

DEVELOPMENTS IN SEDIMENTOLOGY 25A

DIAGENESIS IN SEDIMENTS AND SEDIMENTARY ROCKS

EDITED BY

GUNNAR LARSEN

AND

GEORGE V. CHILINGAR

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Dedicated to

*N.M. STRAKHOV, W.D. KELLER, N.B. VASOEVICH, R. SIEVER,
F.J. PETTIJOHN and W.C. KRUMBEIN*

for their important contributions to the field of diagenesis

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Chapter 1

INTRODUCTION—DIAGENESIS OF SEDIMENTS AND ROCKS

GUNNAR LARSEN and GEORGE V. CHILINGAR

The book *Diagenesis in Sediments* was published in 1967, almost a hundred years after introduction of the term "diagenesis" in geological literature, i.e., in 1868, in Von Guembel's major work *Geognostische Beschreibung des ostbayerischen Grenzgebirges*. Many decades passed, however, before research into diagenetic processes and products really got underway. It could be stated that up to the 1950's, the topic of diagenesis formed only a very minor part of geological research literature (see for example, Trask, 1951, and Sűjkowski, 1958). Rapid development took place during the next fifteen years, as illustrated by the scope and contents of the above-mentioned work *Diagenesis in Sediments*.

The demand for that book was such that the need arose for a new and revised edition. Because of the scope of the subject and the proliferation of literature on the subject, it has been necessary to publish the new edition in two volumes. This reflects the growth which has occurred in the research into diagenetic phenomena since the publication of the first edition.

DEFINITION OF DIAGENESIS

Diagenesis can be defined as the changes which occur in the character and composition of sediments, beginning from the moment of deposition and lasting until the resulting materials (rocks) are either moved into the realm of metamorphism or become exposed to the effects of atmospheric weathering. Other, more restrictive, definitions can be found which, for example, consider that diagenesis ceases when the sediment becomes a sedimentary rock. For practical reasons, the latter definition is strongly recommended by one of the editors (G.V.C.), whose speciality is in the field of carbonate oil and gas reservoir rocks. This definition is used in the USSR and some other countries (see Table 1-I, obtained from the Russian translation by N.B. Vassoevich of the first edition of *Diagenesis in Sediments*), and is briefly discussed in this chapter.

According to the *Glossary of Geology and Related Sciences* (1962) sedimentation can in short be defined as "... that portion of the metamorphic cycle from the separation of the particles from the parent rock, no matter what its origin or constitution, to and including their consolidation into

TABLE 1-I

Classification of various stages in postsedimentation alteration of sedimentary rocks according to different Soviet authors (after Vassoevich, 1971, p. 14.)

Strakhov (1957)	Vassoevich (1957)	Kosovskaya, Logvinenko, Shutov (1957)	Strakhov and Logvinenko (1959)	Vassoevich (1962)	Vassoevich, Vysotskiy, Guseva, Olenin (1967, 1968)	Logvinenko (1968)
diagenesis	diagenesis	diagenesis	diagenesis	diagenesis	diagenesis (peat stage)	diagenesis
epigenesis	catagenesis	initial deep burial	catagenesis	protocata- genesis mesocata- genesis	protocata- genesis (brown coal stage) mesocata- genesis (coalification stages D, G, Zh, K and OS)	early cata- genesis (coals B, D, G) late cata- genesis (clinkering coals)
early metamorphism or proto-metamorphism	?	early late	metagenesis or initial metamorphism	apocata- genesis (starting with lean coals)	apocata- genesis (lean coal stage T, semianthraxes and anthracites)	early meta- genesis (lean coals anthracites)
	?	?	?	metagenesis (regional metamorphism)	metagenesis (regional metamorphism)	late meta- genesis (ultra-anthraxes, graphitized anthracites)
metagenesis	lithogenesis	regional metamorphism	?	metagenesis (regional metamorphism)	metagenesis	regional metamorphism

* Lithogenesis

another rock . . .". This portion of the metamorphic cycle comprises a large number of richly varied types of events, controlled by factors such as; (a) physical and chemical processes, and (b) tectonic and morphological conditions in both the field of accumulation and in that of denudation. These events can be grouped into a number of more or less distinct stages, as for instance the following three groups:

(1) The disintegration and decomposition of the parent material, i.e., the effect of the mechanical and chemical weathering.

