, composed of frozen methane (methane ice). The radius is within 1 200-1 800 km, and a geometrical albedo is 0.49.

M. Lupo and N. Lewis (1980) have built a number of Pluto's models, the most acceptable being the following one. 21 per cent of the planet, the radius being 1 300 km and the average density  $1.12 \text{ g/cm}^3$ , is made up of a solid rock in the centre, 74 per cent of water ice and 5 per cent of a frozen methane.

In 1978 J. Christy and R. Harrington discovered Pluto's satellite that was named Charon. Pluto-Charon represent a double planetary system, in which the ratio between the satellite's mass and a central body is the highest equalling  $1/10$  (it is  $1/81.3$  for the Moon—the Earth). The radius of Charon is approximately estimated at 600-700 km, the density is approximately  $1.0 \text{ g/cm}^3$ , the orbital period 6.39 days, an average radius of the orbit being approximately 20 000 kilometres.

The above data on the origin and constitution of the planets allow one to draw conclusions having a direct relationship to the evolution of the Solar System.

1. The planets differ in their chemical composition that is most clearly expressed in the difference between the inner and outer planets. The inner planets are mainly solid bodies mostly composed of gases.

2. The inner planets also differ between themselves depending on the heliocentric distance. The closest to the Sun planets are denser than the distant ones.

3. The difference between average densities of inner planets is governed by a different proportion of metallic and silicate material. Hence, the closest to the Sun planets contain

more metallic material than those that are more distant.

4. The composition of asteroids within their belt also depends on the heliocentric distance. Less oxidized bodies of the type of common chondrites are located closer to the Sun, then follow more oxidized ones that are similar in composition to carbonaceous chondrites.

5. Gigantic outer planets originated from matter that is similar in composition to the Sun and fractionation processes during their formation were manifested less intensively. At the same time the chemical differences are observed within the satellites of outer planets depending on the distance to the central planet.

6. All bodies of the Solar System change their composition as influenced by heliocentric distance: the bodies, closest to the Sun, are enriched with high-melting elements and their compounds, the distant ones, mostly with volatile elements and their compounds. If we compare a number of planetary bodies of similar sizes (inner planets, large satellites of big planets, Pluto), their main constituents (metal + silicate +  $H_2O$  +  $CH_4$ ) will increase their proportion from left to right as they move away from the Sun, from the complete absence of water and methane on Mercury to the complete absence of metal (?) on Pluto.

7. The difference in the composition of planets indicates the fractionation of elements during the formation of the Solar System. The fractionation was substantially determined by

a different degree of the material oxidation and the properties of volatile elements and their compounds depending upon the distance to the Sun.

## Composition and Constitution of the Earth

The globe is made up of concentric shells of varied density and composition. The Earth's upper shells are the atmosphere and hydrosphere. The atmosphere borders space. The solid body of the planet consists of three principal shells: the crust, the thick mantle, and the core at the centre.

The surface of the solid Earth is quite irregular. Mountains and mountain ranges alternate with vast plains on continents, all of which are crustal segments raised above sea level. The disposition of continents is extremely asymmetrical. Thus, if we divide the globe along the Pacific coast of continents (along the margins of East Asia, and the western margins of North and South America), it will be composed of two hemispheres: the continental, where nearly all continents, as well as the Atlantic and Indian Oceans, will be located, and the oceanic, embracing the entire Pacific Ocean. This character of the planetary topography is far from being casual; it is primarily related to crustal composition and constitution within the continental and oceanic hemispheres.

The Earth's crust is taken to mean the upper layer of the solid Earth between its surface and the so-called Mohorovičić discontinuity. At a certain depth, this discontinuity is marked by an abrupt jump in the increasing seismic wave velocities produced by strong earthquakes. On passing through the Mohorovičić boundary, the longitudinal (primary) seismic waves speed up from 6.5 to 8 km/s, and transverse (secondary) waves, from 3.7 to 4.5 km/s. The lower boundary of the Earth's crust, drawn along the M-discontinuity, lies at depths ranging from 70 km beneath the continents to 10 km under the oceans. On the average, the continental crust is 35 km thick and the oceanic crust, 5-10 km thick. This is due to the different composition of the rocks that constitute these two crustal types. The oceanic crust is largely composed of basaltic material and the continental crust of the material similar to granite in composition. The modern constitution of the Earth's crust is shown in Fig. 14. Granitic rocks contain more silica and less magnesium and iron than basalts. It can be concluded, therefore, that one of the two hemispheres of our planet is richer in silica in its upper horizons than the other.

The asymmetric constitution is characteristic not only of the crust of the Earth but also of its upper mantle, but possibly runs to a depth of 700 kilometres. It should be emphasized, therefore, that the irregular constitution and probably composition to a depth of 400-500 kilometres could have not originated in the inferred past epoch of the wholly mol-

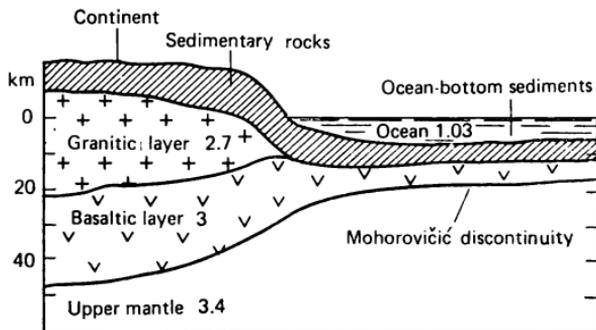


Fig. 14. The constitution of the Earth's crust.  
Figures stand for the density of materials, in  $\text{g/cm}^3$

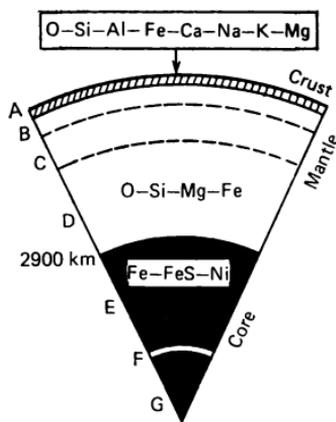


Fig. 15. The internal constitution of the Earth:  
A—crust; B—upper mantle; C—transition layer; D—lower mantle; E—outer core; F—boundary between the outer and inner core; G—inner core

ten Earth. The shells would then have been uniform in both composition and thickness whatever the differentiation process,

Figure 15 shows a detailed subdivision of the entire Earth.

A question arises because the shells are quite real parts of the planet: what is the zonal character of the Earth's interior? Two standpoints on the subject have been put forward during the last decades. In other words, two basic models of the composition and constitution of the Earth were designed. One of them assumes that each deep zone of the globe has its own chemical composition differing from the composition of other zones. This model is called the Goldschmidt-Fersman one. It represents the Earth as a chemically layered spherical body. According to the other model, the Earth as a whole is a chemically uniform body and the deep zones, identified by geophysicists, differ solely in the composition of matter, becoming progressively denser towards the Earth's centre. Thus, the core of the Earth is a highly compressed silicate material converted to a "metallized" state. This model can be called the Lodochnikov-Ramsey one. It was highly popular for some time because of the ideas of a cool origin of the Earth and a uniform accumulation of dust particles. Of course, the chemical differentiation could not have taken place over the whole Earth at low temperatures of its origin. At present, however, new geophysical evidence suggests that the Earth's interior is involved in both chemical partition of matter and its transformation into different polymorphic states, of deep matter, the distinction being most prominent between the core and mantle. Changes

in polymorphic modifications refers to separate parts of the mantle and probably core.

The model of the Earth's constitution that embodies the most recent data is presented in Table 9, in which the shells of our planet are characterized.

TABLE 9. Basic Characteristics of the Earth's Shells

Shell	Depth interval, km	Density interval, g/cm <sup>3</sup>	Percentage of Earth's volume	Mass, 10 <sup>23</sup> g	Mass, %
Crust	A 0-33	2.7-3.0	1.55	5	0.8
Mantle	B 33-400	3.32-3.65	16.67	62	10.4
	C 400-1 000	3.65-4.68	21.31	98	16.4
	D 1 000-2 900	4.68-5.69	44.28	245	41.0
Core	E 2 900-5 000	9.40-11.5	15.16	188	31.5
	F 5 000-5 100	11.5-12.0	0.28		
	G 5 100-6 371	12.0-12.3	0.76		

*The crust* is the most nonhomogeneous shell of the Earth, consisting of different mineral associations in the form of sedimentary, igneous, and metamorphic rocks. It is the result of the geological evolution of our planet and is the dynamically most active layer in the upper part of the solid Earth. This is where geological processes operate with both direct and indirect participation of the living matter of the planet.

The crust is, in general, of a layered structure, being composed of three rock complexes: sedimentary, constituting a sedimentary layer

or stratisphere; metamorphic, making up a metamorphic geosphere; igneous or magmatic, composing a granitic geosphere; and an underlying basaltic layer (see Fig. 14). All layers are discontinuous and lacking in places. Thus, no granitic layer is present beneath the Pacific Ocean. Within continents, sedimentary rocks are occasionally absent within the so-called Precambrian shields.

Sedimentary rocks are materials deposited on the bottoms of water reservoirs and in lows on land. They are extremely common, covering more than 80 per cent of the modern continents. These are sand, clay, limestone, and sandstone. Some sedimentary rocks are derived from breaking up and redeposition of older rocks, others (chalk, limestone, coal, peat) are direct products of activity of living organisms in the biosphere. A certain part of sediments was chemically formed by precipitation of salts in drying closed water reservoirs. The deposits of gypsum and rock salt were appeared.

Igneous rocks have crystallized from magma, which is an aluminosilicate melt enriched with gases. Magma solidification at depth at 500-800 °C gives rise to crystalline plutonic, or intrusive, rocks. Most rocks of this kind in the Earth's crust are granites and their varieties. The granites are composed of pink and grey feldspars, quartz, and mica. Flowing out onto the surface, the magma loses gases and becomes lava which forms such volcanic rocks as porphyrites, rhyolites, and basalts. Basalts are most common of these rocks.

The effusive rocks are made up mostly of small minerals and are, as a whole, a fine-grained mass. In violent volcanic eruptions, much volcanic ash is thrown out (air-cooled varying-size lava spatters), which settles down to produce the so-called volcanic tuffs.

Metamorphic rocks are initially sedimentary or igneous rocks that then underwent recrystallization under the action of pressure and temperature on their sinking to certain depths. Thus, unconsolidated clay is transformed into a rock with a compact crystalline structure, and sedimentary limestone into marble. Metamorphic rocks are often thinly stratified, or foliated, which is related to a one-sided crystal growth due to vertical pressure onto the rock. Examples of common metamorphic rocks are gneisses and schists. Gneisses are similar in mineral composition to granites but the minerals in them are stratified. It should be noted that the distinction between metamorphic and igneous rocks disappears in the case of intense metamorphism with partial melting. There is a good reason to believe that continental granites are largely of metamorphic origin.

The chemical compositions of continental and oceanic crust, as well as those of the whole crust, are given in Table 10 (A.B. Ronov and A.A. Yaroshevsky, 1976). Obviously, the chemical composition of the crust is in general defined by only eight chemical elements: O, Si, Al, Fe, Ca, Mg, Na, and K. The leading one is oxygen, which constitutes nearly half of its mass. By volume, however, its ions

TABLE 10. Chemical Composition of the Earth's Crust, wt. %

Component	Continental crust	Oceanic crust	Entire crust	Component	Continental crust	Oceanic crust	Entire crust
SiO <sub>2</sub>	56.23	48.17	55.24	K <sub>2</sub> O	1.98	0.33	1.61
TiO <sub>2</sub>	0.71	1.40	0.86	P <sub>2</sub> O <sub>5</sub>	0.16	0.22	0.17
Al <sub>2</sub> O <sub>3</sub>	14.46	14.90	14.55	C <sub>org</sub>	0.08	0.05	0.07
F <sub>2</sub> O <sub>3</sub>	2.36	2.64	2.42	CO <sub>2</sub>	1.48	1.37	1.44
FeO	5.41	7.37	5.86	SO <sub>3</sub>	0.12	—	0.09
MnO	0.13	0.24	0.15	S <sub>org</sub>	0.08	0.05	0.08
MgO	4.77	7.42	5.37	Cl	0.03	0.02	0.03
CaO	6.98	12.19	8.12	F	0.03	0.02	0.03
Na <sub>2</sub> O	2.40	2.58	2.44	H <sub>2</sub> O	1.57	1.05	1.46

being large, it composes 92 per cent of crustal volume. The Earth's crust is thus a realm of oxygen. The typical lithophile elements have here the maximum concentrations.

All modern geological, geophysical, and geochemical data indicate that the continental crust of our planet is the product of a more drastic chemical differentiation of the mantle as compared with the oceanic crust. This is evidenced by the chemical compositions of the different crustal types given in Table 10.

*The Earth's mantle differs* in composition from the overlying crust. Information about its chemical composition was derived from the analyses of the deepest igneous rocks intruded into the upper layers of the Earth as a result of intense tectonic uplifts with a removal of the mantle material. These are dunites and peridotites, ultrabasic rocks occurring in moun-

TABLE 11. Chemical Composition of the Upper Mantle, wt. %

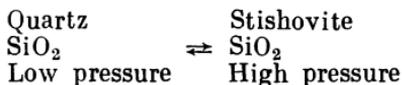
Component	Mantle-derived pyrolite of A. Ringwood	Rock from St. Paul Islands	Mantle composition calculated by L. Dmitriev (1969)	
			1	2
SiO <sub>2</sub>	45.16	43.16	45.5	45.8
Al <sub>2</sub> O <sub>3</sub>	3.84	3.69	3.8	5.1
Fe <sub>2</sub> O <sub>3</sub>	0.46	1.45	5.3	4.8
FeO	8.04	6.64	3.0	3.3
TiO <sub>2</sub>	0.71	0.28	0.3	0.3
Cr <sub>2</sub> O <sub>3</sub>	0.43	0.51	—	—
CaO	3.08	2.61	2.1	3.0
MgO	37.45	38.45	42.2	39.3
Na <sub>2</sub> O	0.57	0.33	0.4	0.5
K <sub>2</sub> O	0.13	0.10	0.1	0.1
MnO	0.14	0.14	0.2	0.2
CoO	0.01	—	—	—
NiO	0.20	0.27	—	—
P <sub>2</sub> O <sub>5</sub>	0.06	0.13	—	—

Note: 1, 2—data calculated for two alternatives of relative proportions of ultrabasic and basic rocks.

tain systems. On geological evidence, the rocks from the St. Paul Islands in the middle part of the Atlantic Ocean are mantle materials. The same is true of rock fragments collected by the Soviet oceanographic expeditions from the floor of the Indian Ocean in the area of the Mid-Indian Ridge. (The investigation results have been summarized by L. Dmitriev.) Some scientists derived the composition of the mantle from that of chondrites. However, this method of investigation is now open to question. Based on rock compositions at depth, the chemical composition of the mantle is presented in Table 11. As to the mineral com-

position of the mantle, we can expect drastic changes due to a pressure growth. The upper mantle is mostly composed of the silicates (olivines, pyroxenes, garnets) stable under relatively low pressures, and the lower mantle, of highly dense minerals (see Table 8).

The most common mantle component is the silica of silicates. Under a high pressure, however, the silica may be transformed into stishovite, a denser polymorphic modification. This mineral has been produced by the Soviet investigator Stishov and is named after him. While common quartz has a density of  $2.53 \text{ g/cm}^3$ , stishovite, derived from quartz under a pressure of 150 000 bars, has a density of  $4.25 \text{ g/cm}^3$ . Both minerals differ in the internal structure. Thus, common quartz consists of combinations of  $\text{SiO}_4$  tetrahedra, in which each silicon ion is surrounded by four oxygen anions, whereas stishovite is a combination of structural units in which each silicon ion is surrounded by six oxygen anions, i.e. is in the so-called sixfold coordination. Therefore, pressure changes cause transformation of polymorphic silicon modifications:



Moreover, the lower mantle may also contain more compact mineral modifications of other compounds. It definitely follows from the above that common ferromagnesian silicates decompose, with growing pressure, into the oxides, each of which is denser than the

silicates. Thus we can assume conversion of magnesian olivine,  $Mg_2SiO_4$ , to magnesian oxide (periclase) and stishovite. While the density of olivine is  $3.1 \text{ g/cm}^3$ , that of periclase is  $3.9 \text{ g/cm}^3$ , and that of stishovite,  $4.25 \text{ g/cm}^3$ . With the possibility of such transformations in mind, we can attempt to explain the nature and mineral composition of the mantle of our planet.

The upper mantle (B) is made up mostly of ferromagnesian silicates (olivines, pyroxenes). Some aluminosilicates may pass here into denser minerals, such as the garnet, grossular,  $Ca_3Al_2(SiO_4)_3$ . The mantle has different properties and probably composition beneath continents and oceans. We can only assume that beneath the former the mantle is more differentiated and contains less silica owing to its concentration in the aluminosilicate crust. Below the oceans, the mantle is less differentiated. Denser olivine modifications with spinel structure, etc. may arise in the upper mantle.

The transition layer (C) of the mantle is characterized by a steady seismic velocity growth with depth, which suggests denser polymorphic modifications of matter. Here, probably, appear FeO, MgO, CaO, and  $SiO_2$  as wüstite, periclase, lime, and stishovite. Their amounts increase with depth while the amounts of common silicates decrease so they are in minute amounts below 1 000 km of depth.

The lower mantle (D) in the 1 000-2 900-km depth interval consists practically

exclusively of dense mineral varieties, oxides, as suggested by its high density—4.68-5.7 g/cm<sup>3</sup>. Under elevated pressure, the dense oxides are compressed, their density becoming even higher. In all probability, the lower mantle contains more iron.

*The Core of the Earth.* The knowledge of the composition and physical nature of the core of our planet is among the most exciting and puzzling geophysical and geochemical problems. A slight progress in solution of this problem has been achieved only recently.

The big central core of the Earth, lying deeper than 2 900 km, is composed of the large outer core and small inner core. The outer core, according to seismic data, has the liquid properties. It does not transmit tensional (secondary) seismic waves, as established long ago. The absence of cohesion between the core and lower mantle, the character of tides in the mantle and crust, the peculiarities in the motion of the Earth's axis of rotation, and the character of seismic wave transmission deeper than 2 900 km points out that the outer core is liquid.

Some authors assume that the core in the chemically homogeneous model for the Earth is silicate in composition and that under a high pressure the silicates have been transformed into a "metallized" state, in which the outer electrons are common, as in metals. The above geophysical data are, however, inconsistent with this assumption. In particular, the lack of cohesion between the core and the mantle is incompatible with the "metallized"

solid core, as implied in the Lodochnikov-Ramsey hypothesis. Highly important indirect evidence on the core were obtained from experiments on silicates under high pressures. There have been achieved pressures of 5 mln atmospheres, whereas the pressure is 3 mln atmospheres at the centre of the Earth and approximately 1 mln atmospheres at the core boundary. Therefore, the pressures in the experiments exceeded those present in the deepest interior of the Earth. Under these conditions, the silicates underwent only linear compression without any jump and transition into a "metallized" state. Moreover, at high temperatures and pressures in the 2 900-6 370-km depth interval the silicates, along with oxides, cannot be in a liquid state. Their melting point rises with pressure.

Very interesting results have been obtained in recent years from experiments under the influence of high pressures on the temperature of metal melting. It has been found that some metals pass into the liquid state under very high (300 000 atmospheres and higher) pressures at relatively low temperatures. According to some calculations, under a high pressure an alloy of iron with nickel and silicon (76% iron, 10% nickel and 14% silicon) must be in a liquid state at a depth of 2 900 km even only at temperature 1 000 °C. All the more so that, according to the least estimates of geophysicists, the temperature at this depth must be much higher.

Therefore, in the light of modern high-pressure geophysical and physical evidence, as

well as cosmochemical data, indicating the leading role of iron as the most prolific metal abundance in space, one can assume that the Earth's core is largely made up of liquid iron with nickel admixture. The estimates of the American geophysicist F. Birch have shown, however, that the density of the core is 10 per cent lower than that of an iron-nickel alloy at temperatures and pressures prevailing in the core. Then it follows that the metallic core of the Earth must contain a considerable amount (10-20%) of some light element. Silicon and sulphur are most probable out of the lightest and widespread elements. The presence of one or the other element explains the observed physical properties of the core. Therefore, whether some silicon or sulphur is present in the Earth's core is debatable and associated with the way of formation of our planet as a whole.

In 1958 A. Ringwood assumed that the core contains silicon as a light element, proving that elemental silicon constitutes several weight per cent in the metallic phase of some reduced (enstatite) chondrites. No other arguments have been present, however, in favour of silicon existence in the core of the Earth.

The probable presence of sulphur in the Earth's core stems from a comparison of its distribution in the chondritic material of meteorites and in the mantle material of the Earth. Thus, a comparison of elemental atomic ratios, in relation to  $10^6$  of silicon, in a mixture of crust and mantle and in chondrites shows

a considerable sulphur deficiency. The sulphur content of the mantle and crust is three order of magnitude lower than that of the average material (chondrites) of the Solar System.

It follows from the above that much sulphur may well have been introduced into the Earth's core. Moreover, other conditions being equal, the melting point of Fe-FeS is much lower than that of iron or mantle material. Thus, under 60 kbar, the melting point is 990 °C for the Fe-FeS eutectics, 1 610 °C for pure iron and 1 310 °C for mantle pyrolite. Therefore with temperature rising in the interior of the initially homogeneous Earth, the sulphur-rich iron melt will form first and, because of its low viscosity and high density, will flow inward to produce a ferrosulphur core. Thus the sulphur in the iron-nickel material acts like a flux, reducing, on the whole, the melting point. The hypothesis of the high sulphur content of the core is very attractive and does not contradict the all known geochemical and cosmochemical data.

V. Rama Murthy and H. Hall (1970), who proved most convincingly the presence of sulphur in the core as a light element, assume that the core/mantle ratio is 31/69 and the Earth's core contains 15 weight per cent sulphur. In their theoretical model, the composition of the Earth can be presented as a mixture containing 40 per cent carbonaceous chondrites, 50 per cent common chondrites, and 10 per cent iron meteorites.

The current estimate of the bulk elemental composition of the Earth on the basis of mod-

ern geochemical and cosmochemical data is given in Table 12.

TABLE 12. Chemical Composition of the Earth, wt. %

Major element	V. Rama Murthy & H. Hall, 1970			Major element	V. Rama Murthy & H. Hall, 1970		
	R. Ganapathy & E. Anders, 1974	J. Smith, 1979			R. Ganapathy & E. Anders, 1974	J. Smith, 1979	
O	30.25	28.5	31.3	Ni	1.65	2.04	1.72
Fe	29.76	35.87	31.7	Ca	1.64	1.93	2.28
Mg	15.09	13.21	13.7	Al	1.32	1.77	1.83
Si	14.72	14.34	15.1	Na	0.30	—	—
S	4.17	1.84	2.91				

As to the inner core of the Earth below 5 000 km of depth, its nature and composition remain to be most enigmatic. It cannot be ruled out that the core has the same composition that the outer core has but is in a solid state. Possibly, it consists solely of nickelous iron without sulphur admixture.

The modern views on the nature of the interior of our planet thus imply a chemically differentiated globe divided into two different parts—a thick solid silicate-oxide mantle and a liquid, largely metallic core. The Earth's crust is the lightest upper solid shell composed of aluminosilicates and having the most intricate structure.

Summing up, the following conclusions can be drawn:

1. The Earth is stratified, zoned. It consists of a solid silicate-oxide shell, mantle (2/3), and a metallic liquid core (1/3).

2. The basic properties of the Earth suggest that the core is liquid and only iron (among the most common metals) with some light elements, most probably sulphur, can have this property.

3. The Earth's crust and upper mantle are asymmetric. The oceanic hemisphere is less differentiated within the upper mantle than the opposite, continental hemisphere.

The purpose of any cosmogonic theory of the origin of the Earth is to explain these basic features of its internal nature and composition.

## The Present and Past Radioactivity of the Earth

Radioactivity is the most important property of our planet, and has the basic and profound properties of its material. While solving so important a problem as the origin and chemical evolution of the Earth, we must consider the properties of the planet's radioactivity. As spontaneous decay of unstable atoms radioactivity reflects the history of the Earth's material in the remote cosmic past, when different atoms of chemical elements, both stable and unstable, were formed.

Modern radioactivity of the Earth is mainly associated with radioactive isotopes  $^{238}\text{U}$ ,  $^{235}\text{U}$ ,



gators resulted in the models of the radioactive Earth that generate from  $2.3 \times 10^{20}$  to  $10 \times 10^{20}$  calories of radiogenic heat per year.

However, the Earth continuously loses its heat to the world space through thermal conductivity and radiation. At present the entire surface of the Earth, including the ocean floor, is covered with geothermal measurements of a varying density. The value of heat flows per unit surface proved to be the same above continents and ocean floors. It follows then that continental and oceanic segments must contain, on the average, an equal amount of disseminated radioactive elements per square unit surface (from the surface to the centre of the planet). However, in the area of oceans the radioactive elements are deeply buried. On the basis of the data of heat flows, thermal properties of rocks and radioactivity, MacDonald has calculated the deep-seated distribution of temperatures beneath the oceans and continents (Fig. 16). The temperatures in the mantle under the oceans have been found to exceed by  $100^\circ\text{C}$  those under the continents to a depth of 700 km.

