THE DIAGENETIC RHYTHM DEVELOPMENT

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Feasibility of diagenetic development of carbonate intercalations in argillaceous deposits with the originally uniformly distributed carbonate material is considered in the instance of middle Miocene deposits in the East Ciscaucasus. A multiple recurrence of this process may lead to emergence of a rhythmically constructed argillaceous sequence with marl stringers. The probable mechanism of diagenetic differentiation of the argillaceous sediment consists of two phases: argillaceous and carbonate. The effectiveness of this mechanism depends to some extent on changes in HCO_3^- concentration in ooze waters and on the phenomenon of calcium carbonate redeposition, in diagenesis.

Rhythmic structure of sedimentary sequences and their several horizons is fairly common in nature. The presence of rhythms in a section often implies a cyclicity of deposition. At the same time, some investigators doubt that rhythms encountered in sedimentary sequences always reflect the nature of sedimentation processes. At times, the rhythms are conceded to have originated at the diagenetic stages (Botvinkina, 1959; Daff et al., 1971; Sujkowski, 1958). The process of diagenetic differentiation of a sediment into layers of different composition has been modeled in laboratory experiments, at times with interesting results (Denisov, 1948; Smirnov and Fedorova, 1974, 1977).

However, as long as the mechanism of diagenetic development for rhythms remained unclear, and also because of the absence of criteria for reliable differentiation between the diagenetic and originally deposited layers, the concept of diagenetic rhythmicity has not gained popularity among the geologists.

The present article discusses a conceivable mechanism of rhythmic differentiation in diagenesis of argillaceous sediments into argillaceous and carbonate layers, and some of the implications of this concept.

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Rhythmic structure often is associated with horizons carrying carbonate concretions. Being typical diagenetic formations, the latter provide information necessary for identification of conditions under which the concretion-enclosing formations have developed.

The middle Miocene Chokrakian-Karaganian deposits in the East Ciscaucasus contain concretions of various mineral compositions, the most numerous being zonal calcite and calcite–siderite varieties.

The concretions of this type are associated with horizons of black claystones, almost free of silt but enriched in organic matter (C_{org} = 3-10%). These horizons are 2-4 m thick; at the base of the Chokrakian, they make up a sequence several tens of meters thick (Fig. 1).

It has been established that single layers of calcite and calcite–siderite concretions are almost nonexistent; as a rule, 5-8 layers are traceable in the concretion horizons (Fig.

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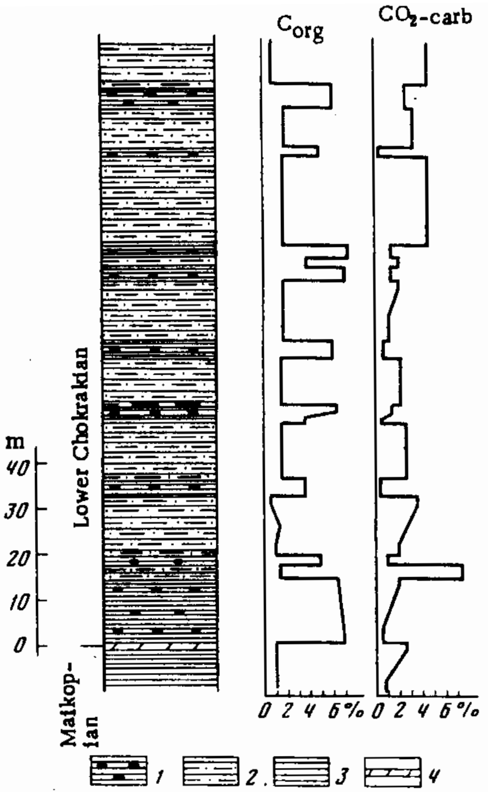

Fig. 1. Lithological and geochemical column of the lower part of the Chokrakian section along the Elistanzha River: 1) black claystones with calcite and zonal calcite–siderite concretions; 2) brown silty claystones; 3) gray Maikopian claystones; 4) marl bed (Tarkhan horizon).