(2) The separation of the weathering products, i.e., the effect of the processes of erosion, transportation and deposition, leading to the formation of the many different types of sediments.

(3) The consolidation and cementation of the deposited material, i.e., the diagenetic processes.

It must be emphasized, however, that the above clear classification is at the same time artificial, because distinct systems and sharp boundaries are scarce in nature. For example, the development of typical weathering profiles (Goldich, 1938; Wahlstrom, 1948) evidently is the result of not only weathering processes but also of removal of weathered material, i.e., leaching of soluble salts starts during the weathering itself. Thus, the events which give rise to typical weathering profiles are transitional between the above mentioned groups 1 and 2. The boundary between groups 2 and 3, i.e., between deposition and diagenesis, also can hardly be drawn clearly. It can be stated that diagenesis does not start until the moment the material is deposited, for instance on the sea floor. At the same time, however, it must be added that the diagenetic processes at work between the newly formed sediment and the overlying sea water do not have to be fundamentally different from the processes already acting between the sea water and the particles suspended in it. The processes which comprise halmyrolysis can possibly be considered to represent the even transition between the processes of deposition and those of diagenesis. Strakhov (1953, p. 12; 1960) divided the history of sedimentary rock into the following three different and distinct stages:

(1) Sedimentogenesis, namely formation of sediment.

(2) Diagenesis, or transformation of sediment into sedimentary rock.

(3) Catagenesis, which is a long stage of secondary changes in already formed sedimentary rock.

In Strakhov's classification, which is based on recognition of different stages of transformation of sediments into hard rocks, diagenesis is considered as only one of the stages in this development. Thus, one can say that the concept of diagenesis is used by Strakhov in a "restricted sense".

Like many other authors, Williams et al. (1955), on the other hand, are using the concept of diagenesis in a more "broad sense". They include the

catagenesis stage of Strakhov in diagenesis under the term of "late diagenesis", which represents a transition to metamorphism. The same point of view is held by Sijkowski (1958), who stated: "Diagenesis, after all, is but the introduction to metamorphism." Some authors go still further: for example, while speaking of the definition of the metamorphic zeolite facies, Coombs (1960) stated that this facies includes the products of not only conventional metamorphism but also those of hydrothermal activity and diagenesis. An attempt at drawing a borderline between diagenesis and metamorphism is found in the article by Fyfe et al. (1958): "Diagenesis of sandstones results in minor changes in the clay matrix and crystallization of cement minerals in the hitherto open pores. When the coarse clastic grains are also extensively involved in reaction so that the rock becomes substantially recrystallized, the process is classed as metamorphic." Thus, it is impossible in a pressure-temperature diagram to fix a boundary of universal validity between diagenesis and metamorphism, because some types of sediments are less stable than others and, consequently, during deep burial will cross the boundary faster than the more stable sediments.

It is important to mention here that the processes of diagenesis in sub-aerial environment and in shallow stable seas differ from those in subsiding basins, and were termed "exodiagenetic" by Shvetsov (1960). He also pointed out that in addition to dehydration, the coagulation of colloids, rapid growth of crystals (recrystallization), formation of concretions, and preservation of textural properties of sediment (such as fissures and borings) are characteristic features of "exodiagenesis".