In conformity with modern geothermal evidence as a result of thermal conductivity the Earth annually loses  $1.9 \pm 0.1 \times 10^{20}$  calories of heat, which is somewhat less than the amount being produced by a radioactive model of the Earth according to the least estimates ( $2.3 \times 10^{20}$  calories per year). Thus it is easy to conclude that radioactivity plays the leading role in the modern heat balance of our planet and is a powerful energy factor

that can rise the temperature of the Earth's interior.

Such a conclusion is not surprising. It resulted naturally from the first determinations

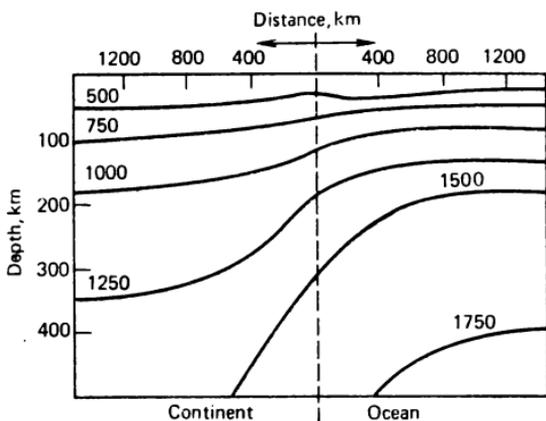


Fig. 16. Temperature distribution beneath continents and oceans

of radioactivity of the Earth's material made by R. Strutt and J. Jolly in the early 20th century and was most vividly expressed by V. Vernadsky in the following way: "...the amount of heat energy, generated by a radioactive process, is sufficient not only to account for the Earth's loss of heat and all the dynamic and morphogeological effects of the planet's internal energy on its surface, the Earth's crust, but also to increase the temperature of the Earth."

However, the Earth's radioactivity in the remote geological past was higher than now. The known decay rate for each radioactive iso-

tope is, in particular, expressed by the half-life period  $T$  ( $T$ , a half-life period equal to a time interval during which any amount of radioactive substance decay to half of its previous amount). Having this in mind, it is not difficult to calculate the amount of the given isotope in the past with respect to its modern

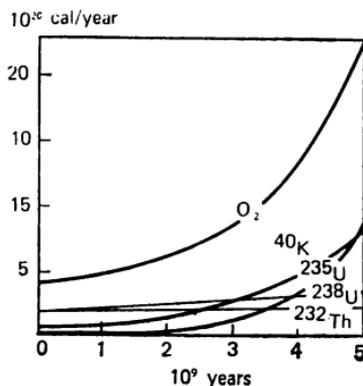


Fig. 17. Heat evolution by radioactive isotopes in the Earth's past.

The values of radiogenic heat are plotted on the ordinate axis

concentration. So 4.5 billion years ago there was twice more  $^{238}\text{U}$  on Earth than now, and it respectively released twice more energy. The total amount of radiogenic heat released in the past is shown graphically in Fig. 17.

It inevitably follows that in the past radioactivity played a considerably greater role in the heat regime of our planet than at present. Since radioactivity has been discovered in all the bodies of the Solar System, this

conclusion can be extended as follows: radioactivity of the Solar System's material during the epoch of its formation was much higher than now. However, relatively short-lived radioactive isotopes, with a half-life period of some  $10^6$ - $10^8$  years, were present in the composition of young Earth. They had resulted from nuclear fusion of heavy elements and later became part of young bodies of the Solar System. Some properties of these isotopes are given in Table 13.

TABLE 13. Extinct Radioactive Isotopes

Radioactive isotope	Half-life period, years	Type of decay	Product of decay
$^{92}\text{Nb}$	$3.3 \cdot 10^7$	$e$ -capture	$^{82}\text{Zr}$
$^{107}\text{Pd}$	$7 \cdot 10^6$	$\beta$	$^{107}\text{Ag}$
$^{129}\text{I}$	$1.7 \cdot 10^7$	$\beta$	$^{129}\text{Xe}$
$^{146}\text{Sm}$	$5 \cdot 10^7$	$\alpha$	$^{142}\text{Nd}$
$^{205}\text{Pb}$	$5 \cdot 10^7$	$e$ -capture $\alpha$	$^{205}\text{Tl}$
$^{236}\text{U}$	$2.4 \cdot 10^7$		
$^{244}\text{Pu}$	$8.2 \cdot 10^7$	fragmentation	$^{232}\text{Th}$
		fission, $\alpha$ -decay	$(^{131-180})\text{Xe}$
$^{247}\text{Cm}$	$1.64 \cdot 10^7$		

$^{244}\text{Pu}$  and  $^{247}\text{Cm}$  are the most long-living isotopes of transuranium elements. It is these isotopes that still existed at the origin of the Earth and during differentiation of planetary material. Some amount of these isotopes could retain to the present day. The traces of  $^{244}\text{Pu}$  decay were definitely found in several ancient meteorites. The data on the existence of  $^{247}\text{Cm}$  in the early history of the Solar System have

recently been obtained by M. Tatsumoto and T. Shimamura (1980).

At present, the following rather valid assumption can be put forward: early in the existence of solid bodies of the Solar System superheavy transuranium nuclei that have not yet been obtained artificially were likely to be also present.

The study of the known transuranium elements has revealed that their instability rather rapidly increases as the atomic number,  $Z$ , increases. However, extrapolation of this tendency into the field of superheavy transuranium elements appears to be arbitrary. Thus, according to S. Nilsson's calculations, most isotopes within  $Z = 106-116$  with  $N = 184$  possess unexpectedly long life periods with respect to both spontaneous and alpha decay. If heavy transuranium elements undergo fission into fragments in solid bodies (minerals), they leave tracks, that is, traces of trajectories of fission fragments. Owing to a high energy of fission of superheavy transuranium elements, the tracks of their fragments have a greater length than that of the tracks of plutonium or uranium fission fragments. Thus, if the tracks resulting from the fission of plutonium and uranium are 13 to 16  $\mu\text{m}$  long, those produced by the fission of superheavy transuranium nuclei with  $Z = 114$  should be within 18-25  $\mu\text{m}$ .

The study of tracks in some lunar rocks and meteorites has shown that many of them have the length exceeding 20  $\mu\text{m}$ . Specific isotopic anomalies of xenon have also been

discovered indicating that they were derived from a spontaneous fission into fragments of superheavy transuranium elements with  $Z = 112-116$ .

From the above it follows that the chemical history of the Earth and other bodies of the Solar System is associated not only with the decay of currently retained radioactive isotopes  $^{235}\text{U}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{40}\text{K}$ , but also with extinct radioactive isotopes. Most of these isotopes decayed during the star epoch of nuclear fusion and only their insignificant amount had survived to the epoch of generation of our Solar System.

In view of the foregoing it is important to emphasize that even the insignificant amounts of rapidly decayed radioactive isotopes that occur in the young Earth could cause its internal radiogenic heat, along with uranium, thorium and  $^{40}\text{K}$  of which our knowledge is much greater. By way of illustration, we compare the specific energy of  $^{238}\text{U}$  with that of some extinct radioactive isotopes:

1 g of $^{238}\text{U}$	releases	0.71 cal of heat per year
1 g of $^{244}\text{Pu}$	releases	14.07 cal of heat per year
1 g of $^{247}\text{Cm}$	releases	66.8 cal of heat per year
1 g of $^{129}\text{I}$	releases	1.32 cal of heat per year

The above values indicate that if the concentration of  $^{244}\text{Pu}$ ,  $^{247}\text{Cm}$  and  $^{129}\text{I}$  in the young Earth had been in total two orders of magnitude lower than that of uranium, even then the atomic energy of their decay would have been commensurable with the decay energy of uranium itself.

Unfortunately, we cannot yet estimate the original content of extinct isotopes in the material of the young Earth. We cannot either ignore the possible presence of still other radioactive isotopes ( $^{10}\text{Be}$  and  $^{26}\text{Al}$ ) produced by solar proton irradiation of the dispersed material that gave rise to primary planets.

Radioactivity provides valuable information about the age of solid bodies in the Solar System and about that of elements. The study of isotopic ratios of  $^{266}\text{Pb}$ ,  $^{267}\text{Pb}$  and  $^{268}\text{Pb}$  in the Earth's crust and meteorites has enabled one to suggest that the age of the Earth is  $4.60 \pm 0.05$  billion years. Besides,  $^{207}\text{Pb}/^{206}\text{Pb}$  being a function of the life of  $^{235}\text{U}/^{238}\text{U}$ , the age of U in the Solar System is close to 5 billion years! The anomalous contents of  $^{129}\text{Xe}$  as a product of decay of extinct  $^{129}\text{I}$  in stony meteorites indicate the time interval between the completion of the natural synthesis of radioactive nuclei and the formation of meteorites. True, this calculation is tentative as we do not know the initial  $^{129}\text{I}/^{127}\text{I}$ . The most probable values range from 50-150 million years. The age of the Earth and meteorites being 4.6 billion years, that of radioactive nuclei in the Solar System does not exceed 4.8 billion years. This value indicates a prolonged existence of the Solar System, as in modern conditions no fusion of  $^{129}\text{I}$  and  $^{238}\text{U}$  is possible in its bodies. In other words the natural synthesis of heavy radioactive nuclei had been completed on the eve of the Earth formation and other planets of the Solar System. This leads us

to conclusion that the origin of the Solar System was related to that of its constituent chemical elements. The heaviest nuclei of thorium, uranium, transuranium elements had immediately been formed before the generation of the planets of the Solar System.

The data on radioactivity considered here in a concise form make it possible to come to definite conclusions of cosmogonic and geochemical significance.

1. The radioactivity of the Earth is an important source of its internal heat and can cause melting of material in the Earth's interior.

2. The relatively high radioactivity of the young Earth contributed to the rise in its temperature and melting of material, and was one of the leading factors of chemical differentiation of the planet.

3. The isotopes of the most long-lived radioactive elements, including the transuranium ones ( $^{244}\text{Pu}$ ,  $^{247}\text{Cm}$ ,  $Z = 112-116?$ ), existed for some time in the early history of the Solar System, and the material that gave rise to it was highly radioactive.

4. The modern radioactivity of the Earth and of all the studied bodies of the Solar System is a natural consequence of the nuclear evolution of matter in star cosmic conditions. The construction of heavy atomic nuclei had mainly been completed not long before the formation of planets.

## The Birth of Atoms in Space

All the bodies surrounding us are changeable and retain the signs of the processes from which they have resulted. Modern natural science has revealed a number of the most important trends in the development of individual forms of material accumulation.

The atom is the basis for many cosmic accumulations of the material. It provides the possibility of establishing the stable genetic ties between the forms of material accumulation with sharply differing properties. Therefore the history of the formation and destruction of any body is at the same time the history of atoms that compose it. Using the language of atomic theory, we can say that the birth, development, and death of any form of existence of the material are concentration and dissemination of atoms that form it. But the history of atoms of chemical elements in nature is not limited exceptionally by the processes of their connection and dissemination by the formation of their infinite combinations in the form of different simple and complex compounds. The atom itself is a changeable particle in the boundless history of the universe.

The atoms of chemical elements have their own history that is of an ambiguous character. On the one hand, this is the history of ready atoms that combine with each other according to chemical laws, eternally moving in the dif-

ferent parts of the Universe, creating all the beauty of our terrestrial nature, and on the other, there are processes of creation and destruction of the atoms themselves in extraordinarily contrasting thermodynamic conditions of space and in its electromagnetic fields. And if the first, mainly the external aspect of the history of atoms has been studied and to a large degree involves the range of interests of geochemistry, cosmochemistry, biochemistry, and other sciences, then the second aspect, touching upon a deeper essence of the material and dealing with evolution of atomic nuclei in the nature, has been studied very poorly and only in the last few years positive results were obtained in this field.

A new problem is being posed, i.e. the problem of the origin and evolution of chemical elements. Every year the investigations in this field are extended and the idea of the eternity and immutability of atoms has long become a legend, leaving as a legacy only the term itself, i.e. "atom" (indivisible). Particular hypotheses on the origin and evolution of an atom in the nature are being advanced while considering the problems of the theory of nucleus, relative distribution of nuclear types, isotopic composition of elements and also astrophysical investigations concerning the sources of energy and the structure of stars.

The problem of natural evolution of atoms verges on nuclear physics and the physics of the cosmos being most closely related to a thorough study of the material of our planet and the related material of meteorites.

In his brilliant generalizations in the field of geochemistry and cosmochemistry A. Fersman distinguished three epochs of existence of the Earth's atoms: star, cosmic and geological. The star epoch incorporating the processes of the natural synthesis of atomic nuclei was evidently the first in the historical sequence of the evolution of the Solar System's material. Based upon the composition of nuclei we can imagine some of the general features of this process.

Thus, a successive construction of atomic nuclei as the number of their constituents—nucleons ( $Z$  and  $N$ )—increases can take place either by merging the charged particles (protons,  $\alpha$ -particles) with each other and with newly formed nuclei or by a successive addition of neutral particles, i.e. neutrons. According to modern concepts, the conditions necessary for these processes to occur are created in the interior of massive stars of different types. The charged particles in these stars acquire a high velocity, corresponding to temperatures of the order of tens-hundreds of millions of degrees. The charged particles in the upper rarefied shells of the stars can be hastened by electromagnetic fields probably followed by nuclear reactions of protons with protons and protons with other nuclei. If neutrons appear in the process of star evolution as a result of nuclear reactions, they later easily penetrate into other nuclei promoting the formation of heavy nuclear types. With any one of the mentioned methods of construction, the atomic nuclei are initially formed

with anomalous neutron-proton ratio in comparison with a stable ratio that is shown in Fig. 18. Stable isotopes are depicted in this

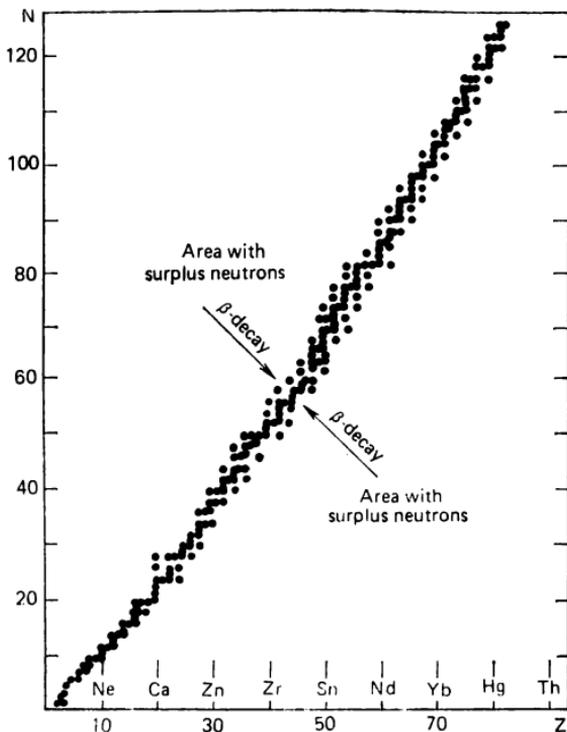


Fig. 18. Neutron-proton ratios of natural stable isotopes.

Stable isotopes are designated by circles

figure with a fully determined content of protons and neutrons. Evidently they form quite a limited stability band. It is easy to imagine that if the addition of protons played a leading

role the nuclei appeared with their surplus relative content. These newborn nuclei were getting rid of the surplus positive charges by means of positron  $\beta^+$ -radioactivity. If a successive capture of neutrons took place, the nuclei appeared that were maximally enriched with them and later they were getting rid of the surplus neutrons by means of common  $\beta$ -radioactivity that some of radioactive isotopes of the Earth's crust are known to have now.

The ratios considered above suggest that any method of the natural synthesis of elements caused the formation of radioactive isotopes as primary products that later equalized the neutron-proton ratios till they acquired a definite stable value by means of  $\beta$ -decay. The heaviest nuclei overcharged with neutrons also underwent  $\alpha$ -decay and a fragmentation spontaneous fission. Thus, modern radioactive isotopes in the material of the Solar System directly bear witness to the processes of nuclear fusion with neutron participation.

Relatively light elements  $Z < 35$  have a maximum content of a light isotope, i.e. they are mostly enriched with protons, which indicates their origin by adding neutrons or other charged particles (deuterons,  $\alpha$ -particles).

Different hypotheses on the origin of chemical elements due to different types of nuclear reactions were put forward long ago. According to one group of hypotheses the formation of atomic nuclei results from a superdense state

of the material during the epoch of early pre-star existence of the material when the Universe began to expand. According to another group of hypotheses it results from the evolution of massive stars.

At present, when nuclear physics and astrophysics are gradually being developed, the theory of the star epoch of elements fusion is more and more confirmed. In 1931 R. Atkinson and F. Houtermans attempted to attribute the sources of star energy to the conversion of light elements into heavy ones. In 1938 H. Bethe and C. Weizsacker put forward a theory of thermonuclear reactions in stars according to which conversion of hydrogen into helium is a probable source of energy of the most widespread stars of the so-called principal sequence. This related the stars evolution to the change in their composition. The release of energy during the conversion of hydrogen into helium is enormous. So, the conversion of only 10 per cent of the Sun's mass would have given enough energy to maintain its glow on the modern level during 10 billion years, that is approximately twice the age of the Solar System. In 1940-1941 V. Cherdyntsev was the first to put forward the theory of the origin of chemical elements with the participation of a neutron phase in massive stars.

However, as the calculations of a great number of studies revealed, the fusion of heavy elements, heavier than helium and oxygen, requires extremely high temperatures that are impossible in the interior of most

of the stars. In 1946 F. Hoyle calculated that an enhanced distribution of elements in the area of iron (see Fig. 1) may be due to thermonuclear reactions in extreme conditions of exceptionally high temperatures and pressures in the interior of rare massive stars. These conditions are created at the final stages of star evolution and manifest themselves in the outburst of the supernova.

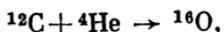
In recent years further accumulation of astrophysical data relating to nuclear fusion took place. So, the element technetium ( $Z = 43$ ) that is absent on the Earth and whose all isotopes are radioactive has been discovered in the shells of some of the stars. Its presence in star atmospheres definitely indicates the possibility of elements fusion in star conditions. The character of luminescence fall of supernovas after their bright outburst is in good agreement with a half-life period of some of the transuranium isotopes ( $^{254}\text{Cf}$ ) in time that astrophysics consider to be an indirect indication of the possible fusion of heavy transuranium elements in some of the stars. At last, Cameron's theoretical calculations have revealed that at a certain stage of the development of stars-giants in their interior the generation of neutrons, extraordinarily active particles in respect to heavy elements formation owing to neutrons themselves by merging with the medium and light elements, is principally possible.

As a result of correlation between astrophysical data and theoretical calculations, V. Cherdyntsev, D. Frank-Kamenetsky,

G. Burbidge, E. Burbidge, W. Fowler and F. Hoyle have shown that chemical elements resulted from superposition of a number of processes interconnected with star evolution. These processes can briefly be characterized in the following way.

1. *The conversion of hydrogen into helium* results from thermonuclear reactions with the participation of carbon and nitrogen as original catalysts. This is a widespread process characteristic of the majority of stars of the main sequence.

2. *The conversion of helium into light elements* is effected by thermonuclear reactions of helium with  $^{12}\text{C}$ . Thus, the nuclei can appear that are multiples of four and are the most widespread over among light elements:



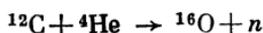
3. *Reactions with the participation of  $\alpha$ -particles ( $\alpha$ -process)*. Rapid nuclei of helium ( $\alpha$ -particles) that react with previously formed light nuclei and form the following isotopes are freed from the light nuclei at superhigh temperatures as a result of severe radiation:



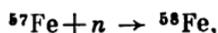
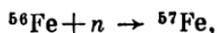
4. *Equilibrium process (e-process)* occurs as the hottest thermonuclear process at temperatures of  $3 \cdot 10^9$  °C, at which static equilibrium is created between the nuclei present and ele-

mentary particles. As this takes place, the elements appear that are adjacent to iron with the most stable specific nuclear bond.

5. *The processes of neutron capture* occur when free neutrons appear. The neutrons themselves may probably appear in the interior of stars during nuclear reactions of the type



The construction of heavy elements, including transuranium ones, occurs during further successive capture of neutrons by more widespread nuclei. If one considers the distribution curve (see Fig. 1), it is evident that the distribution of heavy elements is  $10^{10}$  times smaller than that of hydrogen. Consequently the process of their construction on a common scale can be regarded as a relatively rare event. Neutron generation inevitably causes the fusion of heavy nuclei according to the scheme



Heavy elements  $\rightarrow$  Pb

The fact that nuclei with unlikely neutron capture have an enhanced distribution confirms the reality of neutron reactions in the history of the material of the Solar System. This occurs because a nucleus, whose neutron capture is highly probable, will easier become the next member of the series than the nucleus whose capture is slightly probable.

6. *The processes of proton capture* result

in the formation of nuclear types with an increased proton content as compared with a minimum stable proton-neutron ratio. Protons that are necessary for nuclear reactions pick up high speeds in electromagnetic variable fields of star atmospheres. The reactions can occur during the outburst of supernovas containing much hydrogen in shells.

The processes considered above qualitatively, and possibly, in some cases quantitatively account well for the distribution of elements observed in the Solar System and their isotopic composition. Therefore there are grounds to believe that the material of the Solar System before the formation of planets has passed a prolonged stage of development including different processes of nuclear fusion.

The appearance of the material consisting of atoms dates back to the earliest events in the history of the Universe. At present its expansion has been established as a real fact. Different galaxies representing the clusters of thousands of millions of stars are scattered. The birth of the first atoms of hydrogen, and probably, helium is associated with this effect of expansion in the remote past. The discovery of cosmic radio emission in the field of heat waves, uniformly embracing the entire Universe provides the first piece of information on physical conditions of its existence at the early stages of development.

During the epoch of stars formation by the flat component of our Galaxy (which at present incorporates the Sun) the initial material for constructing the cosmic clusters, as it

follows from the foregoing, was mainly presented by hydrogen dominating up to the present in the cosmochemistry of the Universe. The duration of era of pre-planetary existence can hardly be estimated even approximately, since we have not got a reliable evaluation of the time measurement for the epoch when there were no radioactive nuclei.

Our knowledge concerning nuclear processes in the stars makes it possible to assume that the natural nuclear fusion was at first consecutively following a path of constructing light, then medium and in conclusion heavy transuranium atoms. Therefore the first stage of the ascending evolution of elements had to pass a phase of hydrogen-helium combustion at a temperature exceeding  $10^8$  K. Hot and massive Wolf-Rayet stars, according to astrophysics, are prototypes of this stage of development of the Earth's material. The stage of hydrogen-helium combustion ends mainly with  $^{20}\text{Ne}$ . Less abundant isotopes ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{17}\text{O}$ ,  $^{18}\text{O}$ ,  $^{19}\text{F}$ ) were formed during interaction with  $^{12}\text{C}$ ,  $^{16}\text{O}$  and  $^{20}\text{Ne}$ .

The next stage is that of  $\alpha$ -process, when gravitational energy, compressing stars, causes heating of their central nuclei up to the temperatures of about  $10^9$  K. Drastically increased energy of  $\gamma$ -radiations causes photo-disintegration of light atoms with the escape of  $\alpha$ -particles having the energy of 4-5 million MeV.  $\alpha$ -particles interacting with  $^{20}\text{Ne}$  successively result in the formation of isotopes of  $^{24}\text{Mg}$ ,  $^{28}\text{Si}$ ,  $^{32}\text{S}$ ,  $^{36}\text{Ar}$ ,  $^{40}\text{Ca}$ , possibly  $^{44}\text{Ca}$  and  $^{48}\text{Ti}$ . Some of the white dwarfs with sharp lines

in calcium spectra probably exemplify element-forming stars with the  $\alpha$ -process.

The stage of an equilibrium process at temperatures of about  $3 \cdot 10^9$  K most satisfactorily accounts for terrestrial and meteoritic abundance of the "iron maximum" on the curve of cosmic distribution of elements, in this case the generation of isotopes of Cr, Mn, Fe, Co, Ni, Cu takes place. The stage of an equilibrium process is extremely short and its analogue cannot yet be indicated for the studied stars of Galaxy. The time scale of the processes signifies a distinctive leap in the life of a massive star related to a catastrophic explosion and dissemination of already formed atoms from hydrogen to titanium into space while the elements of the "iron maximum" are preserved in its central part.

If we consider the composition of the Earth's crust and mantle, only 13 most abundant elements will constitute a major portion of the planet's mass. These include C, O, Na, Mg, Al, Si, S, K, Ca, Ti, Mn, Fe, Ni. The isotopes of these elements were formed in three processes of nuclear genesis discussed above. Thus, the products of hydrogen-helium fusion, the  $\alpha$ -process and equilibrium thermonuclear reactions had determined the composition of the main mass of the globe in the remote past. All other elements, taken together, represent a small quantity. The main products of hydrogen-helium combustion and the  $\alpha$ -process predominate even in the Earth's crust that is the lightest differentiate.

The further stage, the processes of neutron

capture, was rather important in that during this stage the main isotopes of elements with  $A > 60$  were formed, including all well-known and existing now  $\beta$ -active natural radioisotopes. The conditions for effecting the processes of neutron capture could be created in the interior of a large star, considerably exceeding the mass of the modern Sun. But this massive star was probably the Sun's ancestor to which it turned having ejected the surplus mass by catastrophic explosion or gradual outflow of the material mainly in the area of an equator.

The similarity between the atomic composition of different bodies of the Solar System indicates that in respect to nuclear evolution the material of the Sun and that of the Earth (as well as of other planets of the Solar System) had had a common history till a certain stage of development. This stage was distinguished by the differentiation of a certain common system, i.e. the change (of primordial star) for primordial Sun and the near-Sun protoplanetary material. A similar process began soon after the fusion of heavy atomic nuclei.