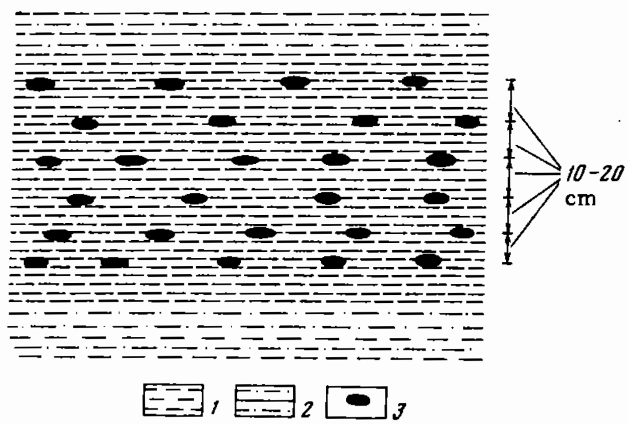

Fig. 2. Constitution of a black claystone horizon with stringers of calcite concretions: 1) black claystones enriched in organic matter; 2) brown silty claystones; 3) carbonate concretions.

Fig. 3. Constitution of concretion horizon with large calcite concretions (hammer 70 cm long).

2). A distinctive feature of such horizons is their rhythm, with the layers alternating in approximately the same spacing (0.1-0.2 to 1.0 m). There often is direct relationship between the size of concretions and the layer spacing. While layers with ellipsoid nodules, diameter 0.15-0.25 m, are most commonly spaced 0.1-0.3 m (Fig. 1), there are horizons spaced 1 m with concretion diameter increased to 1.0-1.5 m (Fig. 3).

There are numerous indications that calcite nodules, as well as the cores of zonated concretions, developed in the uppermost horizons of loose and watery ooze, at depths of a few decimeters. The siderite developed later on, in a more compact sediment (Gavrilov, 1977). An answer to the question as to what has brought about a rhythmic structure of black claystones is invariably related to factors of the origin of each individual layer.

In a majority of instances, diagenetic carbonate concretions in the argillaceous deposits occur in layers. The appearance of such layers within a section may be the effect of various factors. According to Strakhov (1960), one of these may be outflow of CO_2 from the ooze, along the bedding planes; that would lead to a concentration of carbonate material along these planes. As observed, the effect of this factor usually is manifested when the claystones contain sandy-silty intercalations that act as "ventilation channels" in the sediments. It turns out that carbonate nodules are "strung up" on the intercalations of material coarser than in the enclosing rock.

Another factor in development of concretion stringers is the change in primary sedimentation conditions during deposition of the sequence — in consequence of a relative or absolute intensification of carbonate accumulation with a subsequent redistribution of carbonate material within the newly developed stringer and its concentration in concretions.

It is hardly probable that stringers of calcite concretions in the Chokrakian-Karaganian deposits have developed as the result of sediment degassing along the bedding planes: the black claystone horizons are quite consistent, areally. Furthermore, a loose and water-saturated ooze would not favor lateral degassing of sediment over the vertical, in development of calcite nodules. Finally, the black claystones do not contain silty material in lentils and intercalations for CO_2 escape from the ooze.

Nor is it probable that some of the stringers were enriched in $CaCO_3$ as the result of changes in sedimentation conditions. Careful comparison of claystones from concretion horizons and from their separating layers has not revealed any difference between them. However, even though stringers with diagenetic concretions are traceable for kilometers, they are not quite as consistent as, e.g., the obviously sedimentary marl beds that extend for tens and hundreds of kilometers. Finally, a sedimentary origin of rhythmically arranged concretion horizons implies a rapid and recurrent change in sedimentation conditions for the very deposits accumulating under the most subdued and stable conditions.