The scale of different stages of alteration of sediments is first developed for clays, because of (1) their most common occurrence (clay deposits constitute not less than half of the volume of the stratisphere), and (2) their sufficiently distinct response to changing conditions, which influence development of lithogenesis. Clays are especially good indicators of pressure. On the other hand, the most sensitive indicators of temperature are coals and coaly organic matter (kerogen), in general, which is widely distributed in sedimentary rocks including clayey deposits. Consequently, the most detailed subdivision of catagenesis is based on properties of organic matter, especially on reflectance and index of refraction of vitrinite.

The role of time (geologic scale) is also of utmost importance. For example, Kossovskaya and Shutov (1963) and Kopeliovich (1965) pointed out a considerable shift of the border between initial and deep-burial epigenesis (catagenesis) in deposits of various ages: (1) in Neogene deposits of the Apsheron peninsula, this border is situated at a depth less than 5 km; (2) in Mesozoic deposits of Siberia, at a depth of 2.5 km; (3) in Paleozoic deposits of the Russian Platform, at a depth of about 1.3–1.7 km; and (4) in Riffian deposits, at a depth of less than 1 km. The role of time on changes which

occur in coaly organic matter was quantitatively evaluated during the past few years.

In 1922, A.E. Fersman (in: Vassoevich, 1971, p. 12) introduced two new terms, *hypergenesis* and *catagenesis*, into geochemical literature. The first term rapidly gained popularity in the USSR, whereas the latter became popular in the USSR only in the 1950's as a result of the efforts of N.B. Vassoevich. Fersman recognized: (1) *syngenesi*s: formation of sediment, (2) *diagenesis*: changes of sediment, and (3) *catagenesis*: transformations of sedimentary rocks until beginning of deep-burial metamorphism (or *hypergenesis*).

In 1934, M.S. Shvetsov (in: Vassoevich, 1971, p. 12) proposed to distinguish between *initial diagenesis*, or diagenesis of *sediments*, and *late diagenesis*, or diagenesis of *rocks*. In 1940, L.V. Pustovalov (in Vassoevich, 1971, p. 12) recognized five main stages in the history of sediment deposits: (a) destruction of source rocks; (b) transportation of products of disintegration of rocks; (c) sedimentation (accumulation) of sediments; (d) syngenesi

s, or early diagenesis; and (e) epigenesis, or late diagenesis. Vassoevich (1971, p. 12) objects against using the term epigenesis, because it was used in studies of ore deposits to designate *all* secondary processes and/or their products. Reference is made in the literature to *epigenetic* minerals, textures, and deposits in contrast to primary *syngenetic* ones.

Strakhov (1953) proposed the term *sedimentogenesis* to designate the first stage of formation of sedimentary rocks, including formation of loose sediment at the earth's surface as a result of reworking (weathering), transportation, and deposition of previously existing mineral masses. In 1956, Strakhov described in detail the diagenetic stages involving the following processes: (1) mineral formation in oxidizing environment in unstable components of sediments; (2) mineral formation in a reducing environment in the unstable components of sediments; and (3) redistribution of authigenic minerals and appearance of concretions together with local compaction of sediments.

In 1957, the term *metagenesis* was proposed almost simultaneously in three published works. Unfortunately, however, the definition of this term was not the same in all three cases. Vassoevich (1957), in using it, referred to metamorphism, whereas A.G. Kossovskaya, N.V. Logvinenko and V.D. Shutov (in: Vassoevich, 1971, p. 14) defined metagenesis as early metamorphism, prior to regional metamorphism. Strakhov (1957, in: Vassoevich, 1971, p. 14) agreed with the latter authors as far as the lower boundary of metagenesis is concerned, but included catagenesis in this term.

Strakhov and Logvinenko (1959) distinguished the following stages of rock formation: hypergenesis, sedimentogenesis, diagenesis, catagenesis, metagenesis, etc. According to them, based on tradition, the terms progenesis, syngenesi

s, and epigenesis can be used loosely to designate the

time and stage of successive rock-forming processes, without definite boundaries (sliding scale). (See Table 1-I.)