The formation of numerous radioactive isotopes directly resulted from the process of neutron capture that had most probably occurred directly before the isolation of the Sun from the rest of protoplanetary material.  $\beta$ -active isotopes that had been preserved until the present time in the planetary material probably originated during neutron capture directly from some of the stable isotopes formed earlier by other nuclear processes.

The formation of isotopes of transbismuth elements inevitably occurred under conditions of rapid neutron capture as there were short-lived isotopes in radioactive series, whose chain of appearance could be effected with a rapid and powerful flow of neutrons. The value that may be in the range from 50 to 150 million years is a time interval between the completion of the process of fusion of radioactive nuclei and the beginning of the Earth's formation. It is possible that some of the light isotopes that rapidly burn out in thermonuclear reactions of the star interior (D, Li, Be, B) have been formed within this interval. D. Burnett, W. Fowler and F. Hoyle advanced the hypothesis of the formation of D, Li, Be and B in solid bodies (planetesimals) having surrounded the early Sun under the effect of proton irradiation accelerated by a magnetic field. This proton irradiation interacted with carbon, nitrogen, oxygen and also caused the formation of neutrons. In this case it is assumed that the early Sun has been noted for a high magnetic activity.

Chronological sequence in the history of formation of chemical elements of the Solar System in A. K. Lavrukhina's interpretation (1976) is presented in Fig. 19. According to this sequence, the main nuclear synthesis had occurred 11 billion years ago in the epoch of a single galactic nuclear genesis (nuclear fusion). As this takes place, 99 per cent of the modern abundance of isotopes were synthesized. The last act of the nuclear fusion had directly preceded the formation of the Solar

System planets. The time interval between the completion of the last act of the nuclear fusion and the formation of solid bodies in the Solar System is marked by  $\Delta t$ .

The stage of the material transition from the genesis of heavy atomic nuclei to the planetary existence of common chemical elements

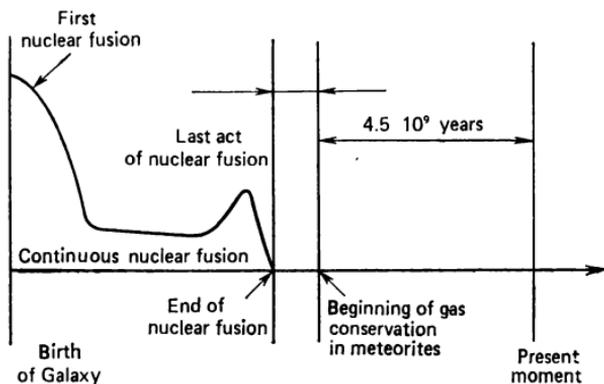


Fig. 19. The diagram showing the sequence of events of the formation of elements and the formation of material of the Solar System bodies for 11 billion years

presents a problem that is, in fact, within astrophysics and cosmogony. It is not so important for us as yet. The main conclusion from the foregoing is the inevitability of material that had gone through a number of stages of nuclear fusion that determined henceforth the chemical composition of the Earth, the observed now isotopic ratios, the radioactivity that had decreased and the radioactivity of isotopes that had retained up to now.

In considering the historical sequence of the processes of natural evolution of atomic nuclei it is easy to come to the conclusion that the primary protoplanetary material immediately after the completion of the nuclear fusion was presented in the form of separated, not related atoms that appeared under conditions of high temperatures as a mixture of atomic nuclei and separated electrons. In other words, only after a significant drop in temperature the newborn bare atomic nuclei were clothed in electron shells, thus creating a prerequisite for effecting chemical reactions and the appearance of the first chemical compounds. Thus, a cosmic dust composed of solid particles and repeatedly used not long ago in cosmogonic hypotheses as the building material of planets, must be a secondary object having resulted from the chemical evolution of the plasmatic star material as it cooled down.

## Chemical Evolution of the Protoplanetary Material

The formation of the Earth and other planets of the Solar System was not only explained by the laws of mechanics, on which classical cosmogonic hypotheses were based not long ago, but was associated with the properties of the material itself, with physicochemical

processes in the broad sense of the word. The appearance of atoms in their cosmic history was governed by the laws of nuclear physics and thermodynamics. The formation of chemical compounds, consisting of atoms, was caused by the structure of their electron shells and physical conditions within relatively low temperatures as compared with the conditions of nuclear fusion. The protoplanetary material, from which primary planets had been immediately accumulated over all the space of the Solar System, acquired a real inhomogeneity in the course of its chemical evolution that affected the composition of the planets themselves.

As was already noted, a striking similarity between isotopic composition of different bodies of the Solar System indicates that the material of the Sun developed in the same way as that of the Earth to a certain stage. This crucial stage was expressed in dividing a general system (primary massive star?) into the primary Sun and the circumsolar material originally having the composition of the solar gas. We do not know a particular mechanism of separating this material, it was apparently related with centrifugal forces that appeared when the velocity of rotation of the primary massive star changed. In this way protoplanetary solar nebula was formed as a gas disc coinciding with the plane of the solar equator. The initiation of this disc was inevitably due to the expansion of the solar (star) material and its cooling to the temperatures promoting the birth of molecules, chemical compounds

and metal phases. Below we shall try to follow what processes could occur during cooling of the gas disc of the solar composition and how they resulted in the appearance in it of chemically inhomogeneous areas.

Primarily such an important physical factor as the pressure of solar rays should be noted. Probably primary gas underwent a certain spatial differentiation under the effect of the beam pressure of the bright primary Sun. Thus, the lightest gas components of the primary disc were thrown off to its marginal parts. We observe the same in increasing gas tails of comets as they approach the Sun. Large planets of the type of Jupiter, Saturn, Uranus, Neptune, consisting mainly of gases appeared afterwards in these marginal peripheral parts of the gas disc. The pressure of solar rays was a permanent factor having by now a part in classifying the material of the Solar System.

The differences in the chemical composition of a primary nebula were additionally determined by the effect of fast particles being thrown out by the primary Sun. According to G. Kuiper, the most effective mechanism of gas removal from inner parts of the Solar System was knocking out light atoms and molecules in the rarefied part of the primary nebula as a result of impacts of solar corpuscles of high energies.

The problem of varying compositions of inner planets is most important. A. Ringwood considers that this is explained by a different intensity of the processes of iron reduction

that was represented by oxides in the period of planet formation. In this case the scientist assumed that the reduction itself occurred because of different heating of the planets soon after their formation had been completed under the effect of hydrogen and carbon, whose content in their composition was large. However, approaching the solution of the problem from the viewpoint of different possibilities, two probable ways of the formation of chemical composition of the planets of the Solar System can be distinguished:

(1) the composition of planets was determined from the moment of their formation and their differences arise from varying chemical compositions of some areas of the protoplanetary material (disc, nebula);

(2) at first the planets were of a similar constitution but later on after having lost a number of materials they changed to chemically different bodies.

In the light of modern data on cosmochemistry the first way of the formation of chemical composition of planets seems to have been more probable and of decisive importance. The second way is not in principle excluded, it holds true for some elements also in the modern epoch (hydrogen and helium are being lost by inner planets), but as a whole it played a secondary role in the history of the Solar System.

In order to clearly imagine the ways of chemical evolution of the protoplanetary material it is necessary to consider most completely the distribution of all chemical elements

in the studied bodies of the Solar System, and this will allow to establish their migration in the past and to elucidate certain basic trends that can be interpreted from the standpoint of chemical laws.

The study of a number of chemical elements in chondritic meteorites of different types by means of modern precise methods of analysis (neutron activation, mass spectrometry, etc.) resulted in the essential improvement of the data on their distribution. One third of the elements of Mendeleev Periodic Table in all studied chondrites proved to be markedly deficient in carbonaceous chondrites of the C1 type as compared with their distribution. We can consider the latter to be the bodies that are most similar to the material of the protoplanetary substance in atomic composition.

As was already noted, when meteorites are chemically characterized, carbonaceous chondrites of the C1 type are most similar to the solar material in composition. Unlike the other meteorites, they contain much carbon (up to 3-5 per cent), bound water and a relatively large amount of gases. As a result many investigators regard carbonaceous chondrites of the C1 type as the least differentiated and fractionated material of the Solar System, whose composition is most similar to the protoplanetary substance, from which planets and asteroids had originated in the process of fractionation and chemical differentiation.

The data on atomic distribution of a number

of elements in carbonaceous chondrites are presented in Table 14. As seen from the table, the content of Au, Cu, F, Ga, Ge, Se, Sn, Mn, K in common and enstatite chondrites is decreased and amounts to 0.25-0.5 of their content in carbonaceous chondrites C1. The content of other elements (Ag, Bi, Br, C, Cd, Cl, Cs, H, Hg, I, In, Kr, Ne, N, Pb, Te, Tl, Xe, Zn) is much smaller. By and large it is two or three orders of magnitude smaller.

A marked shortage of many chemical elements relative to carbonaceous chondrites is noted in the Earth's crust with the exception of alkali metals (Na, K, Rb, Cs) and Sb, Pb, Tl. However, the Earth's crust is in the long run a product of differentiation of deep-seated parts of the Earth, where the most lithophile elements have been concentrated, including primarily alkali metals, easily forming 8-electron ions and being closely bonded to oxygen. Ultrabasic rocks, the most probable equivalents of the mantle, making up two thirds of the planet's mass, to a considerably larger extent indicate the average chemical composition of the Earth, in any case relative to atomic proportions (the ratio between any element and silicon). The analyses of lunar rocks of elements indicated in Table 14 revealed a similar picture of the shortage of many of them. They proved to be the same for the Earth's mantle and for the most widespread chondrites. The conclusion can be referred also to the material of the Moon. Consequently, the distribution and fractionation of elements when form-

TABLE 14. Indicators of Deficiency of Some of the Chemical Elements Relative to Carbonaceous Chondrites C1 (the content of each element in carbonaceous chondrites C1 is assumed to be unity)

Element	Carbonaceous chondrites		Common chondrites	Enstatite chondrites	The Earth's substance	
	Type C2	Type C3			Ultrabasic rocks	Earth's crust
Si	1.00	1.00	1.00	1.00	1.00	1.00
Mn	0.67	0.53	0.72	1.00	0.43	0.21
Na	0.58	0.47	0.70	1.00	0.61	1.61
K	0.63	0.52	1.1	1.1	0.35	18.00
Rb	0.68	0.47	0.87	—	0.57	27.00
Cs	0.56	0.16	0.14	—	0.003	6.00
Cu	0.62	0.52	0.28	0.72	0.05	0.08
Au	0.75	0.79	0.64	1.30	0.017	0.06
Ga	0.61	0.44	0.26	1.1	0.09	0.6
Ge	0.60	0.30	0.16	0.89	0.016	0.022
Sn	0.39	—	0.15	0.29	0.15	0.4
S	0.45	0.25	0.20	0.60	0.0008	0.002
Se	0.38	0.25	0.21	0.54	0.0013	0.0008
Te	0.46	0.24	0.11	0.59	0.000017	0.0001
Ag	0.35	0.30	0.095	0.74	0.072	0.063
Zn	0.42	0.16	0.084	0.68	0.045	0.081
Cd	0.57	0.26	0.08	1.7	0.031	0.05
Hg	0.33	0.089	0.07	0.024	0.0004	0.0025
F	0.69	0.38	0.31	0.44	0.21	0.333
Cl	1.1	0.93	0.021	1.6	0.10	0.22
Br	0.30	0.30	0.024	0.41	0.044	0.13
I	0.45	0.18	0.041	0.28	0.008	0.011
Pb	0.44	0.28	0.02	0.59	0.024	2.30
Bi	1.1	—	0.0055	0.38	0.005	0.027
In	0.46	0.20	0.0018	0.64	0.016	0.37
Tl	0.69	—	0.0018	0.49	0.04	2.70
Kr	0.65	0.56	0.023	0.068	—	—
Xe	0.62	0.022	0.022	0.05	—	—
H	0.55	0.074	0.016	—	—	—
C	0.54	0.10	0.013	0.069	0.015	0.021
N	0.54	0.15	0.016	—	0.0013	0.0027

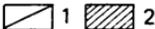
Note: The data on chondrites are assumed according to J. Larimer and E. Anders (1967), the data on the Earth's crust and ultrabasic rocks, according to A. P. Vinogradov (1962).

ing solid bodies was due to cosmochemical reasons.

In the Earth's mantle the deficit of sulphur, selenium, tellurium, mercury is especially pronounced, their relative concentration in the Earth's material being less than 0.001 as compared with the substance of carbonaceous chondrites Cl. With what properties of chemical elements is their shortage connected in a number of studied bodies of the Solar System? The corresponding deficient elements are presented in the Mendeleev Periodic Table (Table 15).

TABLE 15. Deficient Elements in the Earth's Substance and Meteorites in the Mendeleev Periodic Table

I	II	III	IV	V	VI	VII	VIII			I	II	III	IV	V	VI	VII	
																	H He
Li	Be	B											C	N	O	F	Ne
Na	Mg	Al	Si	P											S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Tr	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Tb	Pa	U												


 1    2

1—elements of normal deficiency (0.5-0.1)

2—elements of sharp deficiency (0.1-0.001)

According to J. Larimer, these elements can be of normal deficiency, when their content relative to Cl is 0.5-0.1 (i.e. their concentration is 2 to 10 times smaller) and of abnormal deficiency, when their content is with-

in 0.1-0.001. Thus, their concentration is 10 to 1 000 times lower than an average cosmic one. Table 15 shows that deficient elements occupy quite certain places in the Mendeleev Periodic Table, embracing the fields of chalcophile, atmophile and volatile lithophile elements. Hence, their deficiency is not accidental and is associated with certain physicochemical properties.

It is easy to see that most of the deficient elements are volatile. Their melting and boiling temperatures are relatively low and therefore they easily migrate at high temperatures in a gaseous state. The separation of elements into volatile and nonvolatile is presented in Tables 3, 4. However, not all elements are deficient due to the volatility alone. Such metals as silver, gold, copper are non-volatile. But their scarcity in the Earth's crust and mantle may be due to their siderophile properties and concentration in the metallic core of the Earth. Probably sulphur and its chemical equivalents were also supplied to the Earth core and their deficit in reality is probably not so sharp.

A great shortage of volatile elements on our planet relative to the average material of the Sun is the result of processes of the Earth formation as a physicochemical system. The process that caused the loss of volatiles and fractionation of elements could occur in two ways: in the past the Earth had passed a stage of a high-temperature molten state and volatile elements evaporated and were dissipated in space. The Earth appeared due to conden-

sation of the material, in which volatile elements were present in small amounts and thus it inherited the composition of a certain part of the protoplanetary disc.

The first process could not provide a different degree of the loss of volatiles observed in reality. The temperatures necessary for heavy atoms of mercury, thallium and lead to acquire a cosmic velocity (11.2 km/s) and to escape the Earth forever prove to be extremely high and would result in the explosion and dissemination of the whole terrestrial material. Therefore this process of the loss of volatiles should be abandoned as unreal.

The second way, the successive condensation of elements and their compounds in the order opposite to their volatility, is most probable. So, if a temperature rise results in the increase of volatiles mobility, a temperature decrease of an incandescent gas system of the solar composition causes a successive condensation first of nonvolatile high-melting elements (see Table 4), then of low-volatile elements and finally of the most volatile elements and their compounds. This process of condensation of the hot gas of a solar composition was quantitatively studied and calculated according to the formulae of chemical thermodynamics by J. Larimer and L. Grossman and other investigators (Fig. 20).

The constructed diagram characterizes a succession of the condensation of elements and their compounds in the course of the temperature decrease of a solar gas and the pressure drop from 1.00 down to 0.007 atm. As seen

from the diagram, the condensation of elements and their simplest compounds in the form of oxides, silicates and sulphides occurred in a certain strictly systematic order. Iron,

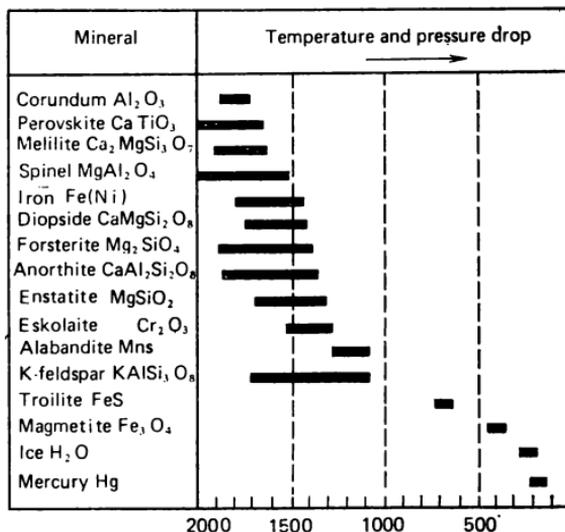


Fig. 20. Condensation temperatures of elements and their compounds on cooling of the solar gas

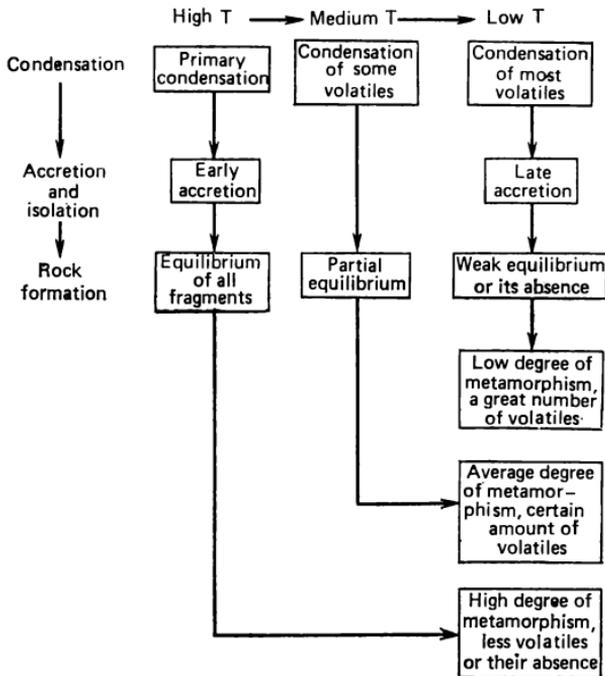
nickel, silicates consisting of the most abundant elements (O, Si, Fe, Mg, Ca, Al) were the first to condensate, then came sulphides and such volatiles as water and mercury were the last to condensate at negative temperatures. Drops of silicates cooled down, passed a crystallization stage and were turned to solid bodies, i.e. globular particles. There is a good probability that chondrules of most of the stony meteorites are direct residues of the drops having appeared in the process of con-

densation of the solar gas.

It should be noted that in 1958 J. Wood proposed the idea that chondrites had condensed at a high temperature from the protoplanetary gas cloud having contained vapours of iron, magnesium, silicon, and other elements. At the temperature decrease below 2 000 K liquid droplets were formed and during further cooling they produced small specks of dust that served as the material for the formation of the Solar System planets. Thus, a thorough investigation of the meteoritic material allows one to conclude that the initial high temperature and a subsequent quite rapid cooling are necessary for its formation.

The calculation results were based on the assumption that in the course of the solar gas condensation there was a continuous equilibrium between a condensing liquid phase and the surrounding gas. However, this case should be considered ideal. In the process of the solar gas condensation the equilibrium could be disturbed. Silicate particles that had been formed could undergo a repeated heating, metamorphism and recrystallization. The study of the structure of chondrules themselves indicates a great reality of these processes. Microscopic investigations and the analysis of individual chondrules made by M. Blander and A. Monet (1969) have shown that chondrules could be formed as overcooled droplets. The scientists compiled an idealized scheme of different stages of condensation and accumulation of chondrites at the same pressure regime (Scheme 1).

The sequence of condensation (see Fig. 20) depends on pressure in a primary solar nebula



Scheme 1. The scheme showing different stages of condensation and accretion of chondritic meteorites at the similar pressure regime (according to M. Blander and A. Monet)

that is in essence unknown to us. This dependence is not essential to the change of the order of condensation. Thus, according to L. Grossman's calculations iron-nickel alloys have higher condensation temperatures than magnesium silicates (forsterite  $Mg_2SiO_4$ , en-

statite  $\text{MgSiO}_3$ ) at all pressure values exceeding  $10^{-5}$  atm ( $\text{kgf/cm}^2$ ). But at lower pressures forsterite and enstatite are the first to be distinguished.

However, the C/O ratio has the most essential effect on the sequence of condensation processes of different compounds in a cooling nebula. All the above temperatures of condensation were based on the solar ratio  $\text{C/O} = 0.6$  that was ubiquitously assumed to be the same in the entire homogeneous solar nebula. In fact we have not got convincing proofs of this being exactly so. A slight change of the C/O ratio from 0.6 to 1.00 causes a significant change of the sequence of condensation processes of different substances. The change in condensation temperatures depending on the C/O ratio at the pressure of  $10^{-4}$  atm ( $\text{kgf/cm}^2$ ) is given in Fig. 21. It shows that condensation temperatures of iron and its alloys do not change. At the same time, when the C/O ratio changes from 0.4 to 0.9, the condensation temperatures of such compounds as  $\text{Al}_2\text{O}_3$ ,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{Mg}_2\text{SiO}_4$ ,  $\text{MgSiO}_3$  are decreased by  $50\text{--}100^\circ$ . When the C/O ratio increases from 0.9 to 1.0, these temperatures are decreased by  $300\text{--}400^\circ\text{C}$ . In this case high-temperature compounds, for example, graphite,  $\text{CaS}$ ,  $\text{Fe}_3\text{C}$ ,  $\text{SiC}$  and  $\text{TiN}$  are among the first to appear. They really occur in the most reduced meteorites of the type of enstatite chondrites and in some iron meteorites.

Generally we can assume fractionation of carbon and oxygen in the primary solar nebula.

la, though particular reasons for such fractionation are not clear. The C/O ratio varied in the course of condensation and accretion of substances. Solid phases of carbon (graphite

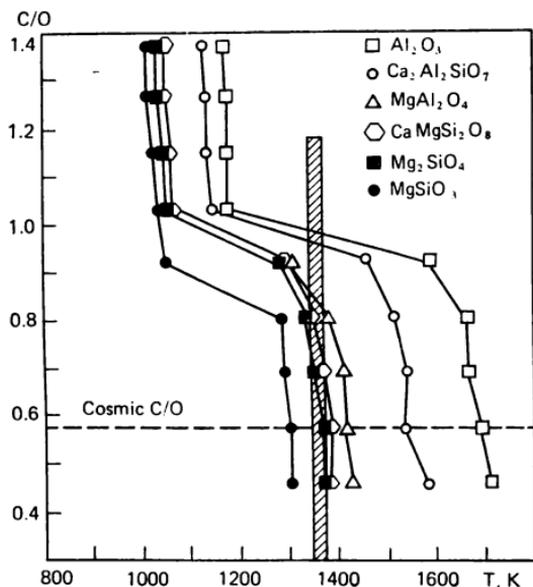


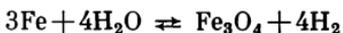
Fig. 21. Condensation temperatures of high-melting silicates and oxides when the C/O ratio (pressure  $10^{-4}$  atm) increases. The condensation temperature of metallic iron remains constant (according to J. Larimer)

and carbides) were parts of nuclei of planets, thus decreasing the C/O ratio in the remaining nebula, where later the chemical processes came to be mainly determined by the cosmochemistry of oxygen.

The formation of the Earth's chemical composition was caused by certain physico-chemical processes in a protoplanetary gas nebula and naturally was a variant of a more common process of condensation, then thickening (accumulation, accretion) of condensed systems to form planets and asteroids.

The products of gas condensation of a solar composition can be divided into two main fractions: low-temperature that retained in its composition a great quantity of volatile elements and their compounds, and high-temperature, containing no volatiles and consisting of chondrules in chondritic meteorites and metallic iron as a constituent part of a number of meteorites and of inner planets.

When the temperature of gas of a solar composition is decreased, the equilibria of many chemical reactions between components of the solar cosmic substance varied. One of the most important chemical reactions in a gas nebula having determined the composition of planets of a terrestrial group was that of a redox type.



H. Urey and W. Latimer who studied this reaction for the substance of a solar composition calculated the temperature of its equilibrium that proved to be equal to 400 K. Below this temperature iron is oxidized to magnetite. However, small quantities of iron silicates could appear in the process of cooling of a protoplanetary substance. R. Mueller has shown in 1964 that the reduction of iron from

silicates to the metal should occur at the temperature exceeding 1 100 K, and iron silicates could form below this temperature.

One might imagine that the material of the Earth, inner planets and parental meteoritic bodies was formed by condensation from the solar gas that was being cooled down. It is quite permissible that inner planets that are closer to the Sun were formed under conditions of its heating and the heating slackened farther from the Sun. Therefore inner planets located closer to the Sun appeared as a result of thickening of a high-temperature fraction. But farther from the Sun in the area between Mars and Jupiter in the so-called asteroidal belt parental bodies of meteorites were formed—mainly chondritic asteroids, in which the proportion of a low-temperature fraction of condensates was rather high and generally increased to the peripheral part of the belt. Thus, in the central and marginal parts of the asteroidal belt the condensation occurred during rapid cooling of the substance, which resulted in a leading role of a low-temperature fraction and the formation of the composition of the substance of the carbonaceous chondrite type that almost entirely retained the atomic ratios of the Sun. Finally, outer planets that are remote from the Sun—Jupiter, Saturn, Uranus, Neptune, Pluto—were formed completely from the indivisible and non-fractionated solar substance mainly retaining gases in its composition (hydrogen playing a leading role).