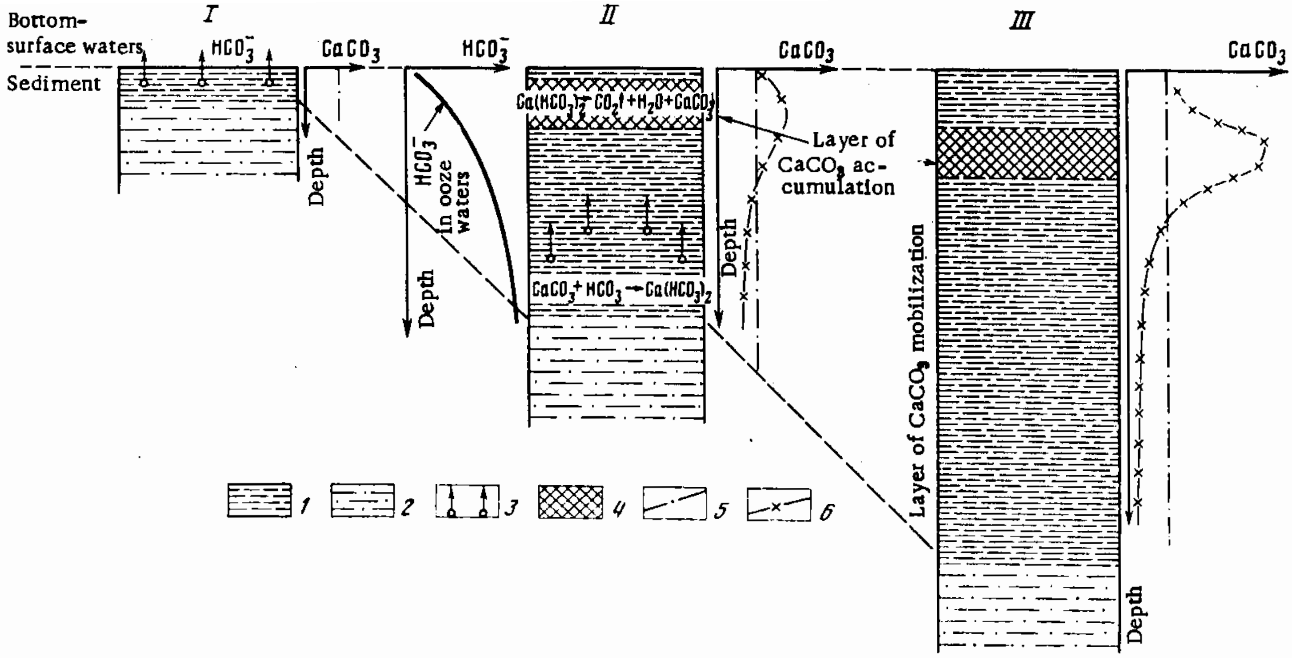

Fig. 4. Diagenetic development of the carbonate layer in argillaceous sediments: 1) argillaceous sediment enriched in organic matter; 2) clayey silt; 3) direction of diffusion for Ca bicarbonates and HCO_3^- ions; 4) layer of diagenetic accumulation of Ca carbonates; 5) original content of $CaCO_3$ in sediment; 6) probable change in $CaCO_3$ content in sediment, in the course of diagenesis.

Analysis of the constitution of concretion horizons leads to the conclusion that diagenetic processes not only determined the development of concretions as the result of material redistribution within layers enriched in carbonates but also actively produced these stringers in sediments with an originally uniformly distributed carbonate substance.

The behavior of calcium carbonate in sediments, and consequently in the course of carbonate concretion development, is known to be controlled by the carbon dioxide regime of ooze waters. It is therefore important to know the behavior of carbon dioxide in the active zone of diagenesis.

Study of present sediments shows that, in the majority of instances of sulfate reduction in oozes, the loss of sulfates in ooze waters is accompanied by an increase in HCO_3^- (the sum of HCO_3^-, CO_3^{2-}, and CO_2) at the expense of reduction processes (Shishkina, 1972, and others).

In considering the dynamics of reduction processes, Strakhov (1972, 1976) noted that, although HCO_3^- generation is particularly intense in upper horizons of ooze, its content here is at a minimum, because the bulk of ions is removed to bottom-surface waters. At the same time, its concentration rises in deep horizons of the sediment, owing to the difficulty of its removal. The alkali reserve also increases here, due to solution of $CaCO_3$ dispersed in ooze.

As also noted by Strakhov (1976), the HCO_3^- ion renders incidental service in recrystallization of calcium carbonate. First, it transfers into solution the more soluble (usually aragonite) phase of $CaCO_3$; then it is removed from oozes as diagenetic $CaCO_3$ is precipitated.

These two aspects of the geochemistry of ooze processes (higher content of HCO_3^- in ooze waters, with depth; and action of HCO_3^- on redeposition of calcium carbonate) most probably played a critical role in the development of diagenetic carbonate layers.

A generalized mechanism of diagenetic stratification is illustrated in Fig. 4.