It has not been the wish of the editors to impose a particular definition on the contributing authors. As in the first edition, the intention has been to describe the processes and conditions which prevail during the period covered by the broad definition of diagenesis, regardless of the terminology used.

No matter how this phenomenon is defined, diagenetic alteration can be characterized as the reaction of a sediment or sedimentary rock to its physicochemical environment. The most important factors involved are the Eh and pH of the environment, the concentration of various anions and cations, pressure, and temperature.

In Chapter 2 of the first edition, Professor R.W. Fairbridge presented a comprehensive model of the sequence of diagenetic events within the broad spectrum of the term diagenesis (Fairbridge, 1967). His elegant approach is briefly presented here.

Taking deposition in a normal marine environment as a starting point, with sufficient water circulation to provide oxidizing conditions on the sea floor, Fairbridge's model describes diagenesis as a cyclic process in which the main events are referred to as *syndiagenesis*, *anadiagenesis*, and *epidiagenesis*.

For a given sedimentary particle, *syndiagenesis* commences at the moment of deposition on the sea floor. The processes which operate on the newly deposited particle are similar to the halmyrolytic processes which affected it during transport and sedimentation in the marine environment. *Halmyrolysis* can thus be considered as the link between the sedimentation and the first stage of diagenesis (*syndiagenesis*).

Syndiagenesis is subdivided into two stages: the initial stage and the early-burial stage. During the initial stage, oxygen is present in the sediment pore fluids. Oxygen allows organic activity, e.g., that of aerobic bacteria, the essential nutrient of which consists of organic substances present in the sediment. The aerobic activity of bacteria leads to the production of CO_2 , with a consequent decrease in the pH of the pore fluids. The environment, therefore, becomes hostile towards CaCO_3 , which may be present as calcareous shells in the sediment. As a result of the aerobic activity, the oxygen content is eventually used up. Consequently, oxygen disappears at a certain depth below the sediment-water interface. This boundary ($\text{Eh} = 0$) defines the transition from the initial to the early-burial stage. Obviously, in stagnant marine basins, having oxygen-free bottom water, the initial stage is not present.

Reducing conditions prevail during the early-burial stage, with active population of anaerobic bacteria. The pH increases as a result of this activity, and the calcareous material, which survives the initial stage of *syndiagenesis*, is protected against further dissolution. A characteristic product forming

during the early burial stage is FeS_2 . The lower limit for the occurrence of anaerobic bacteria marks the boundary between syndiagenesis and anadiagenesis.

The most characteristic feature of the syndiagenetic stage is, thus, the biological activity. The resulting bacterial effects produced on the sediments are largely controlled by the chemical conditions brought about by this activity.

Anadiagenesis comprises the compaction and maturation stages of diagenesis. In contrast to syndiagenesis, which operated in a restricted depth range and over a geologically short time interval, anadiagenesis occurs down to a great depth (e.g., 10 km) and operates over a long period of time (e.g., 10^6 yr). A negative Eh and moderately alkaline to high-pH environments are typical of anadiagenesis. The controlling factors in anadiagenetic processes are the increasing pressure and temperature with depth. The pressure of the overlying sediments results in compaction and simultaneous expulsion of pore fluids. A large-scale migration of pore fluids through sedimentary sequences results from compaction. The migrating solutions may react chemically with the sediments and rocks resulting in either dissolution or precipitation of various minerals. Structural closures resulting from the compaction can be accentuated by cementation processes. Compaction, dehydration, and cementation, which are the major features of anadiagenesis, can all be considered as the effects of pressure increase with depth. As mentioned previously, whereas clay sediments are sensitive indicators of pressure, organic matter, including both coal and other organic materials (e.g., kerogen), which may occur in a dispersed form in, for example, a clay matrix, is particularly sensitive to changes in temperature. The effect of temperature is mainly responsible for the maturation of carbonaceous rocks and hydrocarbons, whereas the migration of hydrocarbons is a result of the pressure effect.