So, according to the ideas discussed above

that are based on the data of cosmochemistry, meteoritics and thermodynamics, the formation of the chemical composition of planets had occurred in two stages. The first stage was distinguished by cooling of a gas disc and condensation of a part of its substance to liquid drops and then to particles. In this manner a gas-dust nebula appeared. It was unstable and owing to different velocities of its cooling down, depending on the distance from the Sun, had acquired chemical inhomogeneity that additionally increased under the effect of solar rays pressure. The second stage was expressed in the thickening of condensed particles of a dust component of a protoplanetary disc in separate blobs, i.e. protoplanets. It can be assumed that these two stages were not sharply separated from each other in time. On the contrary, it is more probable that accumulation in separate parts of the protoplanetary disc began when condensation had not been yet accomplished.

Evolution of a protoplanetary nebula is schematized in Fig. 22. Inner planets of a terrestrial type that are close to the Sun mainly resulted from the thickening of a high-temperature fraction, containing a significant amount of metallic iron. Therefore, Mercury, the closest planet to the Sun, is two-thirds metallic iron, and Mars, the most distant from it among inner planets, is probably only one-fourth metallic iron.

On physical grounds one can assume that the protoplanetary gas disc cooled down rather rapidly. The gas disc that was formed around

primordial Sun in its equatorial plane was partially dissipated and partially condensed in the form of drops rapidly passing into solid particles. The gas disc was in general an unstable formation and was quickly disseminated in the world space by diffusion, overcoming the Sun's force of attraction. Evidently only its small part was condensed to become solid bodies and gas accumulations that gave

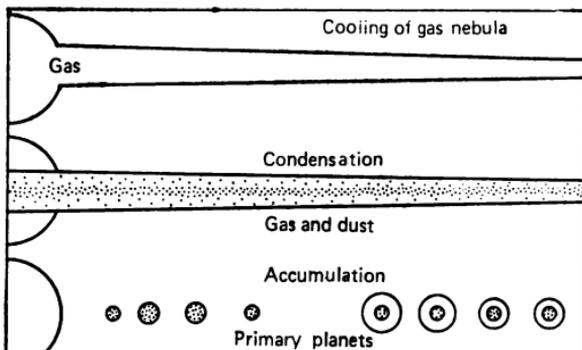


Fig. 22. Evolution of a protoplanetary nebula

rise to planets. Using the data on chemical fractionation of the meteoritic substance as the base, J. Larimer and E. Anders calculated the velocity of cooling down of a gas nebula and its condensation in two variants: without regard for and with regard to solar heating. In the first case the formation of meteorites had not exceeded 10 thousand years. In the second case the process occurred slower, i.e. of the order of 1.0 million years. Because of the strong so-

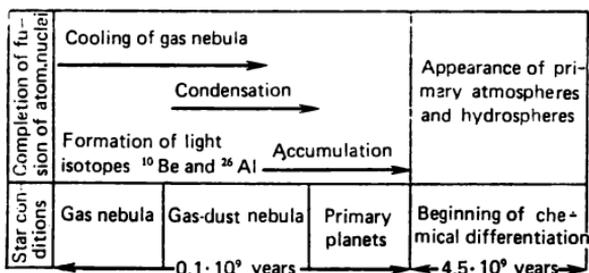
lar heating in the area of inner planets the process of cooling down was prolonged probably to 2-5 million years.

Thus, a primary gas nebula as it cooled down was turned to a gas-dust one. A dust component served as a building material for inner planets, meteoritic bodies, and a gas-dust mixture, for outer planets (see Fig. 22). Closer to the Sun, at a distance of 0.5-1.5 AU the primary protoplanetary substance was cooling down relatively slowly. Condensed drops were formed, as well as particles mainly of a high-temperature fraction with a maximum portion of metallic iron and a minimum one of a low-temperature fraction. By accretion of this material inner planets were formed with a minimum content of volatiles. But farther from the Sun the material with an increased proportion of volatiles of a low-temperature fraction was condensed.

It can be assumed that parental bodies of enstatite chondrites appeared from the material found near the Earth's orbit. The parental bodies of common chondrites were formed near the orbit of Mars, approximately at a distance of 1.2 AU and in the inner part of asteroid ring. The greater part of the asteroid ring was the most favourable place for the formation of parental bodies of carbonaceous chondrites.

A general chronological sequence of events that had occurred in the Solar System after the finishing of processes of nuclear fusion is presented in Scheme 2. It is easy to assume that the substance of our planet in the remote

past underwent successively the stages of nuclear fusion, gas nebula, condensation of the gas nebula resulting in the formation of solid particles, of accumulation, of its own development accompanied by chemical differentiation into separate shells. A subsequent course of the above events is based on the modern study of meteoritic material, the Earth and planets. However, it is natural that the data obtained are incomplete and make it possible to draw a qualitative picture that requires further confirmation.



Scheme 2. Chronological sequence of events in the history of formation of the Solar System

Thus, we can put the main question: to what extent can modern data on observational astronomy and physicochemical investigations of an experimental character confirm the accepted process of cooling of a solar (star) gas with the formation of chemical compounds and their subsequent condensation to solid particles?

Indeed, the spectral studies of distant stars of our Galaxy reveal that as the gas of a star

composition cools, the first chemical compounds appear in the form of diatomic molecules. In the spectra of the coldest stars with a surface temperature of about 3 000-2 000 K numerous molecular bands have been discovered indicating the presence of AlO, MgO, TiO, ZrO, CO, SiO and other compounds.

Condensation of solid particles or liquid drops from the solar nebula have long been considered to be one of the most important physicochemical processes occurring in the early history of the Solar System.

According to astrophysical observations, enstatite or olivine grains are in the interstellar space and surround the areas of cold stars of spectral classes K and M. A thorough study of the spectra of different stars in ultra-violet and infrared areas has made it possible to make rather interesting conclusions relating to the composition of the circumstellar dust. Wide bands in the infrared area of the spectrum of giant and supergiant cold stars indicate that many of them have a surplus of emission within the limits of the light waves that correspond to the radiation peak of the silicate material, and that of a star dust is composed of silicates. It should be noted that the particles of moissanite SiC, graphite and metallic iron have also been found in the composition of the circumstellar dust. It has recently been established that the particles of moissanite are formed around carbon-rich stars and are the main condensates of stars with the C/O ratio close to unity. Mainly silica will be a leading component

of dust particles in the neighbourhood of stars relatively enriched with oxygen (Ney, 1977).

In spite of the fact that at present the data on the chemical composition of grains of the circumstellar dust are very limited, they show the composition of a high-melting fraction of the star substance of a central stellar body. Since the chemical composition of different types of stars is different, it is natural that the composition of the circumstellar dust is individual and depends on that of high-substances in a parental star. Therefore if solid bodies of the Solar System (meteorites, asteroids, and inner planets) reveal to a certain extent a chemical composition of a high-melting portion of the Sun, disseminated dust material surrounding the stars of different types reveals to the same extent a chemical composition of a high-melting portion of these stars.

Thus, the formation of graphitic, moissanite silicate and iron particles from the substance thrown away by the stars is a rather abundant process in our Galaxy.

Of course, a particular mechanism of formation of solid particles from a cooling star gas is not clear yet. But one does not have to doubt that this process occurred in the past.

Considering a modern state of the technique of a physical experiment, separate units of condensation processes of the solar gas can be modelled experimentally. The results of such experiments can confirm general thermo-

chemical calculations of the solar gas condensation and account for mineral paragenetic associations observed in meteorites of different types. Unfortunately, investigations that have been carried out in this line are rather few in number. Nevertheless, it has been possible under conditions close to cosmic to synthesize silicate minerals and metallic phases directly from a vapour phase. Physicochemical experiments with vapours of metals and oxides under low pressures have recently yielded rather interesting results.

Polymorphic alloys (for example, Fe-Ni, etc.), magnetite, graphite, metal carbides, magnesian silicates, polymorphic varieties of silica can increase directly by condensation from partially ionized gas in radiation equilibrium with this gas. Experiments with a Fe-Ni system have demonstrated that the phases of this composition increase simultaneously from the plasma of a gas system in the form of discrete well-shaped crystals at a substrate temperature below 600 K.

The experiments carried out by Ch. Meyer in 1971 under conditions similar to circumstellar condensation have revealed that crystalline silicates can really condense from a hot vapour. Condensation of Mg, Si, Fe, O at different temperatures of substrate also results in fractionation of Mg, Fe, Si relative to Ca and Al, but Ca and Al are separated from each other with difficulty at temperatures below 1 300 K.

The results of these experiments confirm the assumption that a total chemical compo-

sition of chondritic meteorites of different classes can indicate primary fractional condensation of high-melting oxides in the Solar System. The direct synthesis of crystalline silicates during vapour condensation supports the conclusion that, according to their mineral and chemical composition, carbonaceous chondritic meteorites belong to the pattern of bodies having formed as a condensation product in the near-Sun space.

Thus, the observational astronomy data and those of physicochemical experiments under conditions similar to cosmic definitely reveal that the appearance of solid dust particles directly from the star substance during its cooling is a natural and rather widespread process in the course of stars evolution. Hence our main conclusion is reaffirmed that in the history of the Solar System the primitive substance of a solar composition was subjected to the condensation of solid particles that later became a building material for terrestrial planets and parental meteoritic bodies.

## Formation of the Earth's Principal Shells

As mentioned earlier, the Earth was derived from the thickening of the mostly high-temperature fraction of solar condensates containing much metallic iron. Generation of meteoritic (silicate, sulphide and metallic) phases in the form of achondrites and stony-iron and iron meteorites within the parental me-

teoritic bodies, as well as metallic cores and oxide-silicate mantles in the inner terrestrial planets, is commonly regarded as a secondary process experienced by far from all asteroids. It is assumed that the inner planets are zoned owing to radiogenic heating and chemical differentiation of initially homogeneous material.

The early history of the Earth is not traceable in the geological record used successfully by geologists to reconstruct the Earth's evolution. Even the most ancient rocks, 3.9 billion years old, are products of much later events subsequent to the generation of the planet itself.

We can postulate, however, that the primordial Earth had experienced its overall planetary chemical differentiation with formation of a core and primordial silicate mantle. An oceanic and a continental aluminosilicate crust formation is related with physico-chemical processes in the mantle itself.

If the Earth had passed through a high-temperature stage, whatever its origin and with its complete melting, the heavier molten iron masses might have flowed toward its centre to form a core, while the silicate masses might have floated upward to give rise to a molten silicate mantle which later cooled down to become a solid shell. However, this view of the differentiation of the entire Earth, most completely elaborated by V. M. Goldschmidt, met with a great difficulty. It consisted in the fact that the high viscosity of silicates under high pressures in the Earth's

interior ruled out the possibility of chemical stratification with the movement of matter on a global scale even at temperatures exceeding the melting point of any known silicate material. Hence a hypothesis of the homogeneous chemical composition of the Earth, and some authors related the presence of the solid core to solidification of silicate material with the formation of an extremely dense "metallized" phase. As mentioned above, however, the most recent data on the physics of high pressures, average density of terrestrial planets, and chemistry of meteorites disagree with this hypothesis. In the light of modern geophysical evidence, the model of the liquid Earth's core consisting of iron with admixture of sulphur and nickel is in closer agreement with all known to date.

In an attempt to discern the chemical differentiation of the Earth, connected with high viscosity of silicates, the following two alternatives can be presented:

1. as a result of radiogenic heating, the Earth underwent chemical differentiation with a release of liquid iron masses in the upper horizons. Being heavy, they broke through viscous silicate masses in some place of one of the hemispheres and flowed down to the centre of the Earth;

2. when forming by concentration of high-temperature condensates of the solar gas, the Earth first accumulated primarily from iron particles (droplets) to form its interior and then from silicate particles to produce a primordial mantle.

At the present state of knowledge we cannot definitely select one of the above alternatives. We discuss both, although the latter is, in principle, more probable.

According to the former, the Earth was derived from accumulation as a chemically relatively homogeneous ball. It was a more or less uniform mixture of particles of iron, silicates and, to a lesser extent, sulphides dispersed throughout the Earth's volume. While accumulating, the Earth also captured some gases, among them  $H_2O$ ,  $CO_2$ , N and Hg from the primordial nebula. The cause was its own gravity when it had become massive enough. In the opinion of some investigators, the Earth as a primitive planet was originated at temperatures below the melting point of its material 5-4.6 billion years ago. We can very approximately delineate the temperature limits of formation of the young Earth. Its mass undoubtedly formed mostly below the condensation point of high-temperature (metallic and silicate) fractions, i.e. below 800 K. The particle impacts, however, during accumulation could have risen the temperature of the Earth under generation. It is true that a quantitative estimation of this process cannot as yet be sufficiently reliable. On the whole, the formation of the Earth could not have been completed below 400 K, which was due to its distance from the Sun.

Once the primitive Earth had formed, its fast radiogenic heating began owing to a decay of short-lived radioactive isotopes, among

them an insignificant amount of transuranium ones left behind by the epoch of nuclear fusion, and a decay of the present radioisotopes of uranium, thorium and  $^{40}\text{K}$ , which were then more than now in amount (see Fig. 17). In general, the amount of radiogenic energy was enough early in the Earth's existence for its material to melt with subsequent degassing and outward movement of the light-weight constituents.

With the relatively homogeneous distribution of radioactive elements and uniform dissemination of radiogenic heat throughout the Earth, the temperature grew highest at its centre, with subsequent peripheral leveling out. The pressure at the Earth's centre was, however, too high to expect melting there. The radiogenic heat-induced melting began at certain critical depths (Fig. 23). It occurred where the temperature exceeded the melting point of some part of the primordial material of the Earth. In this process, iron with some sulphur admixture started to melt earlier than pure iron or silicate material.

According to the American geophysicist F. Birch, the chondritic model for the Earth implies melting in a depth interval of 100-600 km. Here, a molten layer began to grow, whose thickness continuously increased both inward and outward. Because of decisive importance of iron, which is the most common metal, chemical stratification—differentiation in a liquid state—started in the molten layer. The result was a division of layer at least into two parts, the upper, silicate, and the

lower, metallic (iron, iron-sulphur). Remember that the specific gravity of liquid iron

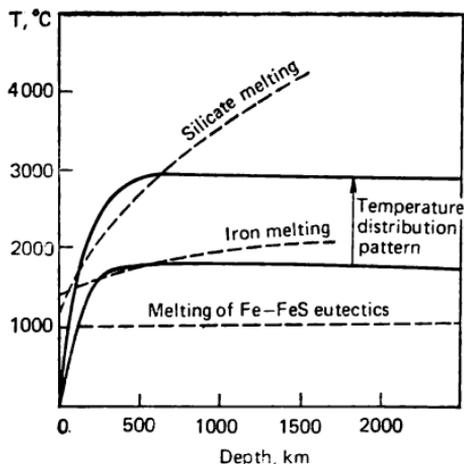


Fig. 23. Melting of material in the Earth consisting of a homogeneous mixture of silicate, metallic and sulphide matter

is more than twice as large as that of the most common silicates. Further melting continuously thickened the molten iron layer thus hinder-



Fig. 24. The formation of the Earth's core (after W. M. Elsasser).

ing cooling at the planet's centre. At the same time, this layer could not have had an equal thickness everywhere. Under the gravity of the newborn Moon, tidal deformation arose, with a tidal wave (Fig. 24). According to

W. M. Elsasser, the tidal effect was very large at that distant time because of the proximity of the Moon. As a consequence, one of the bulges of the tidal wave exerted a high pressure on the substratum and, in the final analysis, pushed it down towards the Earth's centre. A downwarp formed (Fig. 24a), and the liquid iron began to move into the Earth's interior, replacing the other, undifferentiated material containing a great amount of silicates. Although this material was not in a liquid, molten state, it possessed elevated plasticity and fluidity. The further growth of the giant "iron drop" led to its fall to the Earth's centre (Fig. 24b). It squeezed out the plastic silicate masses, which moved upward through the melting zone to undergo differentiation. Along with iron, related siderophile elements and probably sulphur and its chemical equivalents concentrated in its melt. According to F. Birch, the full submergence of the "drop" produced an energy release of some 600 cal per gram of terrestrial material, which is equivalent to a 2 000 K temperature rise. The global-scale energy release was  $3.6 \times 10^{30}$  cal. According to other estimates, the reconstruction of the Earth from a homogeneous silicate-metallic mixture to the modern state with a metallic iron core must have produced  $3.58 \times 10^{30}$  cal (E. N. Lyustikh) or  $4.78 \times 10^{30}$  cal (H. Urey). Thus the differentiation of the whole Earth material caused a strong heating of the entire planet. All this occurred geologically rather rapidly, for the huge masses of molten iron could not have been in an unstable state

for long in the upper parts of the Earth. In the final analysis, all liquid iron flew on one side and asymmetrically into the Earth's centre to form a metallic core whose internal portion was transformed into a solid dense mass under a high pressure with the generation of a small core below 5 000 km of depth.

With this mode of core generation, which was mainly completed 4.5 billion years ago, an inevitable process was asymmetrical differentiation of material with far-reaching consequences in the form of appearance of a continental and an oceanic hemisphere (segment). Probably, the hemisphere of the modern Pacific Ocean was a segment where the iron masses submerged to the centre, whereas the opposite hemisphere was the site of silicate material rise with subsequent melting out of aluminosilicate masses and volatiles. Because the silicate masses could have melted not in the entire Earth but only in its upper horizons, the silicate material underwent zone melting in the would-be continental segment during its rise in the process of Earth differentiation. The mechanism of zone melting was well studied by Academician A. P. Vinogradov and his coworkers on the basis of chondrites. The most typical lithophile elements concentrated in the low melting-point fractions of mantle material; these elements were then supplied, along with gases and water vapour, onto the Earth's surface. On the completion of planetary differentiation, the silicates mostly formed a thick mantle, whereas the products of its melting

began to form an aluminosilicate crust, a primordial ocean and a primitive atmosphere with respect to carbon dioxide. Whereas the hot molten iron masses flowed towards the centre within the segment of the Pacific Ocean in the distant past, the opposite hemisphere was the site where silicate masses mostly rose and differentiated, with an enrichment of the upper horizons in silica, and continents later originated.

The other cause of the zonal structure of our Earth, as mentioned above, may be related to the very mechanism of planet accumulation, with changes at that time in the composition of major components of the globe. Thus, when the primordial gas nebula of solar composition cooled and condensed, the principal components of the inner planets and meteorites—iron-nickel alloys and magnesian silicates—precipitated in the following order:

	<i>T</i> , K		<i>T</i> , K
Fe	1790-1620	Mg <sub>2</sub> SiO <sub>4</sub>	1620-1420
Ni	1690-1440	Fes	680
MgSiO <sub>3</sub>	1670-1470		

Thus the most widespread portion of the high-temperature fraction condensed from the solar gas within 1790-1420 K at a chemical equilibrium. Hence the possibility that the Earth started to accumulate when the iron-nickel drops had ceased to form whereas silicate ones only began to originate in the solar gas nebula. Drops of metals touched one another to produce compact masses, because the metallic material has a high thermal con-

ductivity. Therefore, there is a ground to believe that the accumulation of the Earth and terrestrial planets progressed simultaneously with silicate condensation from protoplanetary matter. Nuclei of planets were first produced from metal and then silicate particles settled down around them to form primordial mantles.

On analyzing the metallic phases of meteorites, A.P. Vinogradov and his coworkers (1971, 1975), put forward more physicochemical arguments on the origin of the solid iron-nickel alloy independently and directly from the vapour phase of the protoplanetary cloud and its condensation at 1 770 K. He believes that the iron-nickel alloy of meteorites is of primary nature and, accordingly, characterizes the metallic phase of terrestrial planets. According to A. P. Vinogradov, rather dense iron-nickel alloys originated in the protoplanetary cloud and caked into lumps, because of their high thermal conductivity. These lumps then fell towards the centre of the gas-dust cloud, still continuing to condensate. The mass of the iron-nickel alloy condensing independently from the protoplanetary cloud was the only one that could have formed the cores of terrestrial planets.

We do not know, however, the temperatures of large-scale planet accumulation. If thickening had taken place below 1 000 K, the conditions of growth of the primordial planets would have been quite at variance. Additional factors promoting a selective accumulation of materials of different com-

positions and properties were in action during the growth of these planets.

In general, the whole dust condensed from the solar gas consisted largely of metallic and silicate particles. It is quite natural that they differed in physical properties and could, therefore, combine. On their impact in the primary nebula, three alternative processes could have occurred: divergence of flying particles as a result of an elastic collision, combining through adhesion and fragmentation into smaller particles at the highest collision speeds. T. Matsui and H. Mizutani (1977) have made the relevant calculations whose results are shown in Fig. 25 at the various temperatures and velocities of impact of metallic and silicate particles for divergence, adhesion and fragmentation. When the diagrams are compared, it becomes clear that the metallic iron material distinctly tends to adhere easier, and in a broader temperature interval and collision velocity range, than the silicate material.

Magnetic interaction is also a significant factor of cohesion of metallic particles. The highly active primordial Sun created a magnetic field in the surrounding space, which promoted magnetization of ferromagnetic materials. These are metallic iron, cobalt, nickel and, to some extent, sulphide of iron. The Curie point, below which substances acquire magnetic properties, is 1043 K for Fe, 1393 K for cobalt, 630 K for nickel and 598 K for iron sulphide (pyrrhotite similar to troilite). For fine particles, the magnetic forces

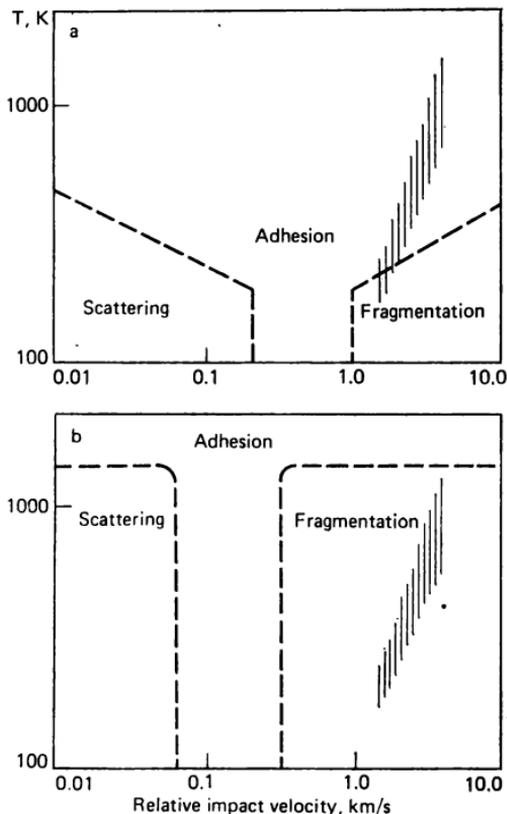


Fig. 25. The diagram showing different temperatures and impact velocities at the time of scattering, adhesion and fragmentation of metallic (a) and silicate (b) bodies.

Data on the terrestrial planets are restricted to the shaded area

are many orders of magnitude stronger than the gravity forces, which depend on masses. Hence accumulation of iron particles from the cooling solar nebula could have begun

below 1 000 K as large clots and have been many times more effective than the accumulation of silicate particles under otherwise equal conditions. Iron sulphide could also have accumulated (below 580 K, under the action of magnetic forces) subsequent to iron, cobalt, and nickel.

With the above in mind, we can formulate the following. The zoned structure of our planet can largely be attributed to a successive accumulation of particles of different compositions, first ferromagnetic, then poorly magnetic, and finally silicate and those of other kinds, whose accumulation was mostly under gravity induced by the grown-up massive metallic clots.

Thus the accumulation process itself was responsible for the chemical inhomogeneity and thermodynamic instability of the Earth. This instability later predetermined the chemical differentiation of the Earth, with the resulting clear distinction between the mantle and core as they look now.

The primordial Earth began to grow with amalgamation of metallic particles. On the achievement of a considerable mass, the primordial metallic core—nucleus—continued a gravity capture of later condensates from the surroundings. In this process, the accumulation was becoming more and more homogeneous, and primordial mantle arose as a thick shell composed of a mixture of metallic and silicate particles, and troilite (Fig. 26). During the continuous accumulation, the content of metallic particles was ele-

vated in the lower parts of the mantle, near the primordial core, whereas they were absolutely absent in its upper horizons. The final stages of accumulation were marked by settlement of the latest components: hydrated silicates (serpentine, tremolite, chlorite) and organic matters, as well as volatiles. As a whole, the order of accumulation repeated that of condensation. It is still unclear whether the accumulation was continuous or discon-

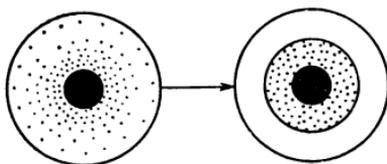


Fig. 26. Model for the primordial Earth derived from heterogeneous accumulation (left) and that for the modern differentiated Earth (right).

Dots indicate the metallic and metal sulphide phases; blank space depicts the silicate phase

tinuous. The former is more probable, as the distinction of the condensation temperatures of the principal materials was not too striking.

Because of adiabatic compression, primary heating produced by particle impacts and radiogenic heating preserved by now and short-lived radioactive isotopes ( $^{244}\text{Pu}$ ,  $^{247}\text{Cm}$ ,  $^{129}\text{I}$ ), the temperature rose rapidly, and the material of the planet began to melt in places. Naturally, the easiest-fusible ferrous-sulphurous masses (eutectics) were first melting, flowing asymmetrically inward. The model

proposed implies, therefore, that the central portion of the core was derived from accumulation of metallic particles, whereas the subsequent melting out of ferrous-sulphurous masses in the lower primordial mantle marked the final stage of formation of the core as a whole (see Fig. 26).