As mentioned above, anadiagenesis is typically of long duration and, theoretically, can last indefinitely. In some instances anadiagenesis may grade into metamorphism. The question of the boundary between diagenesis and metamorphism, as mentioned before, has been discussed by numerous investigators, e.g., Von Engelhardt (1967) stated: "In the diagenetic zone, the sediments contain interstitial fluids as continuous phases which can be moved by normal flow. These fluids (most commonly aqueous solutions) are, therefore, always involved in the diagenetic reactions, the transport of substances occurring through flow and normal diffusion. Because of the intercommunication and mobility of the interstitial fluids, reactions of the open-system type prevail. Some sediments, as, for instance, fine-grained limestones, can already lose all of their porosity at a very shallow depth. Crystallizations and phase transformations in such dense rocks at moderate

temperatures and pressures may be called diagenetic, if other closely associated sediments still have an intercommunicating porosity." . . . "The diagenesis stops at a depth where in all sedimentary rocks the intercommunicating pore spaces have been closed up by physical or chemical processes. In this zone the metamorphism begins, its reactions taking place in the solid state or by diffusion at grain boundaries."

Typically, anadiagenesis occurs in basins during subsidence. In cases where subsidence is replaced by uplift, the sediments may become exposed to the influence of the circulating fresh groundwater, which owes its origin to rain water. The environment during the diagenetic stage in the groundwater (fresh) zone, which is termed epidiagenesis by some geologists, is often characterized by the presence of certain amounts of O_2 and CO_2 , and, therefore, can be aggressive towards a series of components formed during anadiagenesis. Consequently, traces of the earlier stages of diagenesis can be camouflaged or destroyed during epidiagenesis. Upwards, epidiagenesis is replaced by weathering, with the groundwater table being the practical boundary between them. During the transition stage from epidiagenesis to weathering, a new cycle of sedimentation commences.

SOME FEATURES OF DIAGENESIS

The processes of diagenesis, even in the above mentioned "restricted sense" of Strakhov (1953, 1960), go on in the marine sediments for hundreds of thousands of years after their deposition (Zaytseva, 1954; cf. Chilingar, 1958). The processes of diagenesis include: (1) formation of new minerals; (2) redistribution and recrystallization of substances in sediments; and (3) lithification.

The diagenetic minerals include sulphides and carbonates of Fe^{2+} and Mn^{2+} , namely siderite, ankerite, rhodochrosite, oligonite, pyrite, marcasite, alabandine, etc. Strakhov et al. (1954, p. 577) pointed out that their diagenetic origin is evidenced by the fact that Mn and Fe in these minerals are in a bivalent form, which could have formed in a reducing environment that existed in the sediments. Typical diagenetic minerals also include silicates of iron (and manganese), in which iron is present in a bivalent form; all leptochlorites belong in this category. Dolomite and ankerite also form during diagenesis. Many clay minerals are of diagenetic origin, such as montmorillonite (from volcanic ash), beidellite, mountain leather, and series of zeolites (mordenite, chabazite, phillipsite, and others). Illite can also form during diagenesis. The zonation of new mineral formations in Recent seas and in Cenozoic and Mesozoic basins is presented in Fig. 1-1.