At the present state of knowledge, the heterogeneous accumulation of our planet from products of condensation of solar matter seems to be most probable. Rapid radiogenic heating of the young Earth started also in the case of heterogeneous accumulation. This heating rose its temperature and promoted partial melting of material and further chemical differentiation which led to a more distinct isolation of the major shells of the planet. Modern geochemical and cosmochemical evidence indicates that the primordial mantle differentiated along two avenues. On the one hand, melting-out took place of the easily fusible but heavy components — ferrous-sulphurous masses — with their inward subsidence, due to their high density and low viscosity, to produce the outer core. On the other hand, the upper horizons of the primordial mantle were sites of melting-out of less easily fusible but volatile-rich silicate fractions to form basaltic magma and then an ocean-type basaltic crust. While the first, centripetal process led to removal of mostly siderophile and chalcophile chemical elements from the primordial mantle and their concentration in the central core, the second, centrifugal process led to migration of mostly lithophile and atmophile

elements. The basic trends in the migration of elements in the globe with the formation of the Earth's shells are illustrated in Fig. 27.

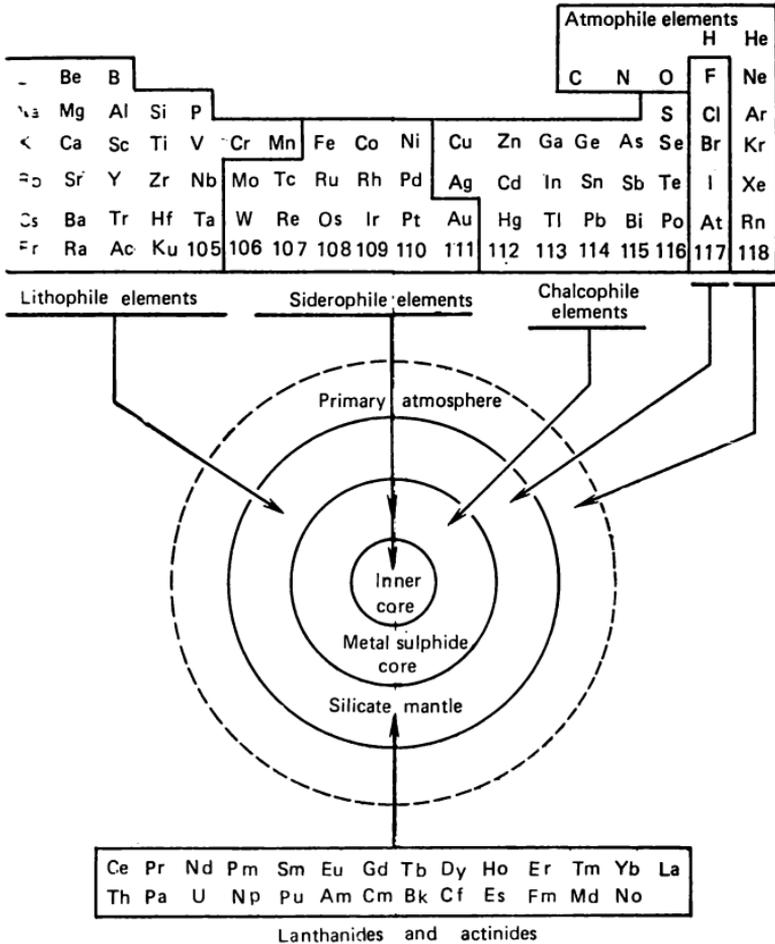


Fig. 27. Basic migration trends of chemical elements in the formation of the Earth's shells

Thus, the zoned structure of the Earth, as well as other inner planets, is the result of both the initial conditions of its generation and subsequent chemical differentiation. The uppermost shells of the Earth—atmosphere, hydrosphere and lithosphere are of secondary nature, being products of the geological history of the planet.

### Origin and Evolution of the Ocean and Atmosphere

All the basic constituents of the Earth's atmosphere and the World Ocean are referred to volatiles. They came onto the surface of the Earth owing to its chemical differentiation. According to the data available, steam and atmospheric gases were generated in the interior of our planet and rose to its surface as a result of internal heating, along with the low-melting point of mantle material in the course of volcanic activity.

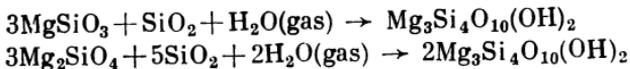
It should be noted that the idea has long prevailed in science that the Earth was first molten and initially surrounded by a thick atmosphere with water vapour which, on subsequent cooling, condensed into liquid water. Rains fell to form the World Ocean, whose water was first fresh. The ocean water became salty and mineralized later, owing to dissolved substances again from the land surface

during a long period of geological time. These ideas, however, once quite popular, are incompatible with modern evidence.

First, it should be borne in mind that, like all inner planets, the Earth contains very little volatiles. Thus the mass of the hydrosphere constitutes merely 0.024 per cent of that of the Earth, and the mass of the atmosphere, only 0.00009 per cent! So little amounts of volatiles is due to the mode and place of formation of our planet on the area of the initial nebula where little volatiles were present.

At present, the initial accretion of volatiles by the Earth is taken to have been as follows. Water and carbon dioxide as constituents of the solar nebula have existed for a long time in molecules when most of the solid condensates had precipitated. Hence the remaining gases were incorporated to some extent into dust particles by adsorption and by various chemical reactions.

After temperature had fallen below 400 K in the gas nebula, the earlier-settled out silicates interacted with water vapour. Some of the olivines and pyroxenes were transformed into hydrated silicates by the following reactions:



Thus the hydrated silicates found in some chondrites were found to be concealed carriers of water, an important volatile. Moreover, having a high adsorption capacity in a finely dispersed state, hydrated silicates

could have caught and adsorbed not only water molecules but also common and inert gases from the environment. Probably, adsorption was the most important process in which the volatiles remaining in the nebula were incorporated by dust and then, during further accumulation, penetrated into terrestrial planets and primordial bodies of meteorites. Hence the observed elevated concentration of inert gases and high-molecular organic compounds in carbonaceous chondrites is due to adsorption.

E. Anders and T. Owen (1977) assume that much of  $^{36}\text{Ar}$  in the Earth is in its atmosphere and can, therefore, be indicative of the meteoritic and terrestrial behaviour of noble gases. The basic inference stemming from the calculation of these authors is that, with the heterogeneous accumulation of our planet, only carbonaceous chondrites could have been suitable to fit the content of terrestrial volatiles. The pertinent data are given in Table 16. The second column presents the amount of meteoritic material in the Earth, which can account for the observed volatile concentration. It is seen that this concentration is relatively low, namely 1.3-6.3 per cent of the mass of our planet. On the basis of some isotopic characteristics, the most suitable material for the Earth's hydrosphere is carbonaceous chondrites C2 or the like. A somewhat rough character of the calculations should be noted. We do not know the amount of volatiles in the mantle. According to A.P. Vinogradov, it constitutes 92.3 per cent of the

total amount, i.e. water largely concentrates in the mantle even now, which is in general little probable. According to J.W. Larimer, the mantle may contain half terrestrial water.

TABLE 16. Chondritic Material as the Source of Terrestrial Volatiles

Object	Earth's mass = 100%	$^{36}\text{Ar}/^{14}\text{Kr}$
Terrestrial material*	—	48
C1 chondrites	2.4	$90 \pm 12$
C2 chondrites	3.9	$77 \pm 23$
C3 chondrites	1.3	$211 \pm 23$
C3V chondrites	6.3	$83 \pm 26$

\* Earth's crust, atmosphere, and hydrosphere.

In any case, the presence of volatiles on our planet is due to the mode of its formation, i.e. mostly to a late accretion of carbonaceous-chondrite material which in the given case was the most probable carrier of volatiles.

It should be noted that all the gases coming to the surface from deep in the Earth undergo in most cases drastic changes and are transformed into other chemical compounds. The principal volcanic gas—water—is condensed as liquid water to replenish the hydrosphere. Carbon dioxide, next common volcanic component, is rapidly consumed by the photosynthesis of green plants. Some of it dissolves in water to produce in the hydrosphere a complex carbonate system from which carbon

dioxide is extracted to form carbonate rocks—limestones and dolomites. Smokes of volcanogenic HCl and HF enter into the atmosphere and hydrosphere and then pass into  $\text{Cl}^-$  and  $\text{F}^-$  ions and are oxidized with the formation of carbon dioxide and water. Thus under present conditions the volatiles of the Earth come to the surface, undergo here severe alteration and not only remain in the atmosphere and hydrosphere but are to a large extent buried in sedimentary rocks.

At present all water on Earth forms a single unity—hydrosphere, a water shell. The importance of water as a strong factor that has long been transforming the face of the Earth and making a tremendous chemical and geological work is well studied. The work of water at the surface and interior of the Earth is due to the crucial capability of water to exist in three aggregate states—solid, liquid and gaseous. The ability of liquid water to dissolve many substances is of great importance. Hence any waters of the hydrosphere contain the varying amounts of dissolved matter. Natural waters are invariably mineralized to some extent or other and can be regarded as natural solutions of different concentrations. Thus even the “purest” rain water contains from 10 to 50 mg/l dissolved substances.

Water is highly mobile and hence penetrates everywhere into various natural formations. It is present in the atmosphere as steam, forms oceans, seas and bodies on continents, and penetrates into sedimentary series to

produce groundwaters in the different forms of occurrence. The greater part of water of the hydrosphere is in the World Ocean (86.5%) and much less of it is related to land, namely to lakes, marshes, rivers and groundwaters in the sedimentary sequence of the Earth's crust. The upper boundary of the hydrosphere is delineated by the surface of open water reservoirs. The lower boundary is rather indistinct. It probably corresponds to the 400 °C level deep in the crust, below which all water is gaseous (critical temperature of water).

The World Ocean occupies two thirds of the Earth's surface. The total mass of its water is  $1\,420 \times 10^{15}$  t, and its average depth is 3.8 km.

Ocean water is a unique solution containing, on the average, 3.5 per cent dissolved substances. Their sum is called salinity. Quantitatively, salinity is defined as the total weight, in grams, of the dissolved substances in a kilogramme of sea water. Among the principal components of salinity ions are the most common ones, which are rather few in number, and the dispersed ions of many chemical elements. The principal ions of ocean water, with their contents in grammes per kilogramme of water are given in Table 17. Ocean water also contains other chemical elements of the Mendeleev Periodic Table, but their concentrations are insignificant (below  $1 \times 10^{-4}\%$ ) and vary widely. These elements can be classified as rare and trace ones. Some of them, however, play an important role in the chemical processes in the sea and

in the life of marine organisms despite their relatively low concentration. In this respect, a prominent role is played by nitrogen, phosphorus and silicon, which are consumed by living organisms, their content in sea water being controlled by the growth and reproduction of marine plants and animals.

TABLE 17. Principal Ions of Ocean Water

Cation	Amount, g	Anion	Amount, g	Cation	Amount, g	Anion	Amount, g
Na <sup>+</sup>	10.7638	Cl <sup>-</sup>	19.3534	Sr <sup>2+</sup>	0.0136	Br <sup>-</sup>	0.0659
Mg <sup>2+</sup>	1.2970	SO <sub>4</sub> <sup>2-</sup>	2.7007			F <sup>-</sup>	0.0013
Ca <sup>2+</sup>	0.4080	HCO <sub>3</sub> <sup>1-</sup>	0.1427			H <sub>3</sub> BO <sub>3</sub>	0.0265
K <sup>+</sup>	0.3875	CO <sub>3</sub> <sup>2-</sup>	0.0702				

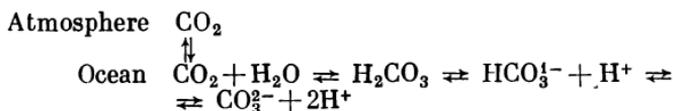
A striking chemical feature of sea water should be emphasized—its principal ions have constant relative proportions throughout the World Ocean. This suggests an extreme stability of the dynamic quantitative equilibrium between the dissolved substances supplied from land into the ocean and their precipitated amounts.

A peculiar role in sea water is played by dissolved natural gases—N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>S—which are closely associated with the atmosphere and living matter of land and sea. The concentration in cm<sup>3</sup>/l of these and other

natural gases vary widely depending on physiographic conditions:

N <sub>2</sub>	8.4-14.5	Ar	0.2-0.4
O <sub>2</sub>	0-9	H <sub>2</sub> S	0-22
CO <sub>2</sub>	34-56		

It is obvious that carbon dioxide, which is in the sea water in different forms, takes the first place in the greatest amounts. Not so much of the carbon dioxide proper is present in sea water. All of its forms in the sea constitute the so-called carbonate system at a dynamic equilibrium as follows:



A complex, temperature-dependent system of chemical equilibria between the links of this chain is established in sea water. The total amount of carbon dioxide in the entire World Ocean is estimated at  $1.4 \times 10^{20}$  g, which is 60 times higher than the amount of carbon dioxide in the Earth's atmosphere. Calcium ions, and indirectly the entire ion complex of sea water, are related to the carbonate system. Precipitation of calcite, CaCO<sub>3</sub>, is largely controlled by the concentration of CO<sub>3</sub><sup>2-</sup>.

The problem of origin of the ocean is associated with that of origin of not only the water itself but also of different types of ions dissolved in it.

We noted at the beginning that the ocean could not have formed owing to steam con-

densation in the earlier suggested primordial atmosphere of cosmic origin. Water is among the volatiles of our planet; naturally, its fate in the Earth's history is related to that of other volatiles. Thus a number of components now making up sedimentary rocks, atmosphere and hydrosphere are volatiles in a broad sense of the word. If we compare their amount in the modern atmosphere, hydrosphere and the whole sedimentary rock complex (stratisphere) with the quantity that could have been released following weathering and reworking of crustal crystalline igneous rocks, a large discrepancy will be obtained which can be called volatiles excess. In 1951 W.W. Rubey calculated the amount of volatiles near the Earth's surface and compared it with the amount produced by weathering of crystalline rocks. The results are shown in Table 18. We see that the volatiles excess is rather large, exceeding for some components tens and even hundreds of times the amount of volatiles produced by weathering of lithospheric bedrocks. Thus the excessive volatiles contain 83 and 60 times more carbon dioxide and chlorine, respectively, than the amount that the primordial Earth's crust could have provide on its intense destruction. This evidence suggests convincingly that the natural gases of the Earth's interior (as an excess) played an extremely great role in the generation of the principal upper shells of our planet embraced by the modern biosphere, a domain of living organisms. This role becomes even more evident if we compare the composi-

tion of the volatile excess with that of volcanic gases and the gases of igneous rocks. A correlation of respective geochemical data indicates that the composition of the volatile excess is generally similar to that of volcanic gases released by the Earth's mantle. This forms a strong foundation for one of the most important geochemical inferences—the water of the World Ocean and the gases of the atmosphere

TABLE 18. Volatile Contents Near the Earth's Surface ( $10^{20}$  g, or  $10^{14}$  metric tons)

	O <sub>2</sub>	C as CO <sub>2</sub>	Cl	N	S	H, B, Br, F
Content in modern atmosphere, hydrosphere and living matter	14 600	1.5	276	39	13	1.7
Content, in a buried state, in ancient sedimentary rocks	2 199	920	30	4.6	15	15
Total amount	16 700	921	306	43	28	16.7
A. Amount derived from igneous rock weathering	130	11	5	0.6	6	3.5
B. Volatile excess not taken into account when estimating crystalline rock weathering	16 600	910	300	42	22	13
Prevalence of volatile excess over amount of material derived from crystalline rock weathering (B/A ratio)	128	83	60	70	3.7	4

are derived from mantle degassing. This idea has gained momentum in science and is elaborated in many studies into the origin of the ocean.

It follows from the above that the history of the surface of the Earth, with prolonged degassing of its interior, was closely associated with that of subsurface volatiles. In other words, the material of the ocean and atmosphere was generated from one and the same source; therefore, the origin of the hydrosphere as such and of the atmosphere of the Earth should be discussed as a single problem. However, the composition of the volatiles excess and volcanic gases differs sharply from that of the present Earth's atmosphere.

The upper boundary of the atmosphere cannot be established precisely. The air is gradually becoming less dense with height. The atmosphere is traditionally subdivided into a troposphere, stratosphere and ionosphere. The troposphere is a zone of vigorously intermixing air masses extending from the Earth's surface to certain heights. Its height varies between 5 and 17 km depending on latitude and season. The troposphere is the thinnest at the poles and thickest at the equator. The temperature of the air decreases with height. The troposphere is overlain by the stratosphere, where air mass mixing is less intense. Above 80 km lies an extensive rarefied gas shell many of whose atoms are ionized. It is called the ionosphere and directly borders the space.

The chemical composition of dry atmospheric air at sea level is given in Table 19.

Obviously, our atmosphere is largely of a nitrogen-oxygen composition. Attention should be given to a tiny amount of inert gases, except argon, and hydrogen, which is in a sharp contrast with their extreme extension in stars, gas nebulae and the atmospheres of the outer planets.

It is accepted to single out stable and unstable air portions in the atmosphere, depending on how long either one component or other has been present in it. This subdivision

TABLE 19. Composition of Dry Atmospheric Air at Sea Level

Component	Content, vol. %	Total mass, 10 <sup>20</sup> g	Component	Content, vol. %	Total mass, 10 <sup>20</sup> g
N <sub>2</sub>	78.0900	38.648	Ne	0.0018	0.000636
O <sub>2</sub>	20.9500	11.841	He	0.00052	0.000037
Ar	0.9300	0.655	CH <sub>4</sub>	0.00015	0.000043
CO <sub>2</sub>	0.0300	0.0233			

is relative in character, for actually all the components of the atmosphere are unstable in the context of tremendous geological time intervals.

By the stability of composition, the Earth's atmosphere can be subdivided into a lower, homogeneous zone, or homosphere, and an upper, extensive inhomogeneous zone, or heterosphere. The boundary between them lies approximately at a height of 100 km. In the homosphere, the composition of air is like that shown in Table 19. The heterosphere is now

a site of several processes related to gas ionization and appearance of free atoms owing to molecule dissociation by solar radiation. Here, the percentage of light gases increases with height.

Under the action of solar ionizing irradiation, oxygen molecules dissociate and recombine at a certain height to produce ozone. Many ozone molecules form between 10 and 100 km of height, with the maximum concentration at about 20 km. Ozone generation provides absorption of most of solar ultraviolet irradiation, which is the lowest at the Earth's surface. This provides the existence of organisms as a whole, because ultraviolet radiation is damaging for them.

However, as we have already mentioned, the composition of the modern atmosphere differs from that of the volcanic gases that gave rise to it in the far geological past of the Earth, though common chemical elements are undoubtedly present. The principal cause of this difference is that the atmosphere evolved under the effect of life. Indeed, any living organism is primarily composed of carbon, oxygen, hydrogen and nitrogen, i.e. the basic chemical elements that constitute the water and air shells of our planet. Hence in their growth, feeding and breathing, all living organisms on Earth transmit through them enormous amounts of gaseous and hydrous components and are responsible for new chemical equilibria and states of matter in the atmosphere and hydrosphere. Therefore it is absolutely impossible to study and under-

stand the chemical evolution of the atmosphere and hydrosphere without taking into account the chemical activity of organisms since they have appeared on the Earth's surface.

Life on Earth is the most striking process absorbing the invigorating energy of the Sun and putting into motion and circulation probably all the chemical elements of the Mendeleev Periodic Table.

Life has been affecting the surface of our planet for billions of years. Because of this, we should pay attention to the fact that life on Earth is extremely ancient. Its oldest traces have been found and recorded in sedimentary, now slightly metamorphosed, units exceeding 3.5 billion years in age. As a consequence, modern science considers the origin of life to be a very ancient event that took place outside the survived stony record of our planet life. Moreover, a scrutiny of geochemical, palaeontological and biochemical information suggests that life on Earth is as old as the Earth itself.

Expanses of the Earth occupied by living organisms at any concentration are termed the biosphere. In other words, it is a part of space involved in life with its active chemical manifestations. The biosphere as a geological shell of the Earth was first defined by E. Suess in 1875. The modern idea of the biosphere is due to the classical Vernadsky's works on geochemistry.

The number of living organisms on the Earth (biomass) constitutes a single unity—the living matter of the planet. The biosphere

proper is the spherical space of the Earth where can exist living organisms in any concentrations possible—from single bacteria per cubic metre of air to thick tropical forests in the equatorial zone and traces of life deep in the World Ocean. In conformity with their requirements to the environment, organisms can settle in various upper horizons of the Earth; hence the actual modern biosphere includes the whole hydrosphere, the upper lithosphere and the lower atmosphere (below the ozone screen).

The living matter is negligible in mass as compared with any of the above-discussed upper shells of our planet. According to current estimates, the total amount of living matter is 2423 billion t, i.e.  $1/2100$  of the mass of the Earth's atmosphere. However, it takes the first place in the effect on the environment and qualitatively differ drastically from all other shells, in the same way as the living matter differs from lifeless.

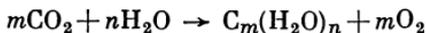
The living matter of our planet is based on compounds of carbon, which can give rise to innumerable organic compounds. In their generation, carbon is primarily combined with hydrogen and oxygen. The remaining elements in living organisms are in small amounts, despite a very important role played by some of them in physiological processes.

The abundance of the leading elements of organisms turns to be elevated, and if we remember the abundance of elements in space, it is easy to conclude that a close similarity is found in this case, except inert gases. Thus,

the living matter of our planet undoubtedly better reflects the chemical composition of space or the volatile fraction of solar matter than any other shell.

The bulk of living matter concentrates in green plants, which entrap solar energy and construct complex compounds in their bodies. This natural construction of organic compounds is called photosynthesis. It forms the basis for all the living on Earth, for plants are food for animals and are indirectly associated with all forms of life in the biosphere. On a global scale, photosynthesis is a vigorous process which involves huge masses of terrestrial material in the yearly cycle and is responsible for the high oxygen potential of the Earth's biosphere.

The principal sources of plant feeding are carbon dioxide and water. In chemical terms photosynthesis is an oxidation-reduction reaction as follows:



Thus carbon dioxide and water are absorbed to synthesize organic matter and release free oxygen. The reduction of 1 gram-molecule of carbon dioxide requires the absorption of 112 kcal of energy. Direct products of photosynthesis are carbohydrates (e.g., glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ ), but proteins are also generated, and photosynthesis is altogether of a rather complicated character.

Photosynthesis involves most of the Earth's surface: the land surface covered with plants, and the upper ocean, where live small algae

as part of plankton. According to the most recent estimates, the intensity of global-scale photosynthesis can be rendered as the amount of carbon dioxide and water consumed by terrestrial plants throughout a year. Individual kinds of matter consumed and created by photosynthesis are presented in Table 20.

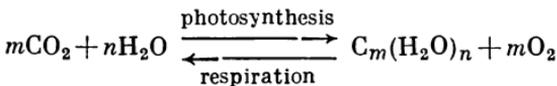
TABLE 20. Photosynthesis Productivity,  $10^9$  metric t/y

Habitat	Used and absorbed		Produced and released	
	CO <sub>2</sub>	H <sub>2</sub> O	CH <sub>2</sub> O	O <sub>2</sub>
Land	253	103.5	172.5	184
Ocean	88	36	60	64
Total	341	139.5	232.5	248

It follows from the Table that 248 billion t of O<sub>2</sub> a year are introduced into the Earth's atmosphere. All in all, about 480 billion t of matter are annually consumed by the photosynthesis of green plants, which is two orders of magnitude larger than the sum of dissolved matter that is transported into the ocean by rivers every year and approximately 28 times larger than the total amount of the material that is annually transported by rivers into the ocean. If we take into account the fact that the biosphere (atmosphere and hydrosphere) of the Earth contains  $1\,440 \times 10^{15}$  t of water,  $233 \times 10^{10}$  metric tons of carbon dioxide, and  $11.8 \times 10^{14}$  metric tons of oxygen, it is easy to calculate that during 10 million years

photosynthesis reworked the amount of water equal to the entire hydrosphere. The whole carbon dioxide of the atmosphere is absorbed during 6-7 years and the entire oxygen can be replaced by the photosynthesis-produced free oxygen during approximately 4 000 years. Taking into account that the biosphere exists for at least 3.6 billion years, the whole water of the World Ocean passed through the biogenic cycle at least 300 times and the free oxygen of the atmosphere was renewed at least 1 million times. All this suggests an enormous intensity of photosynthesis throughout the whole history of the Earth. The biogenic cycle inevitably involved also all other chemical elements that are in plants and animals.

When an organism dies, an inverse process occurs—decomposition of organic matter by oxidation, rotting, etc. to form the decomposition products. Hence the photosynthesis reaction in a general form is



This process in the Earth's biosphere implies that the biomass on Earth tends to a certain stability. Naturally, this conclusion is of relative importance. Because life is extremely intensive, however, its general extension as reflection of the reworked solar energy leads to a global equilibrium between the production of living matter and its decomposition.

The rates of organism reproduction show that the living matter of our planet is in an

extreme tension, striving to extend through a maximum of space. This tension, expressed as rates of growth and reproduction of all the organisms of the globe, is geochemically manifested in a cycle of all biophile elements introduced into the organism from the surroundings and returned back. This is the basic chemical role of the biosphere of our planet and a drastic distinction between the chemistry of the upper shells of the Earth and those of the other planets of the Solar System.

Thus the chemical evolution of the atmosphere and ocean invariably involved living organisms with the leading role played by the photosynthesis of green plants.

Back to the initial radiogenic heating of the Earth, volatiles began to escape onto the surface to form a primary ocean and an atmosphere. As follows from all the data cited here, the primordial atmosphere was similar in composition to volcanic and meteoritic gases. It may survive in the least altered state on Venus. On the whole, many sources of natural gases and vapours worked in the primordial Earth and participated in the setup of the primordial atmosphere. Each source, however, was of its own value. The greatest amount of gases and vapours was concentrated in the very body of the primordial Earth; they were caught there during the accretion of the planet itself supplemented with occlusion and adsorption from the primordial nebula. Then radiogenic heating gave rise to degassing of the Earth, the most volatile elements playing the crucial role in it. Below we present A.P. Vinogradov's

table, which lists the contents of the elements of chondrites that were degassed from the Earth (Table 21).

TABLE 21. The Content of Elements Participating in Degassing in Chondrites (after A.P. Vinogradov)

Element	Possible form of degassing	Content, wt. %
B	B(OH) <sub>3</sub> , etc.	4·10 <sup>-5</sup>
C	CH <sub>4</sub> , CO, CO <sub>2</sub>	4·10 <sup>-2</sup>
N	N <sub>2</sub> , NH <sub>3</sub>	2·10 <sup>-3</sup>
H <sub>2</sub> O	H <sub>2</sub> O, H <sub>2</sub> , O <sub>2</sub>	0.5 %
F	HF	2.8·10 <sup>-3</sup>
Cl	HCl	7·10 <sup>-3</sup>
Br	HBr	5·10 <sup>-5</sup>
I	HI	4·10 <sup>-6</sup>
S	S, H <sub>2</sub> S, SO <sub>2</sub> , etc.	1.8*
Te	Te, H <sub>2</sub> Te, etc.	5·10 <sup>-5</sup>
Ne	Inert gases of different origin	
Ar		
Kr	Ditto	n·10 <sup>-10</sup>
Xe	Ditto	

\* With due account of the troilite (sulphide) phase.

According to A.P. Vinogradov and his coworkers, who have investigated the mechanism of zone melting, the result of this process on the scale of our planet is approximately as follows. Owing to the melting and degassing of the mantle, low-melting point and volatile materials were transported onto the surface; these were mainly three fractions of mantle

material: basaltic magma, water and gasses dissolved in it.

Each basaltic outpouring supplied a definite amount of water to the Earth's surface, since the basaltic magma itself may contain up to 7 wt.% juvenile water in a vapour or liquid state. As a consequence, according to A.P. Vinogradov, the amount of basalts issued and that of juvenile water supplied to the Earth's surface were interrelated. The following gases escaped to the surface of the primordial Earth:  $H_2O$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $NH_3$ ,  $S$ ,  $H_2S$ ,  $H_3BO_3$ ,  $HCl$ ,  $HF$ , and also  $Ar$  and  $He$ . These gases constituted the primordial atmosphere of our planet, although their relative proportions can hardly be disclosed reliably and precisely enough. Hydrogen and carbon dioxide took the first place. If the temperature at the Earth's surface exceeded  $100^\circ C$ , water was in a vapour state in the atmosphere for some time.

The World Ocean was derived from steam coming from the mantle, and the first batches of condensed water on Earth were acid. They contained the anions now also present in sea water, except for  $SO_4^{2-}$ .

It follows inevitably that the initial juvenile waters on the Earth's surface were mineralized, whereas the fresh water proper appeared much later as a result of evaporation (natural distillation) from the surface of the primary oceans, as well as owing to the formation of closed basins on land.

The strong acids in juvenile waters rapidly destroyed primary aluminosilicate rocks, ex-

tracting from them the alkali and alkali-earth metals: Na, K, Rb, Cs, Mg, Ca and Sr, as well as, quite intensely, salts of ferrous iron. The primary land surface was washed by acid rains and was a site of vigorous hydrolysis and hydration of the first-produced minerals. The same processes, but on a different scale, occurred on the ocean floor. In water cycle and removal of the cations Na, K, Mg and Ca, a greater part of them remained in the ocean. Hence we can consider that most of the cations of ocean water are the products of chemical weathering from solid rocks of the primordial lithosphere.

The primordial atmosphere of the Earth was reduced in character and was essentially depleted in free oxygen; only its insignificant part was affected by solar rays as a result of H<sub>2</sub>O steam photodissociation in the upper atmosphere.

On the whole, it is now difficult to restore the amount of gases in the primordial atmosphere of the Earth. However, some qualitative alterations experienced by that atmosphere because of life and photosynthesis can be traced in geological history, when the primordial atmosphere was transformed into the modern nitrogen-oxygen one. The primordial Earth's atmosphere may have been similar, to some extent, to the present atmosphere of Venus, nearest in size to the Earth. The atmospheres of the Earth and Venus are compared in Table 22.

The appearance of life on Earth, and largely the photosynthesis of primitive green

plants, affected most intensely the chemical composition of the primordial atmosphere. The first photosynthesizing organisms were

TABLE 22. Comparison of the Atmospheres of the Earth and Venus

Component	Earth		Venus at present
	at present	initially *	
N <sub>2</sub> , %	78	1.5	1.8
O <sub>2</sub> , %	21	Traces	Traces
Ar, 10 <sup>-6</sup> , %	9 000	190	200
CO <sub>2</sub> , %	0.03	98	98
H <sub>2</sub> O, km	3	3	Traces
Pressure, bars	1	70**	88 ± 3

\* Neither photosynthesis nor carbonates are present on the Earth.

\*\* For crustal carbon (abundance  $9 \times 10^{22}$  g).

probably blue-green algae or their ancestors that appeared at a certain depth in the upper ocean. This depth was controlled by the water layer that absorbed the ultraviolet radiation of the Sun, thus protecting the organisms from the damaging effect.

The main components of the modern Earth's atmosphere are N, O, CO<sub>2</sub>, and Ar. We describe in short the history of their generation.

*Nitrogen* was found long ago in volcanic gases and igneous rocks. On heating these rocks and meteorites, nitrogen is released as

both molecules and  $\text{NH}_3$ . There has been found  $\text{NH}_4\text{Cl}$  in volcanic gases, especially in those escaping in the final stages of eruption. Therefore, ammonia may have been derived from nitrogen and hydrogen in the primordial mantle owing to chemical reactions on heating. It is difficult, however, to expect substantial accumulation of ammonia in the primordial Earth's atmosphere. The ammonia was oxidized to  $\text{N}_2$  in the upper atmosphere by oxygen released in the course of photodissociation of water vapours and other compounds.

Free *oxygen* originated initially in very little quantities owing to photodecomposition of carbon dioxide, carbon oxide and water in the upper atmosphere. But the little amount of oxygen was rapidly consumed to oxidize other gases. All had changed with the appearance of photosynthesizing organisms in the ocean. The amount of free oxygen began to increase, steadily, with an active oxidation of many substances in the environment (Fig. 28). Thus free oxygen rapidly oxidized  $\text{NH}_3$ ,  $\text{CH}_4$  and  $\text{CO}$ , while the sulphur dioxides— $\text{S}$  and  $\text{H}_2\text{S}$ —were converted to the sulphates of ocean water. Till the accumulation of considerable amount of free oxygen in the atmosphere, it also actively became to oxidize many materials at the land surface, in particular promoted the transition of ferrous to ferric iron and sulphides into sulphates. Hence the first batches of photosynthetic oxygen were scanty in the atmosphere. A.P. Vinogradov's study of the isotopic history of atmospheric oxygen has shown that free oxygen was largely

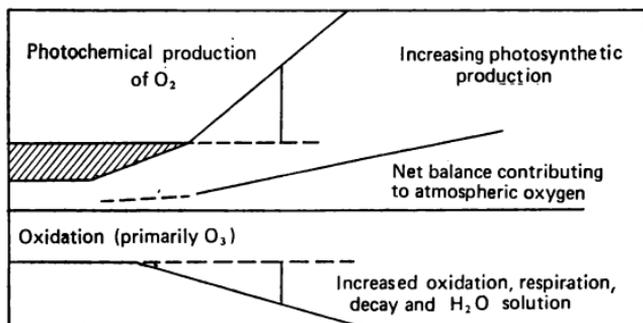


Fig. 28. Factors of early oxygen balance (after L. V. Berkner and I. C. Marshall, 1984)

derived from photosynthetic water decomposition. In the final analysis, the amount of free oxygen in the atmosphere had reached a certain level to become equal to the amount of absorbed oxygen. A relatively constant free oxygen content set up in the atmosphere. According to H.D. Holland, the overall balance of oxygen production and consumption at the Earth's surface is as follows:

Total oxygen production, in $10^{20}$ g.	
Photosynthesis-derived oxygen	181
Steam protodissociation-derived oxygen	1
	<hr/> 182
Modern distribution of oxygen released	
Free atmospheric oxygen	12
Consumption for oxidation into ferric iron	14
Consumption for oxidation into volcanic gases:	
Oxidation of CO to CO <sub>2</sub>	15
Oxidation of SO <sub>2</sub> to SO <sub>3</sub>	8
Oxidation H <sub>2</sub> to H <sub>2</sub> O	140
	<hr/> 189

*Carbon.* Both in the past and at present,

most of the atmospheric carbon occurred in  $\text{CO}_2$  and, much less,  $\text{CH}_4$ . In volcanic gases, carbon also occurs mostly in  $\text{CO}_2$  and, in lesser quantities,  $\text{CO}$  and  $\text{CH}_4$ . During mantle degassing, these gases copiously escaped from the body of the planet. The methane concentration, however, may have been relatively low, not more than the methane content of volcanic gases. From the start of photosynthesis, carbon dioxide was rapidly consumed by plants and also chemically fixed in carbonate sediments. Carbon monoxide was oxidized to carbon dioxide, and methane in the oxygen environment was practically oxidized completely. The whole activity of photosynthesizing organisms was directed at intense removal of carbon dioxide from the atmosphere.

The geochemical history of carbon in the biosphere started with its input into the atmosphere as  $\text{CO}_2$  and  $\text{CO}$  from deep in the mantle as a result of its degassing due to volcanism. The overall carbon cycle in the biosphere is shown in Fig. 29. Carbon dioxide was distributed in the biosphere to form a complex carbonate system in the hydrosphere. As  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were leached from the primordial Earth's crust and introduced in the ocean, carbon dioxide precipitated in the form of carbonates—dolomites and limestones. The other part of carbon dioxide was consumed by photosynthesis to produce organic matter, later experiencing varying transformations, among them generation of buried organic matter and then different types of coal, as well as oil shales and petroleum.

The stable isotopes  $^{12}\text{C}$  and  $^{13}\text{C}$  were being partitioned in the course of the carbon cycle in the Earth's biosphere. Thus, an isotopic

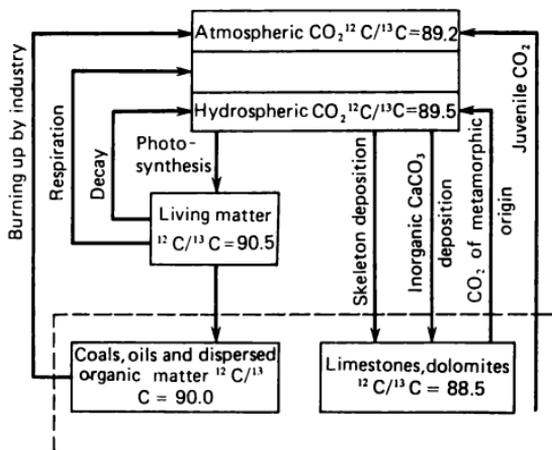
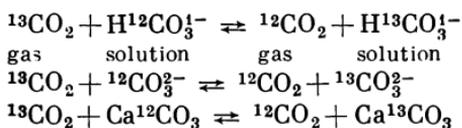


Fig. 29. Carbon cycle in the Earth's biosphere

exchange set up by the following reactions in the carbonate system of the hydrosphere:



In these reactions, isotopic equilibria shift to the right; as a result, marine carbonates acquire the highest amounts of  $^{13}\text{C}$ , which is typical of the calcitic and aragonitic skeletons of marine animals. Hence, the ratio of these two isotopes,  $^{12}\text{C}/^{13}\text{C}$ , is the lowest, 88.5 on the average, for marine carbonates. In contrast, in the course of photosynthesis the

percentage of  $^{13}\text{C}$  decreases because the rate of absorption of  $^{12}\text{CO}_2$  molecules is higher than that of  $^{13}\text{CO}_2$ . An elevated  $^{12}\text{C}/^{13}\text{C}$ —some 90-91 and higher—is observed in plants and their derivatives.

Thus, different carbon isotopes have concentrated in the different compounds of the Earth's biosphere as the result of a prolonged geochemical carbon cycle.

*Argon.* The argon in the Earth's atmosphere is mostly of radiogenic. In particular, this is verified by the fact that it contains here 99.6 per cent  $^{40}\text{Ar}$  while  $^{36}\text{Ar}$  predominates in the usual cosmic argon. The radiogenic argon have long been originating in the mantle by way of a  $^{40}\text{K}$  decay by electronic capture and escaped into the atmosphere during overall degassing of the planet. A similar history is characteristic also of other radiogenic gases, helium in particular. However, as P. Diamond and J.L. Kulp have shown, argon and helium are now predominantly concentrating in the Earth's crust and are introduced in the atmosphere in relatively small amounts. The input of both gases is so insignificant that it could not provide their observed concentration during  $4.6 \times 10^9$  years. One can assume, therefore, that most argon came from deep in the Earth early in its history and much less of it has been added since then owing to rock weathering and volcanism.

The appearance of free oxygen as a photosynthetic product was also responsible for changes in the ocean. The relative proportions of individual parts of the carbonate system

had changed in marine water—sulphur and its compounds had oxidized to form sulphates. This happened very long ago, taking account of traces of photosynthesizing organisms and direct products of photosynthesis in the Precambrian sediments, apparently more than 3.5 billion years ago, in South Africa. Knowing that organisms can generally reproduce themselves and extend rapidly owing to the intensity of photosynthesis, one can assume that the drastic change in the composition of the Earth's atmosphere occurred relatively rapidly on a geological time scale.

Naturally, the degassing of the Earth was most intense very early in its history, when radioactive elements and core formation gave rise to its heating; then the degassing became less intense, but renewed in mobile crustal zones, namely in volcanoes born in mountain belts during orogenic epochs. The composition of the Earth's atmosphere was to a larger extent controlled by the temperature of the Earth's surface.

Therefore, as we can judge from geochemical evidence, unfortunately very scanty, the atmosphere undergoes very slow changes in its chemical composition under the influence of various physical, chemical, and biological factors.

## Principal Trends in the Chemical Changes in the Earth's Crust and Biosphere

The Earth's crust emerged initially as the upper layer of the solid Earth owing to melting-out of mantle material; it has then been reworked substantially by atmosphere, water and living organisms. At present the crust is the upper geosphere with a very complex geological structure and extremely variable composition at some localities, with the resulting variety of relevant rocks and valuable minerals.

The material of the Earth's interior has been reworked and chemically altered at the surface from times immemorial. The first batches of volcanic material were basaltic or the like. Ascending to the surface, the basaltic magma lost gases, which escaped into the atmosphere to become a basaltic lava that spread over the primary surface of the planet. On cooling, it was converted to solid sheets of a primordial ocean-type crust. However, the melting-out of aluminosilicate masses enriched with silica and volatiles appears to have been asymmetric, and their amount is larger in one hemisphere than in the other. In the regions of would-be continents, the young crust was unstable and rose and subsided owing to internal causes whose nature is still very little studied. During the overall oscillatory movements (up and down), parts of the primordial

crust occasionally rose above sea level and underwent destruction by the chemically active gases of the primordial atmosphere, water and other physical agents. The destruction products were transported to lows in land and to water reservoirs to form sedimentary rocks whose particles are mechanically sorted by size and mineral composition. Feldspars gave rise to first clays, magnesium and iron were removed from ferromagnesian silicates into the ocean, and silicon was a source of siliceous sediments—fine-dispersed colloid sediments and coarse-grained sands containing fragments of chemically unaltered minerals and rocks.

Let us discuss, in somewhat more detail, the transition of igneous rocks to sedimentary rocks.

Bedrock changed at the land surface under the action of various geological agents. The biosphere is the most active site of these changes. A totality of rock changes on the surface of continents (they are directly or indirectly associated with living matter) is called weathering. The products of weathering are frequently new minerals, which are then incorporated into new rocks of sedimentary origin. Weathering of fresh igneous rocks and then partition of weathering products in the course of transport and deposition under varying physicochemical conditions make a colossal work on redistribution of chemical elements. As a result, the elements in sedimentary rocks concentrate in mineral associations other than those in igneous rocks. The alteration of principal components of different sedimentary

rock types can be figured out if we compare the data given in Table 23. The transition of principal elements into new mineral species

TABLE 23. Chemical Composition of Sedimentary Rocks

Oxide	Average igneous rock	Clay	Sandstone	Limestone	Average sedimentary rock
SiO <sub>2</sub>	59.14	58.10	78.33	5.19	57.95
TiO <sub>2</sub>	1.05	0.65	0.25	—	0.57
Al <sub>2</sub> O <sub>3</sub>	15.34	15.40	4.77	—	13.39
Fe <sub>2</sub> O <sub>3</sub>	3.08	4.02	1.07	—	3.47
FeO	3.80	2.45	0.30	—	2.08
MgO	3.49	2.44	1.16	7.89	2.65
CaO	5.08	3.11	5.50	42.57	5.89
Na <sub>2</sub> O	3.84	1.30	0.45	0.05	1.13
K <sub>2</sub> O	3.13	3.24	1.31	0.33	2.86
H <sub>2</sub> O	1.15	5.00	1.63	0.77	3.23
P <sub>2</sub> O <sub>5</sub>	0.30	0.17	0.08	0.04	0.13
CO <sub>2</sub>	0.10	2.63	5.03	41.54	5.38
SO <sub>3</sub>	—	0.64	0.07	0.05	0.54
BaO	0.06	0.05	0.05	—	—
C <sub>org</sub>	—	0.80	—	—	0.66

in the formation of sedimentary rocks depends on the stability of rock-forming minerals during chemical weathering. Thus the most resistant minerals of igneous rocks which are preserved in sedimentary rocks are quartz, magnetite and, to some extent, micas and feldspars. The feldspars are mostly transformed, however, into clay minerals (kaolinite, etc.).

As seen from Table 23, the mean igneous rock, which in general corresponds to granite, differs but little in its principal components

from the mean sedimentary rock; therefore, intense metamorphism and melting of sedimentary strata produce crystalline rocks similar in composition to granite and granite gneiss. On the whole, the sodium and magnesium contents of the Earth's sedimentary shell are lower because much of these elements are transported to the World Ocean and remain there. The enhanced contents of  $\text{CO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$  and  $\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3/\text{FeO} > 1$  in sedimentary rocks is due to the fact that their substantial part is formed with the involvement of atmospheric and hydrospheric carbon dioxide, and atmospheric free oxygen which oxidizes iron to a ferric state and sulphur to a trioxide.

In the distant past of the crustal history, with an alternation of oscillatory geological movements, uplift became prominent in one of the hemispheres; its manifestation was relatively long-term existence of land expanses. Nuclei of the first continents emerged, which then began to build up at the expense of belts of thick sedimentary series produced by demolition of the elevated tracts of land. These belts were later folded and raised. Ancient mountain chains grew about the nuclei of continents, and they were later also demolished by external geological agents. However, this process progressed quite unevenly on different continents, and the most ancient segments of the Earth's crust occur in their different parts. This was the way by which, in general, the continental part of the Earth's crust was formed.

The oceanic crust rarely, if at all, emerged above the level of the World Ocean, at least during the early geological periods, and it could not be a site of rapid differentiation of matter, including transport, sorting and deposition of thick and diverse sedimentary rocks.

The Earth's crust evolved chemically by way of a permanent geochemical cycle associated with the formation of sedimentary, metamorphic and igneous rocks as physico-chemical systems with either gradual or discontinuous transitions between them. The geochemical element cycle was especially intensive in the continental hemisphere of the Earth, where thick sediments were accumulated. The bulk of the granites of the continental hemisphere was derived from granitization of these ancient sedimentary series with their intensive metamorphism and melting during their subsidence to depths with high temperatures.

It should be borne in mind that the Earth's crust has progressed to its present state during an extremely long period of time, hence its initial appearance has completely changed.

The geological history was studied quite unevenly on the basis of rocks of different compositions, origins and ages. In this respect it can be subdivided into the Cryptozoic (a long interval in the history of the Earth with a concealed development of organic life) and Phanerozoic (a much shorter time interval distinguished by prolific plant and animal remains as fossils of varying types and charac-

ters). The latter, or aeon, embraces three geological eras: the Paleozoic, Mesozoic and Cainozoic. The general geochronology of the Earth is shown in Fig. 30 (the duration of geological eras and periods is laid in the spiral coils). On the whole, the stony chronicle of the geological history of the Earth is a rather dilapidated book from which all prefaces and at least one third of the initial pages were torn out (pages have survived only in its last part). The last part describes approximately one ninth of the whole period of existence of the planet.

The most common chemical elements of the upper Earth—O, Si, Al, Fe, etc.—are the main builders of the Earth's crust participating in the gross cycle of matter: igneous rock → sedimentary rock → metamorphic rock → melting to form a new magma (Fig. 31). It was first developed by I.D. Lushchikov (1863-1928) in his teaching of metamorphism. This view expressed the idea of a great circulation of matter in the upper horizons of our planet embracing rock masses of different origin. This teaching was later elaborated by V.I. Vernadsky, USSR, and T. Barth, Norway. Concerning the Earth's crust, V.I. Vernadsky writes that most of the crustal material is in constant motion (migration) and forms reversible closed cycles which always regenerate and are identical (geochemical cycles). They are renewed at the surface by solar energy absorbed by living matter and in the interior by atomic energy produced by radioactive decay.

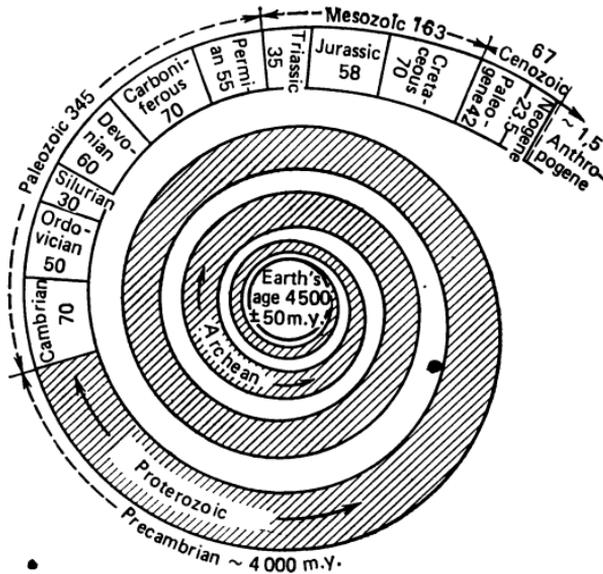


Fig. 30. Geochronological scale of the Earth's history

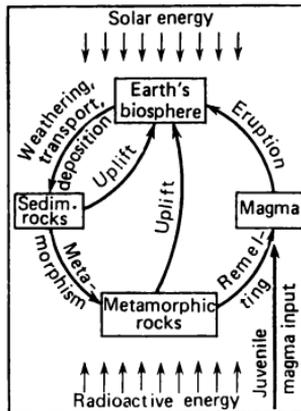


Fig. 31. Major cycle of material in the Earth's crust

The geochemical cycle implies, of course, that lighter molecules, radicals and atoms pass shorter ways and spend less time for their motion than heavier ones. Thus the mobile gas components of the atmosphere, and water experience the fastest cycle. A much slower cycle is characteristic of continental matter. The time required for a full cycle of matter is 7 years for atmospheric carbon dioxide; 4 000 years, through photosynthesis, for atmospheric oxygen; approximately 1 million years for ocean water by way of evaporation; and 80-100 million years for continental matter by way of weathering and removal from the land surface. It is quite evident, therefore, that if no long-term uplifts had occurred in the continental hemisphere, all land would have been worn away and removed into the ocean throughout several geological periods and our planet would have been covered by a continuous water shell. At present, the ocean is 12 times as large as land. The average height of land above sea level is equal to 825 m, and the average depth of the World Ocean, 3 800 m, as seen on the hypsographic curve shown in Fig. 32. Then it follows that the whole modern land reflects a relative balance between its formation by means of uplift and its destruction by removal with external geological agents.

According to T. Barth, the composition of the ocean is at a relative dynamic equilibrium, as evidenced by its constant salt composition. This also implies that the material of sediments laid down in the oceanic

environment returns from sea to continent at the same rate at which the weathering products are transported from continent to sea. Consequently, the average chemical composition of continental rocks must be similar to that of sedimentary rocks.

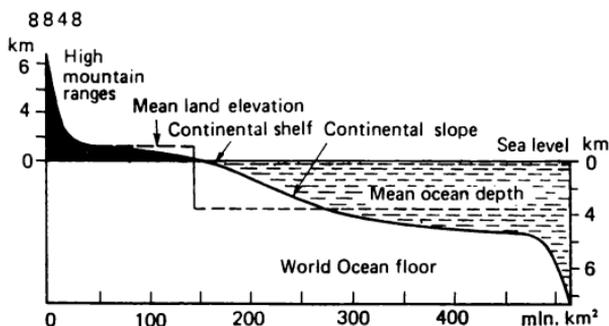


Fig. 32. Hypsographic curve depicting relative areas of the Earth's surface at levels ranging from the highest peaks to the deepest oceanic abysses

The cycle of weathering products involved the marine medium (Fig. 33). The high concentrations of sodium and, to some extent, magnesium in ocean water are due to the fact that they remain in the ocean longer than any other rock-forming element.