The upper 1–2 m of Recent sediments usually reveal two early stages of

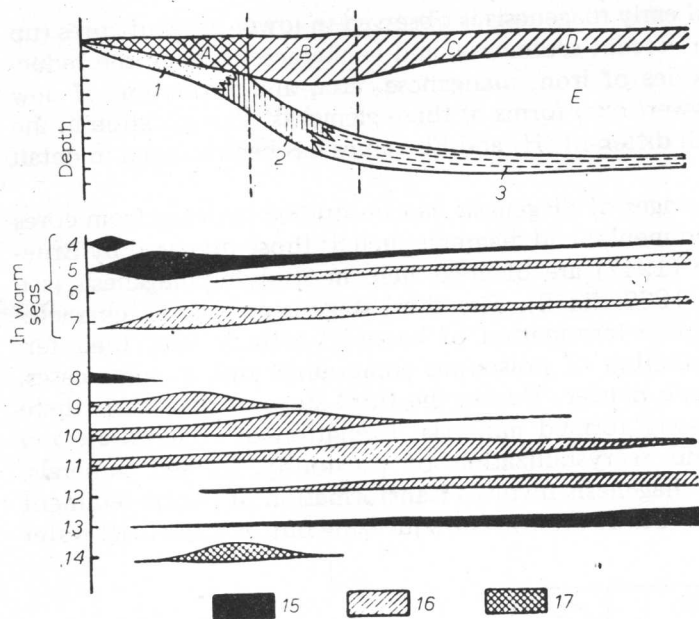


Fig. 1-1. Zonation of new mineral formations in Recent and ancient seas. (After Strakhov, 1954, p. 585.) A = turbid zone of fine-grained material, and its carrying out from near-shore zone into more central parts of the basin; B = areas of currents usually of circular type; C-D = surface zone of agitation and wind currents in central parts of basins; E = deep, quiet (with very slight movements of water) horizons of pelagic part of basins. 1 = sands; 2 = siltstones; 3 = pelites; 4 = CaCO_3 , oölites; 5 = biogenous and chemically precipitated CaCO_3 ; 6 = diagenetic CaCO_3 (bacterial); 7 = various forms of diagenetic dolomite; 8 = Fe_2O_3 , oxides of Mn, Al_2O_3 ; 9 = leptochlorites; 10 = glauconite; 11 = carbonates of Fe and Mn (in muds without CaCO_3 or having very small CaCO_3 content); 12 = sulfides of Fe, Mn (Cu, etc.) in muds with high CaCO_3 content; 13 = biogenically formed SiO_2 ; 14 = primary and diagenetic phosphorites; 15 = minerals forming through direct precipitation from water; 16 = diagenetic minerals; 17 = partly primary, partly diagenetic minerals.

diagenesis. The earliest stage occurs when the upper layer of sediment is situated in the oxidizing or neutral environment. In basins with normal oxygen regime the thickness of this layer is around 10–15 cm and can reach 40 cm and higher (Strakhov et al., 1954, p. 578). In basins deficient in oxygen this layer is only a few centimeters (and sometimes a few millimeters) thick, or is completely absent in the central portions of such basins. The duration of this stage also varies from thousands of years to several days. Some iron–manganese concretions and crusts, glauconite grains, phosphorites, and some zeolites form during this stage.

The second stage of early diagenesis is observed in lower parts of cores (up to 10 m) obtained in Recent sediments, and is characterized by the reduction of sulphates, oxides of iron, manganese, etc., and formation of new minerals containing lower(-ous) forms of these elements. The variation in the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with different $r\text{H}_2$ and Eh values has been studied in detail by Romm (1950).

Only the first two stages of diagenesis can be studied in detail from cores obtained in Recent sediments; and diagrams such as those prepared by Bruevich and Vinogradova (1947) are of great help in studying diagenesis (see Larsen and Chilingar, 1967, fig. 2). The third stage is apparently characterized by almost complete termination of bacterial activity (and their ferments), due to accumulation of poisonous compounds and, in some cases, disappearance of organic matter. During the third stage of diagenesis there is redistribution of newly formed minerals, formation of concretions and local cementation, and recrystallization of previously formed minerals.