According to A. Poldervaart, sedimentary rocks constitute now 6% of the continental crustal mass. In 1966, M. Horn and J. Adams calculated a geochemical balance of elements throughout the geological history and came to the conclusion that the total mass of material weathered and redeposited during that time is equal to  $2 \times 10^{18}$  metric tons.

The mass of the Earth's crust being equal to  $25 \times 10^{18}$  metric tons, nearly 8% of the whole crust were transformed at different times into sedimentary rocks. Other investigations, carried out by K. Rankama and T. Barth (1965), indicate that nearly the whole continental crust has passed through

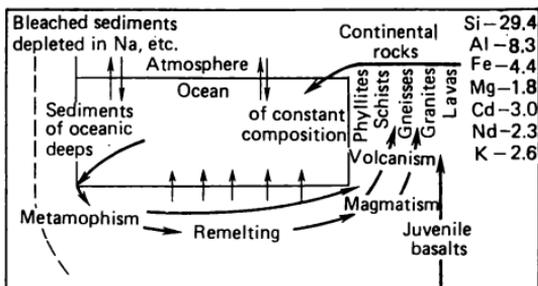


Fig. 33. A complete geochemical cycle. The average composition of continental rocks in the upper right corner corresponds to the middle one of the ancient sediments from geosynclinal troughs (modified from T. Barth)

the weathering zone during 3.5 billion years. In any case, the amount of sedimentary rocks generated throughout the crustal history is enormous. The bulk of these sedimentary rocks (predominantly ancient, Precambrian) has, however, undergone strong metamorphism and melting. Therefore, much of the ancient sedimentary series look like metamorphic and igneous rocks.

It should be noted that the presence of water in pores of sedimentary rocks and in

other forms decreases their melting point at depth and promotes their conversion to magma. Experiments show that water-rich shales melt under 2 kbars to produce magma even at 600 °C. The finely dispersed material of clayey sediments is highly favourable for melting, if they have the appropriate composition, already at 570-580 °C. We believe, therefore, that granite magma may form by way of melting of sedimentary rocks at a depth interval of 10-15 km.

V.I. Vernadsky considered the granitic layer of the Earth's crust to be a segment of the past biospheres. Modern geochemical evidence invariably supports this view. Hence a small, on the whole, proportion of sedimentary rocks in the Earth's crust can be regarded as the part of the sedimentary shell (stratisphere) that has survived metamorphism and granitization in the past geological epochs.

To better understand the basic tendencies in the chemical evolution of the Earth's crust, we shortly discuss the geochemistry of the leading lithospheric elements, silicon and iron, and also the geochemical role of living matter, which has been rising throughout the Earth's history.

*Silicon.* Tetravalent silicon reacts with four oxygen anions to form the complex anion  $[\text{SiO}_4]^{4-}$ , which produces, in different combinations, the whole number of crystallochemical structures that constitute almost all rock-forming minerals. Silicon plus oxygen (silicon as a component) composes 55 per cent by weight of the Earth's crust. Silicon forms

more than 430 mineral species, largely silicates. The silicates are the basic constituents of igneous and metamorphic rocks, except marbles and crystalline limestones, and clayey sediments. Throughout its geochemical history, silicon is practically never divorced with oxygen and migrates together with it. Of extremely high importance for the chemistry of the Earth's crust is silicon oxide, which occurs in various polymorphic modifications, most commonly in quartz.

As magma cools, silicon-oxygen tetrahedra  $[\text{SiO}_4]^{4-}$  combine together. The order of crystallization of silicate minerals begins with the connection of these tetrahedra with magnesium and iron ions in olivines  $(\text{Mg, Fe})_2\text{SiO}_4$ . Then come metasilicate chains  $[\text{SiO}_3]_n^{2n-}$  of pyroxenes, and then even more complex radicals  $[\text{Si}_4\text{O}_{11}]_n^{6n-}$  of amphiboles. Silica,  $\text{Si}_n\text{O}_{2n}$ , in the form of quartz precipitates at the close of magma crystallization. At the same time, the water content of residual melts also rises. As a result, mineralized thermal solutions are formed; they remove dissolved silica, which later precipitates in the form of quartz veins of different size and also silicification of adjacent country rocks, often extensively, takes place. Quartz is the principal rock-forming mineral in many lodes.

When rocks are weathered in a moderately humid climate, quartz remains insoluble while the silica of decomposed silicates is removed by streams more rapidly. Silica removal increases drastically in a humid tropical climate.

In the water cycle, subsurface waters and rivers that drain land remove enormous amounts of silica as suspended clay particles, fragments of aluminosilicates and solutions. In sea water, much of the coarse-grained material precipitates not far from seashore to produce so-called terrigenous sediments. A complex silica migration takes place in the ocean water itself. The bulk of it is rapidly taken up by microorganisms in the upper layers of the ocean. Thus, diatomic algae extract 70-80 per cent of silica from water. Common radiolaria, sponges and some corals also have silicon skeletons. When diatomic algae die, they slowly settle down and gradually dissolve between 2 000 and 2 500 metres of depth. The silicon again is transferred into dissolved form. The undissolved part of silicon is deposited on the floor to form extensive sediments of diatomic muds in the cold seas.

The sedimentary rocks of varying geological age contain silica as quartz derived from mechanical destruction of quartz-bearing intrusive rocks. The generation of pure quartz sediments is related to the intensity of weathering and rewashing of primary material. Pure quartz sands and sandstones are rarely found. They mostly contain some feldspars and other minerals. Enormous masses of silicon precipitated in a colloidal state as diverse clay minerals.

The relative proportions of silica migration forms varied in the geological past. In the Precambrian seas, rhythmic alternation of sediments of fine-dispersed silica and iron com-

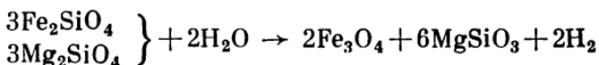
pounds occurred in many places. In this way there deposited banded iron formations which were nowhere found in rock sequences younger than Precambrian. According to Soviet geologists, the purely inorganic migration of silica in the deep Precambrian, had given way to migration with the participation of living organisms which built their silica skeletons more and more efficiently.

*Iron* takes the second place, after aluminium, among the metals concerning its abundance in the Earth's crust. Iron settled down in different geological epochs to give rise to giant deposits whose reserves exceed greatly the known reserves of all other metals taken together.

Iron is a very vivid indicator. It reacts on the physicochemical aspect of the environment by changing its valence. Iron becomes ferric in oxygen-rich solutions to form relatively insoluble oxides and hydroxides.

Among igneous rocks, ultrabasic rocks are most enriched with iron (up to 10%), while acid rocks (granites) are poorest (2-3%). In biosphere iron changes its valence depending on the environment. It occurs in minerals as ferrous and ferric ions. Iron is a chemically active metal that forms over 300 mineral species in the Earth's crust. The iron compounds best characteristic of the biosphere are those with oxygen, such as hematite,  $\text{Fe}_2\text{O}_3$ ; magnetite,  $\text{Fe}_3\text{O}_4$ ; and goethite,  $\text{FeO}(\text{OH})$ . In igneous rocks, the iron is mostly in ferromagnesian silicates, partially in the sulphides: pyrrhotite,  $\text{Fe}_7\text{S}_8$ , and pyrite,  $\text{FeS}_2$ .

The migration and forms of iron occurrence in igneous rocks depend on oxidation processes. In basic and ultrabasic rocks, iron is predominantly ferrous (FeO). Ferric iron originates during oxidation in the upper layers of the lithosphere, a factor of oxidation being water or steam. According to V.M. Goldschmidt, the formation of magnetite on magma cooling is related to water absorption by magma, which is responsible for the following chemical reaction:



Obviously, this reaction produces free hydrogen, which is actually observed in volcanic gases.

During rock weathering, iron sulphides and silicates with ferrous iron are easily oxidized. Magnetite is much more stable. Ferrous iron dissolves easier than ferric iron. Oxidation in natural water reservoirs leads to precipitation of ferric ores. Thus bog iron ores and ferric iron-bearing marine sediments are formed.

Enormous amounts of iron are introduced in the sea owing to weathering and water cycle. It is transported in the form of mineral and rock fragments, colloids, and dissolved compounds. Little iron ( $1 \times 10^{-6}\%$ ) is contained in the marine water itself, which is due to a poor solubility of its oxidized compounds.

One can distinguish in natural water reservoirs the principal reagents that promote

precipitation of iron minerals; these are  $O_2$ ,  $CO_2$ , and  $H_2S$ . Accordingly, ferric iron, and iron carbonate (siderite) and sulphide are laid down.

Huge iron masses have been gradually oxidized throughout the geological history. Thus, whereas ferrous iron is thrice as much as ferric iron in common early Precambrian sedimentary rocks, their amounts are commensurate in the late Precambrian and ferric iron exceeds in amount ferrous iron in Paleozoic rocks. Therefore, ferric iron has been continuously increasing in content with passing geological time while ferrous iron decreasing in sedimentary units under the effect of free biospheric oxygen.

The concentration of iron in sedimentary series is highest in the Precambrian iron formations, which gave rise to iron ore deposits (Krivoi Rog and Kursk Magnetic Anomaly, USSR; Lake Superior, USA and Canada; Minas-Gerais, Brazil; Hamersley, Australia; etc.). Most of these formations have been metamorphosed. However, poorly metamorphosed varieties have also been preserved, so the initial sedimentation environment can be reconstructed. Thus we can observe in them iron sulphides, carbonates, silicates and oxides alternating with finely dispersed silica to form banded ferruginous rocks (jaspilites) and ores.

*Living matter.* During crustal evolution, the role of living organisms has been increasing steadily, primarily affecting sedimentation and ore deposition. The problems con-

nected with these processes were discussed by E.A. Boichenko et al. in 1967-68; they assessed the possibilities of plants to concentrate various chemical elements throughout the biosphere history of the Earth. Of large importance in this process was the capability of living organisms to concentrate certain elements to values many times higher than those in the environment. V.I. Vernadsky called this capability the concentration function. If the environment is taken to be sea water, then the silicon concentration in marine plants is  $10^3$ - $10^5$  times, phosphorus  $10^5$  times and manganese  $10^3$ - $10^4$  times higher than that in sea water. In plant cells many metals form complex compounds with different anion groups. The contents of these metals in plants are tens and hundred thousands of times higher than in the environment. The concentration is especially great for the following metals of the transition groups of Mendeleev's Periodic Table: Ti, Cr, Mn, Fe, Co and Ni. Quite naturally, after plant death most of the elements, that had been concentrated in them, entered into various sediments to participate in the formation of mineral deposits. According to Vernadsky, enormous amounts of metals accumulated by bacteria and other lower plants could have easily become a source of sedimentary ores.

According to Boichenko, a succession of the concentration functions because of the evolution of the organisms themselves can be distinguished. Thus, it is assumed that organisms first appeared in the ocean. They devel-

oped through oxidation of abiogenic organic matter. A break should have set up after spending the reserves of organic matter, namely transition to an autotrophic development by using light energy (photosynthesis). This transition was accompanied by greater concentration of Al, Si, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo and other elements.

The life development on Earth has undoubtedly greatly changed the migration of chemical elements in the biosphere. Studies have been started into the many-sided relations between the evolution of organisms on our planet and ore deposition in sedimentary rocks in the past. It should be noted that the amount of biological mass has been increasing steadily since life origin. The first living organisms developed in the sea; these were apparently planktonic microalgae in the sunlit horizons of sea water, near the very surface. Later on, benthonic marine forms appeared in the relatively nearshore, shallow-water zone. From here, deeper and deeper levels of sea floor were colonized. Later, the spreading of living matter also occurred landward after the increased free oxygen production had resulted in the creation of an ozone screen, which protects the organisms from the damaging ultraviolet radiation of the Sun. Land vegetation started to develop in the humid belts of the ancient continents, and it then began to conquer other, less humid climatic zones.

The total amount of the present-day mass of living matter in the Earth's biosphere is

equal to 2 420 billion t. The Soviet investigators N.I. Bazilevich, L.E. Rodin and N.N. Rozov (1971) present the distribution of this mass in Table 24.

TABLE 24. Biomass of Organisms on the Earth

Habitat	Group of organisms	Mass, metric tons	Percentage
Continents	Green plants	$2\ 40 \cdot 10^9$	99.2
	Animals and microorganisms	$20 \cdot 10^9$	0.8
	Total	$2\ 420 \cdot 10^9$	100.0
Ocean	Green plants	$0.2 \cdot 10^9$	6.3
	Animals and microorganisms	$3.0 \cdot 10^9$	93.7
	Total	$3.2 \cdot 10^9$	100.0
Total amount		$2\ 4232 \cdot 10^9$	

An analysis of geochemical, biochemical and paleontological evidence on the survived parts of the Earth's crust leads to the conclusion that we are still within the biosphere in getting knowledge of the most ancient epochs in the Earth's history. The biosphere was the site of evolution of living organisms, with the production of countless kinds of plants and animals. V.I. Vernadsky thought that the mass of living matter has remained constant throughout the geological history. At present, however, V.I. Vernadsky's conclusion cannot be accepted without reservations. The general distribution of life, its extreme tension as the reflection of the reworked energy of the Sun rays lead to the onset of a global equilibrium between the natural production of living

matter and its decomposition. Therefore, it is now more correct to speak of the biomass tending to remain constant in amount in certain, maybe even prolonged intervals of geological time.

The appearance of life on the land was of large importance for the history of the biosphere. As seen from the Table, the biomass on land now substantially surpasses that in the World Ocean. Since the life conditions are more favourable in ocean, it can be shown that the whole hydrosphere was distinguished by a relative constancy of biomass throughout its existence. In this particular case, the total amount of biomass was controlled by the area of the surface of the World Ocean, which was probably variable and depended on the geological evolution of the Earth's crust.

Life passed on to the surface of continents in the Devonian period of the Paleozoic era. It follows from Table 24 that, as a result, the mass of living matter has grown by almost 800 times. Naturally, so substantial increase of biomass has greatly affected the geochemical processes in the Earth's biosphere.

In M.I. Budyko and A.B. Ronov's (1979) opinion, the dependence of the total mass of living matter on carbon dioxide content has existed all the time within the biosphere. As the biomass was rising, the rate of photosynthesis increased. Hence the suggestion that in the geological periods of the Phanerozoic in which the carbon dioxide concentration was higher than now because of vigorous vol-

canic activity, the mass of vegetation cover must have also exceeded the present-day values. In other words, the changes in the concentration of carbon dioxide may have been accompanied by the changes in the whole mass of living organisms on our planet.

A.B. Ronov (1980) noted that the amount of carbonate sedimentary rocks in the Phanerozoic sections may reflect the carbon dioxide content of biosphere in the relevant periods. Since the fate of carbon dioxide is also connected with the history of free oxygen through photosynthesis, limestone sediments, of course, also reflect the changes in composition of the Earth's atmosphere as a whole.

On the death of organisms in the past, organic matter was buried in both a disseminated state, in various finely dispersed sediments, and a concentrated form to produce rocks rich in organic matter, coals and oil shales. The amount of disseminated organic matter exceeds greatly that concentrated in all known fossil fuel deposits. Thus, according to R. Lawson, the Precambrian Grenville Formation in North America contains more carbon than all coal fields in the world. According to A.B. Ronov's more recent calculations, the amount of disseminated organic carbon is, on the average, approximately 200 times higher than that in all large fossil fuel deposits.

## The Chemical Evolution of the Earth's Crust

We characterize the main trends in the evolution of the crust, with due account of its overall dynamics.

Once the biosphere started to form, sedimentary rocks were deposited in it. This process was closely related to changes in the atmosphere and hydrosphere. The stony records of the geological chronicle provide information on the sequence of chemical and petrographic changes in the Earth's sedimentary shell.

Studies into the composition of ancient sedimentary rocks of different ages have revealed the principal trends in their evolution under the effect of life in the biosphere. The most fundamental investigations in the field of the theory of formation of sedimentary rocks (theory of lithogenesis) were conducted by the Soviet scientists N.M. Strakhov, A.B. Ronov and others. In his summarizing publications on lithogenesis theory, N.M. Strakhov distinguished four stages of chemical-biogenic sedimentation.

The first stage is barely to be restored completely enough, for it encompasses the earliest history of our planet. Various reconstructions of the oldest stage of sedimentation invariably speculative and are based on general physico-chemical considerations. Thus the landscape of the first land expanses was a typical volcanic one. Numerous craters were formed owing to intensive impacts of asteroid fluxes, and

the landscape was in this respect similar to the present-day lunar one. The extensive, relatively flat-lying tracts between volcanoes were covered by a shallow ocean. Volcanic chains emerged as islands. In a humid climate, the volcano-sedimentary type of sedimentation prevailed at that time. No climatic belts similar to the modern ones existed on Earth.

As there was a plenty of carbon dioxide in the atmosphere, igneous rocks were weathered with the formation of K, Na, Ca and Mg carbonates and colloidal particles of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . On introduction in the acid ocean water, the carbonates reacted with free acids to produce K, Na, Mg and Ca chlorides.

As a result, the composition of the primary ocean underwent changes. The solution of the strong acids HCl and HF was being replaced by solutions of Ca, Mg, Al and Fe chlorides. A distinctive feature of this water was its enrichment with aluminium, iron and other heavy metal chlorides.

The character of primary sediments early in lithogenesis is difficult to establish reliably enough. The constituent parts of the Earth's crust were lavas and masses of loose volcanic ash. This material was weathered to give rise to terrigenous (mechanical) sediments. Silica was transported and precipitated chemically. Since copious hydrogen sulphide was present in sea water, sulphides of heavy metals may have been laid down. Iron and manganese precipitated, if at all, as ferrous and manganous forms, respectively. No calcium and magnesium carbonates and sulphates, and

evaporites, such as rock salt, were deposited. The duration of the early stage in the development of the Earth's geospheres is completely unknown; obviously, it was short because the life on the Earth originated very long ago and has severely affected the upper horizons of the planet.

The second stage in the evolution of the Earth's upper geospheres was of longer duration, probably from the start of anaerobic life to the appearance of photosynthesizing organisms. The most ancient findings of these organisms are as old as 3-3.5 billion years. The stony record of this stage has survived to the present. Most rocks whose age exceeds 3 billion years are highly metamorphosed varieties—gneisses, granites and migmatites—in which the traces of primary sedimentation have been completely destroyed. Only one geological section in South Africa, in the so-called Swaziland system, contains weakly metamorphosed rocks in the form of various shales alternating with quartzites, ferruginous rocks and volcanic deposits. The principal geological events in the second stage were a substantial growth of aluminosilicate crust, or sial, and subdivision of the crust into basic structural units known in the entire subsequent history of the Earth. The morphology of the Earth's surface experienced changes. Linear mountain chains and subdued continental expanses in-between originated. The lunar, crater topography gave way to the terrestrial one. As a result, seaward transport of terrigenous material increased, and the ocean-

ward flow became more intense of the dissolved carbonates  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ ,  $\text{MnCO}_3$  and other components derived from chemical weathering of the land surface.

The introduction of carbonates in the World Ocean caused substantial chemical alteration in it. Thus, strong acids had gradually disappeared, and progressive accumulation of carbonate salts became possible. The abundance of carbon dioxide in the atmosphere and water caused the abundance of dissolved carbonates. In this stage, nitrogen and carbon dioxide played an increasing role in the atmosphere.

Sedimentation acquired radically new features under those new conditions. The origin and development of extensive continental masses promoted the generation of the following climatic zones: dry (arid), cold (glacial) and wet (humid). Therefore, the sedimentation conditions became more diverse than before. Carbonate sedimentation set up, owing to accumulation of carbonates in sea water. They were probably dolomites in chemical composition, which purely chemically precipitated in the vast areas of the ocean floor. These same regions, located far from land masses, intensely received silica, iron and manganese. In their appearance they were jaspilites, finely stratified muds, in which thin layers of silica alternate with those of the ferrous iron minerals, siderite and silicates (chlorite).

The next stage of crustal history began approximately 3 billion years ago. It is pro-

vided with an abundant stone record—highly metamorphosed rocks—gneisses, schists, quartzites and jaspilites, on the one hand, and the weakly altered or unmetamorphosed rocks within the Precambrian shields. The Earth's crust had grown extensively by that time and continued to increase. It contained distinct geosynclinal zones with thick folded sedimentary rocks and extensive cratonic regions with a sedimentary cover on a broken crystalline basement. On the whole, the tectonic development of lithosphere controlled sedimentation. The sialic crust built up not only laterally but also vertically, becoming thicker. As a result, the ancient sedimentary rocks subsided to great depths and underwent metamorphism and granitization with a loss of the mobile components concentrated in sedimentary rocks. Thus, the carbonate minerals of sedimentary rocks were decomposed by metamorphism to give rise to silicate minerals with a release of carbon dioxide into the atmosphere and hydrosphere. The same was true of water between fine mineral grains or sorbed on clay particles. Thus whereas water and carbon dioxide were transported from deep in the mantle into the atmosphere and hydrosphere early in the Earth's history owing to mantle degassing, now the supply of regenerated water and carbon dioxide is in progress along with juvenile water supply. The gases of the metamorphic origin supersede the juvenile gases to an increasing extent.

The accreting cratonic areas became exten-

sive continents on which physiogeographic zones set up affecting the differentiation of sedimentation. Clear indications are observed of continental (glacial) sedimentation, as suggested by glacial deposits in the sections of North America, South Africa and Australia. The extensive continental regions are sources of clastic and dissolved materials. However, the growth and development of photosynthesis of green plants in Precambrian seas were of crucial importance for changes in the sedimentation environment. Prominent traces of photosynthesizing organisms have been found in the sediments of this stage.

All these phenomena have changed the hydrochemistry of the World Ocean. The volcanic sulphur and hydrogen sulphide introduced in hydrosphere and atmosphere under conditions of oxygen abundance were transformed into sulphates of sulphuric acid. Reacting with the dissolved carbonates in the hydrosphere, sulphuric acid superseded carbon dioxide, enriching water with  $\text{SO}_4^{2-}$ .

Under these conditions, the mobility of many elements, such as Fe, Mn, V, Cu and heavy metals, reduced greatly. The forms of precipitation of these elements and other multivalent metals also changed. Naturally, they began to precipitate in the oxygen environment mostly in the highest stage of oxidation [ $\text{Fe}(\text{OH})_3$ ,  $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ , etc.]. The lower oxides were becoming less and less abundant in precipitation.

The third stage of sedimentation is characterized by accumulation of huge series of

ferruginous rocks mostly laid down 3 000-2 000 million years ago.

Further chemical precipitation took place of such carbonate rocks as limestone and dolomite. However, alga deposits, stromatolitic strata, indirectly related to the vital activity of diverse colonial blue-green algae, began to accumulate in certain horizons.

The increased amount of living matter in the middle and late Precambrian was responsible for accumulation of organic matter in sedimentary rocks. It became an integral component of sedimentary rocks, especially in late Precambrian sediments. Oil shales are laid down in places; their metamorphosed varieties are called shungites.

On the whole, the sedimentary rocks in the middle and late Precambrian (the Riphean) were becoming more and more varied. Proceeding from the basic features of sedimentation, N.M. Strakhov calls this depositional period a two-stage, higher-lower oxide, dolomite-jaspilite one. First salt-bearing—halide deposits appear.

The last, or historical, stage in the history of the upper geospheres of the Earth, embraces Phanerozoic time. Extensive cratons arose in the southern hemisphere (Gondwana) and northern one (Laurasia). This gave rise to all the known types of formation of sedimentary rocks, among them sedimentation in lows inside the continents. Major changes took place in the hydrosphere and atmosphere. They affected the very character of sediment deposition, primarily owing to life development.

Living matter passed onto the land and occupied areas of a humid climate already at the very beginning of the Paleozoic era. Terrestrial floras and faunas were formed. The onslaught of the continents by living organisms was inevitably accompanied by an increase in the amount of living matter. According to the above estimates, the amount increased nearly 800 times. Living matter extended over the floor to include new regions in the deeper portions of the ocean. This also promoted the growth of living matter.

However, not only simple increase of the biological mass of organisms took place, but its qualitative composition was being complicated. New species of organisms appeared. As a result, more and more mineral substances are absorbed by organisms to construct their internal and external skeletons. Use was made of  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  (Cu, V, etc.), which are involved in the living activity of cells and tissues of different organisms. Therefore, the biological mass of living matter exerted a much greater influence on the whole geochemistry of the ocean, atmosphere and the sedimentary shell of the Earth in Phanerozoic time.

The composition of the atmosphere was approaching the modern one in the relative proportions of nitrogen, oxygen and carbon dioxide. The composition of sea water was also approaching the modern one. Having been chloride-carbonate-sulphate in the third stage of sedimentation, it was gradually becoming chloride-sulphate. At the same time, the

elements with varying valence (iron, manganese) existed as little-soluble, most oxidized compounds; therefore, their concentration in sea water fell sharply. Thus the greater amount of free oxygen in the atmosphere and sea water has sharply limited the mobility of iron, manganese and many trace elements. They were transported as solutions to a much lesser extent, and to a greater extent in fine suspension, inside clay particles or on their surfaces (in an adsorbed state). Their Phanerozoic concentration as ores in different climatic zones tended to occur near the coasts of continental regions. The central parts of seas were becoming more and more barren.

A radically new phenomenon caused by the expansion of continental regions was precipitation of evaporites. Sodium, magnesium, calcium and potassium were not only transported from land to sea but also returned to some extent as a result of sea transgression, precipitating as sulphates and chlorides in closed and semiclosed water reservoirs, mostly in arid climatic zones. In the Phanerozoic, salt precipitation in the World Ocean thus worked along with opposite processes, with some salt removal from, and desalinization of the hydrosphere. Salt precipitation began in the Early Cambrian and alternatively increased and decreased throughout the Phanerozoic. The chemical character of salt accumulation is striking. Sea water entered semiclosed gulfs and extensive marginal portions of intracontinental seas. It evaporated there, and various salts, primarily  $\text{CaSO}_4$ , the

NaCl (in lesser amount but still abundant) and potassium and magnesium chlorides and sulphates (in still lesser amount) precipitated.

Therefore, huge salt masses were removed from the entire salt mass in the ocean and buried in the sedimentary shell of the Earth. N.M. Strakhov believed that the salinity of the ocean could not have remained the same but had reduced when salt precipitation had been especially active and risen in the opposite case. In general, typical salt deposition in the Phanerozoic was periodic in character. The epoch of intense salt precipitation in Early Cambrian, Middle Devonian and Permian times alternated with less intense epochs in Silurian, Carboniferous, Jurassic and Cretaceous times. The approximate estimates made by A.B. Ronov and other investigators show that about 10 per cent of the total sodium and chlorine reserves in the modern ocean precipitated in the Permian epoch of salt deposition.

Quite a distinctive feature of Phanerozoic sedimentation was abundant deposition of organic matter along with ancient marine and continental sediments. Bituminous clays and oil shales were laid down in sea and coal masses, on land.

Coals were also accumulated in a periodic fashion closely related to vegetation evolution, and this affected the texture and petrography of the coals themselves. No coal was accumulated early in the Paleozoic (Cambrian, Ordovician and Silurian), because terrestrial vegetation was still very scanty. Psilophyte

shrubs developed early in Devonian and mid-Devonian time, and true forests, in Late Devonian time. Coal deposits appeared for the first time. Coal deposition was much more intensive, with three maxima, in the Carboniferous and Permian, owing to a rapid progressive development of the vegetable world. In the Triassic, less coal is accumulated, and three peaks of coal deposition took place in the Jurassic, Cretaceous and Paleogene.

The role of organisms in the extraction of a number of metals from sea water rose distinctly. Magnesium carbonate was exclusively extracted biochemically but still on a limited scale. In areas of a humid climate, carbonates on the whole accumulated as limestones. The use of calcium carbonate by organisms to construct their skeletons was increasing with geological time, because new animal groups, ranging from tiny planktonic organisms (globigerines) to mollusks, crinoids, sponges and corals, became capable of extracting calcium carbonate from water. A similar phenomenon is noted in the geochemical history of silica; its purely chemical precipitation gave way to purely biological deposition with participation of many organisms.

The elevated sea water alkalinity favoured precipitation of phosphorites, and their huge accumulations were formed in the last stage in the form of major mineral deposits.

The Phanerozoic witnessed all the types and varieties of sedimentary rocks. On the whole, according to N.M. Strakhov, the Phanerozoic sedimentation can be defined as two-

stage, lower-higher oxide, carbonaceous-carbonate-evaporate, which occurred under a strong influence of living matter, this being not only indirect one, as earlier, but also direct.

The distinguishing and description of the four stages of chemical-biogenic sedimentation is an attempt to discern the principal character of lithogenesis in the history of the Earth. These stages have no distinct boundaries in both space and time. They merely express a certain tendency in the evolution of the planet's sedimentary shell. This tendency is that chemical sedimentation is gradually superseded by partially terrigenous and partially biogenic sedimentation. The living matter of the biosphere exerted an ever increasing influence, both indirect and direct, on the migration of chemical elements in the upper Earth's shells.

It follows from the above that the Earth's sedimentary shell, hydrosphere and atmosphere are an interconnected system. In this system, an exchange of compounds took place continuously, and chemical equilibria changed in the course of evolution of the organic world. As a result, the total content of sedimentary material in the Earth's crust should considerably exceed 10 per cent, or even 30 per cent, according to A.B. Ronov. The long-term growth of the sedimentary shell was due to supply of volcanic materials from depth, of terrigenous materials from the elevated regions of the lithosphere and of oceanic and atmospheric chemogenic materials replenished continuously owing to removal of chemical weath-

ering products from continents and escape of volatiles from the Earth's interior.

Overall changes in lithologic composition and relative proportions of sedimentary and volcanic rocks in continental areas of

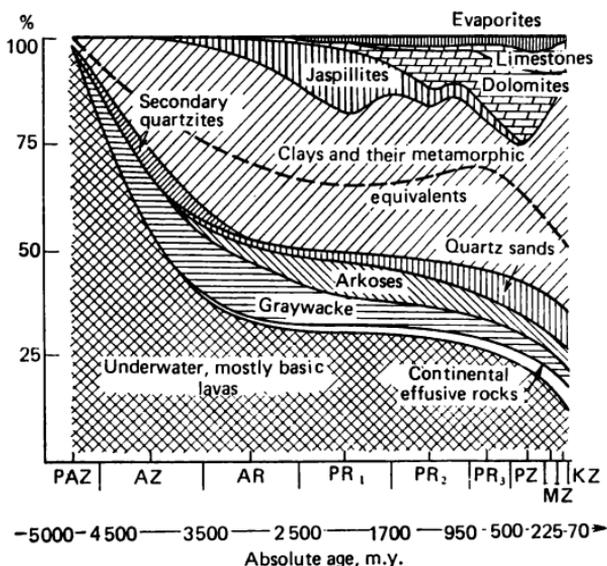


Fig. 34. Diagrammatically presented evolution of the lithologic composition and proportions of sedimentary and volcanic rocks in depositional areas of continents (after A.B. Ronov)

sedimentation with passing time are shown in Fig. 34 (after A.B. Ronov).

Because the ancient sedimentary material has been repeatedly metamorphosed and is now primarily composed of crystalline rocks, various schists, gneisses and granites, and because the continental crust basically consists of these rocks, one can consider that the

evolution of the Earth's sedimentary shell has affected the chemical evolution of the continental crustal segment as a whole.

The chemical evolution of continental crust, or sial, in principle can be discerned by comparing the chemical and petrographic compositions of the most ancient known geological formations with younger ones. Such a comparison has been made for North America. In 1972 A.B. Ronov generalized the voluminous analytical information about geological formations of varying age within the North American and East European cratons. The history of the Earth's crust as follows from the petrochemical data on different continents was studied by A. Engel, S. Eatson et al. (1974). J. Veizer and W. Compston (1976) used the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for Precambrian carbonates as indicators of crustal evolution and came to the following inferences.

Large geological provinces whose age exceeds 2.5 billion years show an average bulk chemical composition similar to that of basalt, i.e. that of oceanic crust. The provinces whose age is less than 2.5 billion years are typical continental crust in composition. A comparison of the petrographic composition of the ancient continental nuclei in North America, South Africa, India and West Australia has shown that so-called greenstone rocks, i.e. altered basic lavas akin to basalt, basaltic andesite and other similar rocks are common there. Therefore, the modern continental crust, or sial, has evolved, throughout geological time,

from basic (basaltic) composition to acid (granitic) one. This general tendency is shown in Fig. 35.

To compare chemical changes, we present the compositions of the oceanic and continental crust (Table 25). It is easy to see that removal of such components as  $\text{TiO}_2$ ,  $\text{FeO}$ ,

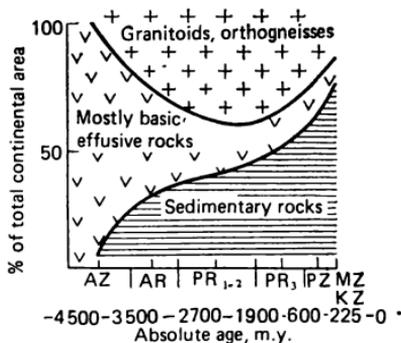


Fig. 35. Diagrammatically presented changes in the principal rock groups in the erosion areas of continents (after A.B. Ronov)

$\text{Fe}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{MgO}$  and  $\text{CaO}$  and conservation of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  are necessary for the oceanic crust to become in composition the continental, sialic crust.

What processes promoted the formation of sialic, continental crust in its present appearance and composition?

The first possible process consists in the general initial asymmetrical differentiation of the Earth probably owing to generation of its core. As a result, primordial basalt issues were more abundant in one hemisphere of the

planet than in the other. In the final analysis, however, this process cannot account for the transformation of basaltic masses into sialic

TABLE 25. Comparison of the Compositions of Oceanic and Continental Crust and Abyssal Oceanic Sediments, wt. %

Oxide	Oceanic crust	Continental crust	Abyssal oceanic sediments
SiO <sub>2</sub>	48.17	56.23	46.6
TiO <sub>2</sub>	1.40	0.71	2.9
Al <sub>2</sub> O <sub>3</sub>	14.9	14.46	15.0
Fe <sub>2</sub> O <sub>3</sub>	2.64	2.36	3.8
FeO	7.37	5.41	8.0
MnO	0.24	0.13	0.2
MgO	7.42	4.77	7.8
CaO	12.19	6.98	11.9
Na <sub>2</sub> O	2.58	2.40	2.5
K <sub>2</sub> O	0.33	1.98	1.0
H <sub>2</sub> O	1.62	0.6	—
P <sub>2</sub> O <sub>5</sub>	0.22	0.16	0.3

ones, enriched with silicic acid and similar in composition to granodiorite.

It is natural to assume that the huge natural cycle and reworking of material from the Earth's upper horizons, with stages of weathering, sedimentation and secondary melting, were responsible for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> accumulation and loss of other components characteristic of primordial basalts.

Both internal, endogenic, and external, exogenic processes have played a certain role in compositional changes in the primary crust, which may now occur as miserable

remnants of basaltic material in the most ancient continental areas.

Magmatism in a wide sense of the word is among internal processes—the melting of volatile-rich mobile silicate material at different levels of the mantle. A characteristic feature of vigorous magmatic processes in the geological history of the crust is their restriction to certain tectonic epochs. Especially intensive magmatic phenomena and volcanism, their external expression, took place in geosynclinal areas. Owing to vigorous tectonic movements, they were later transformed into orogenic areas and then, after long-term erosion, into rigid stable areas with a sedimentary cover produced by prolonged subsidences below sea level.

Radiometric age determinations on igneous rocks have established a sequence of the most ancient magmatic epochs (Fig. 36). A.I. Tugarinov and the present author distinguished the most common Precambrian tectonomagmatic cycles as early as 1966. They confirmed the earlier suggestions that the 1 800-2 000 and 2 500-2 700 million years old epochs of magmatism and metamorphism were of crucial importance in the Precambrian geological history. As seen from Fig. 36, the former epoch (the Svekofenian-Karelian one, or the Hudson cycle) was especially prominent. It encompassed the vast areas of what are now Precambrian shields and the ancient basement of platforms.

According to the most recent calculations of geophysicists, the periods of igneous activity

in the geological history were controlled by those of radiogenic heat accumulation in the upper mantle. The primordial crust of our planet consisted of the mantle-derived basaltic material.

With passing geological time, however, the composition of eruptive products that thicken the Earth's crust within continental segments has changed. Thus basaltic magmas were supplemented by basaltic andesite and andesite eruptions, which are more acid. Indeed, if we compare the composition of typical oceanic (tholeiitic) basalt with that of andesite, we see a substantial difference, as

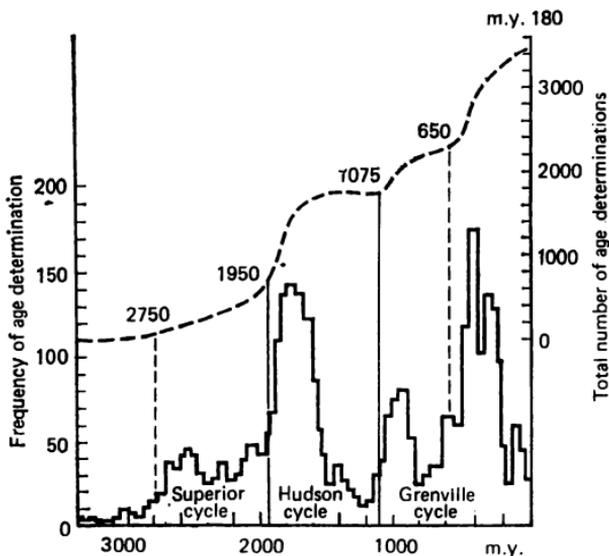


Fig. 36. Histogram of ages based on more than 3 000 determinations (after R. Dearnley)

shown in Table 26. It is easy to infer from the table that introduction of andesitic mate-

TABLE 26. Average Compositions of Volcanic Rocks (after A. Poldervaart), wt.%

Oxide	Tholeiitic basalt	Andesite	Difference
SiO <sub>2</sub>	51.0	60.3	+9.3
TiO <sub>2</sub>	1.4	0.8	-0.6
Al <sub>2</sub> O <sub>3</sub>	15.6	17.5	+1.9
Fe <sub>2</sub> O <sub>3</sub>	1.1	3.4	+2.3
FeO	9.8	3.1	-6.7
MnO	0.2	0.2	—
MgO	7.0	2.8	-4.2
CaO	10.5	5.9	-4.6
Na <sub>2</sub> O	2.2	3.6	+1.4
K <sub>2</sub> O	1.0	2.1	+1.1
P <sub>2</sub> O <sub>5</sub>	0.2	0.3	+1.0

rials into the continental segments of the Earth's crust gave rise to a relative increase in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O and decrease in MgO, FeO and CaO, i.e. sialization of the crust took place, as well as its approach in composition to the modern one. Andesite may have been molten from the horizons in the upper mantle other than in the case of basalt. V.M. Sinitsyn notes (1972) that the acid products of mantle differentiation (basaltic andesites) are more abundant on continents than in the ocean floors because in the former an active zone of magmatic processes (tectonosphere) penetrates far down into the mantle.

The extent of crustal sialization in the course of mantle differentiation rose and became greatest in the late Phanerozoic. However, the role of volcanism in the driving of continental crust towards a more acid composition was, however, insufficiently active.

The second mechanism of crustal sialization is associated with an intense exogenic material cycle, incorporating primordial crust transformation by solar energy, gravitation and the biospheric agent as a whole. The material cycle in the biosphere (see Fig. 31) was the most important crust-forming process. Unlike volcanism, it did not add new material to the crust but vigorously transformed crustal masses, namely their chemical composition and physical state. As we have repeatedly mentioned earlier, the enormous continental crustal masses passed through a state of sedimentary rocks and were eroded and altered by all exogenic geological agents. The extremely prolonged water cycle is responsible for erosion of the continental crust with a removal, once and for all, of some most common soluble simatic (basaltic) elements (Mg and Fe) and conservation of relatively immobile components ( $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ), with its overall sialization.

In comparing the average composition of continental crust with that of deep-sea oceanic sediments (Tables 25 and 26), it is seen that the latter contain more components that were partly lost by the continental crust as compared with the basaltic crust. These pelagic oceanic sediments lie on vast expanses of the

ocean floor; they have practically never returned to continents and are hence irrevocable products of removal of continental crust.

Obviously, long-term erosion of the primary basaltic crust was responsible for the removal of  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$  and  $\text{CaO}$  into the ocean and their laying down both near the shore and very far from where the continental crust was formed. The fates of sodium and potassium are somewhat different. The former was introduced into the ocean in large amounts and retained there in a dissolved state. Its large proportion, however, returned to the continental crust in sediments that had long occurred in the sea. It was then removed from sea water by cation exchange ( $\text{Na}^+ \rightleftharpoons \text{H}^+$ ) with sedimentation water.

The potassium removal into the World Ocean was substantially retarded by sorption in finely dispersed clays. The same is true for this element in plant remains, since it is a component of ashes. This may explain, to some extent, the higher potassium content in the continental crust than that in the oceanic crust. Naturally, however, there were also other causes of potassium concentration in the continental crust.

Thus the volcanic processes producing more and more acid products in their development interacted closely with repeated erosion and redeposition of the direct products of basic and acid volcanism, against the background of alternating uplift and subsidence in one of the segments of the globe. The result is the present-day sialic continental crust

enriched with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and depleted in Fe, Mg and Ca as compared with the original material at the surface of the planet.

## Conclusion

Irrefutable evidence about the atomic structure of chemical elements and their properties has greatly expanded the knowledge of the world around us. At the time of a great revolution in science and technology, man has left the boundaries of his own planet, stepped down on the Moon's surface and acquired for the first time the reliable information on the surface of Venus, Mars and the satellites of Jupiter and Saturn. Hence a new step has been made towards a better knowledge of the origin and history of the Solar System.

Already in the near future, more and more material of celestial bodies will undoubtedly appear in laboratories, and its comparative studies will inevitably be made with due account of atomic laws, both known and those to be discovered.

Modern science postulates a unity of materials in the world on the basis of the most recent advances in atomism; it expresses this unity by means of isotopic ratios of various chemical elements. The whole set of sciences uses the fundamental achievements of physics and chemistry to gain insight into the origin of our planet and the first days of its history

until the ancient known rocks were formed at its surface.

Early in the evolution of the Universe, the interaction between radiation and elementary particles produced light atoms as the most stable entities. Possibly, only hydrogen and helium were dominant at those remote times. The hydrogen atoms later combined to form large celestial bodies that gave rise to massive stars and galaxies. In one of the innumerable stars of the plain component of our Galaxy, hydrogen and then helium were involved in natural fusion to produce other chemical elements. These processes progressed according to the laws of nuclear physics and thermodynamics. It should be emphasized, however, that all the elements heavier than helium have, in general, a low abundance in the Universe, and their genesis can be regarded as an accompanying event associated with star evolution. The heaviest transuranium elements were generated at the end of formation of nuclides in stars. At the same time, this final stage disturbed the element-forming system and caused an outburst of material. The primordial Sun became surrounded by a gas disc that rapidly cooled down and dispersed in space.

The cooling of this disc-shaped gas nebula caused condensation of material into liquid and solid bodies, first droplets and then particles as solidified drops. According to the laws of chemical thermodynamics, high melting-point metals, in particular drops of iron and then of silicates at 1 800-1 000 K, were

first to condense from the material of solar composition. Then, at 1 000-400 K, other less abundant metals and their compounds condensed with sulphur and oxygen. The solidified silicate material drops in the form of small spherical bodies, chondrules, produced a multitude of asteroids—parental bodies of chondritic meteorites—apparently during the later thickening.

The chemical processes and condensation were controlled by dropping temperatures in the different areas of the primordial nebula, and also by the C/O ratio, which was responsible for its chemical inhomogeneity. Near the Sun, the primordial gas cooled slower than away from it. Therefore, the terrestrial planets orbiting closer to the Sun were produced by condensation of the highest-temperature fraction with an enhanced metallic iron content. Numerous organic compounds were formed late in the cooling of the gas nebula, and these gave rise to first primitive living things.

After the Earth had been formed below the melting point of its material, it started to warm up rapidly under the effect of strong radioactivity. This caused initial chemical differentiation with the formation of central core of the planet.

According to one of the hypotheses, radiogenic heating produced melting of material in the upper parts of the young Earth. Iron was the first to melt and then came silicates. An admixture of iron sulphide eased, on the whole, melting of iron, acting as a flux. A thick belt of molten iron was generated in the upper

horizons of the Earth, and this belt was unstable because iron has a high specific gravity. Hence an insignificant thickening of the belt in one place, for instance owing to tidal phenomena, caused a one-sided flow of molten iron masses towards the centre of the Earth. It also cannot be ruled out that much of the Earth's metallic core had been formed even earlier by condensation of metallic particles or drops when the temperature was still too high for silicate compounds to condense abundantly. However, the asymmetric structure and composition of the Earth's crust and upper mantle definitely indicate that the differentiation of the Earth was one-sided and unidirectional. The huge subsiding heavy masses of molten iron superseded lighter plastic silicate masses into the opposite hemisphere. These silicate masses then melted and differentiated to give rise to the lowest melting-point materials along with water vapour and other gases, which were supplied to the Earth's surface by volcanic processes to form primeval aluminosilicate crust, ocean, and carbon dioxide-rich atmosphere.

The further Earth differentiation occurred in the upper mantle and at the surface during the long-term cycle of crustal material under the influence of solar energy, internal forces of the planet, and under chemical and mechanical interaction with the ocean and atmosphere. The appearance of life early in the Earth's evolution had produced a biosphere which later encompassed the hydrosphere, atmosphere and upper lithosphere.

Life rapidly conquered the upper geospheres, involving the increasing masses of materials in the prolonged biogeochemical cycle, which has greatly affected the sedimentary shell of the Earth's crust. The Earth's surface was initially depleted in free oxygen, and ultraviolet solar radiation could have penetrated into the primary ocean to a depth of 10 m. The illuminated surficial layers of sea water were favourable for the development of living matter that gave rise to photosynthesizing organisms. Unicellular photosynthesizing organisms—blue-green algae or their ancestors—may have originated where they were protected from destructive ultraviolet solar radiation, i.e. deeper than 10 m. Therefore, the conditions required for the evolution of photosynthesizing unicellular autotrophic organisms were most favourable where visible solar light penetrated into sea water while ultraviolet radiation did not. These ancient organisms developed at their constant density, because the cell that became heavier descended below the illuminated zone, and if it was light, it emerged, undergoing a damaging action of ultraviolet radiation.

The generation and evolution of photosynthesizing organisms in the illuminated zone of sea were responsible for water decomposition to form free oxygen. As a result, the biosphere became oxidizing in nature. The carbon dioxide was nearly wholly taken from the atmosphere by photosynthesis and carbonatization.

The free oxygen in the atmosphere formed

an ozone screen against destructive ultraviolet radiation. A possibility arose for organisms to disperse rapidly, in particular to extend onto the land.

The world of animals that eat plants arose as a superstructure relative to the photosynthesis of plants in the oxidizing atmosphere of the Earth. Animals can no longer synthesize the organic compounds important for their life, such as amino acids, but consume them from the plant world. At the same time, their life turned to be connected with oxidation by way of breathing and oxygen fixation in the pigments of blood. Hence animals could develop their functions in the cryptozoic interval of the Earth's history, move actively in space and conquer new places of habitat. However, animals have long evolved in marine water, in the zone of sea saturated by oxygen. The animals built then their bodies from soft tissue; they have no rigid skeletons. The evolution of skeletons was strongly hampered, because they made organisms heavier and these submerged below the oxygen layer into the zone unfavourable for their life. Rigid skeletons could, therefore, develop only in the organisms that had acquired swimming organs and could swim independently or move over the sea floor in near shore zones.

After multicellular organisms had acquired rigid skeletons, carbonate rocks became laid down mostly biogenically during further geological history. The surficial layers of ocean water had long been the principal sites of an intense cycle of carbon, hydrogen, oxygen

and other biophile elements. Only with the appearance of land vegetation, the role of the ocean surface in the production of free oxygen had decreased, giving way to the surface of continents.

In connection with life in the biosphere, one should note an important geochemical equilibrium related to the geochemical carbon balance, which is essential but whose essence is still known insufficiently well. As early as 1934, V.I. Vernadsky wrote that a simple, still unknown numerical ratio must exist between the amount of free oxygen on our planet, particularly in its biosphere, and the mass of hard coals, bitumens, oils and carbonates.

A.B. Ronov has recently estimated this ratio, with due account of the limited reserves of carbon dioxide. As the source of food for the whole living matter, free carbon dioxide has been continually replenished by volcanic processes. When these processes cease, however, owing to the exhaustion of the internal energy sources, the supply of carbon dioxide to the surface will cease also. As a result, the biosphere must die off and life will cease, because the sources of internal carbon dioxide will disappear. The free oxygen not replenished by photosynthesis will be gradually involved in oxidation. According to A.B. Ronov, it is hardly probable that life will be able to effect a closed cycle, because the reserves of carbon will also be exhausted, since they are confined to the system atmosphere-ocean-living matter and will be lost inevitably owing

to carbonate sedimentation. The author comes to a general conclusion formulated as the geochemical principle of life preservation: "Under otherwise equal conditions, life on the Earth and other planets is possible until these planets are active and an exchange of energy and matter takes place between their interior and surface. Life must cease when the energy resources of the planets are exhausted."

As to the Earth, we can neglect this conclusion, taking account of prospects of mankind development. With mastering the enormous sources of nuclear energy, the release of carbon dioxide necessary for life and concentrated in carbonate rocks, will not be a perplexing problem.

The conquer of Nature, reasonable and harmonious uses of its resources are impossible without getting insight into the cycle of all the chemical elements in the Earth's biosphere. But this cycle, caused by solar energy and the internal atomic energy of radioactive decay, has an extremely long history. The physicochemical equilibria in the Earth's biosphere and deep interior are continually disturbed by intense energy pulses coming from distant outer space and the interior of the planet.

The Earth's surface is being qualitatively transformed. An antroposphere is arising in the biosphere, a sphere of man's activity, which expands all the time beyond the Earth itself into the near-Sun space. All these huge changes in Nature and society, as we see them today, are the result of the extremely long

history of the planet, its chemical evolution and other forms of development of matter. Only some of the features of this majestic history of our planet, beginning with the origin of its atoms, have been discussed shortly in this book.

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