The fourth stage of diagenesis involves transformation of plastic sediment into rigid compact rock (lithification). The squeezing out of interstitial water

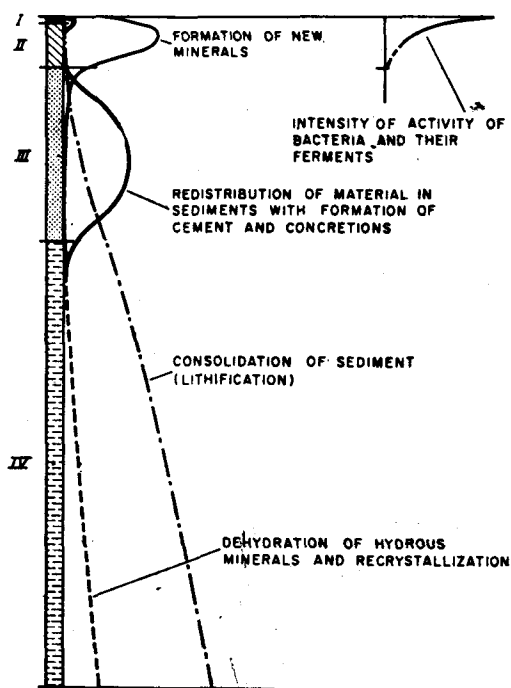


Fig. 1-2. Diagenetic stages in sediments. (After Strakhov et al., 1954, p. 596.)

occurs to a depth of about 300 m (Strakhov et al., 1954, p. 595). Dehydration of minerals occurs during compaction. For example, gypsum changes into anhydrite, hydrogoethite into hydrohematite and hematite, opal into quartz, etc. Fine-grained clays are recrystallized into coarser grains and aggregates, etc., during this stage. The different stages of diagenesis are presented in Fig. 1-2.

One of the earliest diagenetic processes involves consumption of free oxygen by organisms, after which the reduction of hydroxides of Fe^{3+} , Mn^{4+} , V, Cr, etc., and sulphates (SO_4^{2-}) begins. The environment changes from oxidizing to reducing and Eh becomes lower, whereas pH after some initial lowering usually increases (Strakhov, 1960, p. 79). The solid phases present in the sediment (such as SiO_2 , CaCO_3 , MgCO_3 , SrCO_3 , etc.) gradually dissolve in interstitial waters. Base exchange occurs between the cations adsorbed on clays and those in the interstitial water. At the same time the organic matter decomposes forming gases (CO_2 , H_2S , H_2 , N_2 , NH_3 , etc.) and water-soluble compounds, and some complex compounds which remain as solids in the sediment. As a result of these processes the interstitial water becomes devoid of sulphates, and enriched in Fe^{2+} , Mn^{2+} , SiO_2 , organic matter, phosphorous, and minor elements. The O_2 disappears and H_2S , CH_4 , CO_2 , NH_3 , H_2 , etc., accumulate instead. The alkalinity becomes high, Eh sharply decreases (–150 to –330) and pH varies from 6.8 to 8.5 (Strakhov, 1960, p. 80). A pronounced exchange of substances occurs between the bottom waters and interstitial waters at this stage. That is why such components as S and Mg are found in higher concentrations in interstitial waters than in originally buried sea water. The eventual saturation of interstitial waters with some components leads to precipitation of diagenetic minerals such as leptochochlorites, siderite, rhodochrosite, and sulfides of iron, lead, zinc, etc. The variation in Eh, pH and concentration of various ions in different areas of sediments results in subsequent redistribution (lenses, concretions, etc.) of authigenic minerals.

According to Strakhov (1960, p. 81), the depth at which diagenesis ceases varies from 10–50 m to 200–300 m. It obviously depends on the degree of compaction and the closing off of supercapillary, capillary and subcapillary pores. Consequently the diagenetic processes practically cease on reaching a certain degree of lithification. It is important to note here that lithification of carbonate rocks is accomplished more rapidly than that of other sediments.

Compaction, which is discussed in detail by Rieke and Chilingarian (1974), is very important in the case of clayey sediments. N.B. Vassoevich (1960, in: Klubova, 1965, p. 64) recognized four distinct stages of compaction occurring (1) with ease, (2) with difficulty, (3) with considerable difficulty, and (4) with great difficulty. For clays, the porosity varies from 60 to 85%