For simplification, we consider a layer of clayey silt with poorly expressed diagenetic processes, when it begins to get covered with clay oozes enriched in active organic matter. At initial stages of ooze deposition (Fig. 4I), when its layer is but centimeters thick, the bulk of HCO_3^- ions, originated in reduction processes, are removed to bottom-surface waters. No appreciable solution of $CaCO_3$ dispersed in sediment takes place at this stage.

As sediments accumulate (Fig. 4II), removal of HCO_3^- from the deepest subsided parts of the layer becomes progressively more difficult and it begins to accumulate. This sets up a difference in HCO_3^- concentration, in ooze waters, between the near-surface and the deeper parts of ooze. When a certain content of HCO_3^- is attained, calcium carbonate dispersed in the sediment begins to dissolve. The produced calcium bicarbonates diffuse from deeper horizons to the near-surface part of ooze. Here, a reaction reverse to $CaCO_3$ dissolution takes place at the lower content of carbon dioxide in oozes:

$$Ca(HCO_3)_2 \rightarrow CO_2\uparrow + H_2O + CaCO_3,$$

and calcite is deposited. It cannot be ruled out that a portion of bicarbonates is removed to bottom-surface waters. As a result of this process, the lower parts of ooze are rid of $CaCO_3$, while the higher parts are enriched in it. Thus a cumulative layer is created, with a $CaCO_3$ content higher than the original.

However, at the early stages, enrichment of the "cumulative layer" in carbonate material is a rather slow process. Consequently, as sediments accumulate and this layer sinks to deeper ooze horizons, it may dissolve, and the bicarbonates again migrate to the near-surface parts of ooze where calcite is deposited. Thus the "cumulative layer" is pushed upward. At the same time, its $CaCO_3$ content increases because carbonate material is mobilized out of a progressively larger volume of ooze. At a significant accumulation of $CaCO_3$ in the layer, when the available carbon dioxide of ooze is no longer sufficient to dissolve this layer, the latter becomes stationary, no longer pushed upward (Fig. 4III).

The "cumulative layer" evidently is a zone enriched in carbonate substance which gradually becomes less abundant above and below it. The probable difference in carbonate content in sediment, as compared with the original, is illustrated in Fig. 4II-III. Had development of the carbonate layer ceased right there, the outcrop would have exhibited a gradual transition for the marl layer to claystone. The fact is that redistribution of substance continues at the later stages of diagenesis: $CaCO_3$ is drawn to the layer, out of its surrounding clay (from the zone of low $CaCO_3$ content). This contributes to differentiation of sediment into two phases and brings about a sharper boundary between them.

Depending on how much $CaCO_3$ is mobilized from the sediment (from the "mobilization layer"), the degree of carbonate enrichment in the "cumulative layer" varies greatly — from a comparatively slight increase in $CaCO_3$ concentration, as compared with the regional, to a very considerable increase, of tens percent and locally over 50%. Correspondingly, as seen in the section, these stringers can hardly be told apart from the groundmass, in some instances, and are readily identifiable as a marl bed, in others.

In the course of diagenetic stratification, the "cumulative layer" itself lost its uniformity, which led to redistribution of material and its concentration in concretions. The latter are much more resistant to dissolving action of carbon dioxide than the minute aragonite shells and very fine $CaCO_3$ particles dispersed in sediment. They maintain their stability even in deeper ooze horizons.

When a sufficiently thick layer of sediments has been accumulated — at least several times thicker than the "mobilization layer" — the process of diagenetic stratification can continue after the first carbonate stringer has been formed. By the same token, calcium carbonate is redistributed in sediments overlying the newly developed layer. This leads to development of layer two, three, etc. Such a diagenetic reworking of sediments continues as long as this type of sediments is accumulated. The recurrent development of carbonate stringers produces a rhythm in the sedimentary sequence. Figure 5 illustrates the development of a rhythmic concretion horizon.

Thus, the processes of diagenetic redistribution of substance culminate in emergence of a substantial lithological inhomogeneity in the originally uniform sediment.

The Chokrakian-Karaganian black siltstones are abundant in minute pyrite nodules indicative of a significant intensity of reduction processes. We see then that conditions favorable for diagenetic transformation prevailed here.

However, the fact that rhythmicity of the Chokrakian-Karaganian deposits is associated only with a certain definite type of claystones indicates that certain definite conditions are prerequisite for development of diagenetic rhythm. This process evidently is controlled by such factors as the presence of reactive organic matter (OM), the rate of sedimentation,

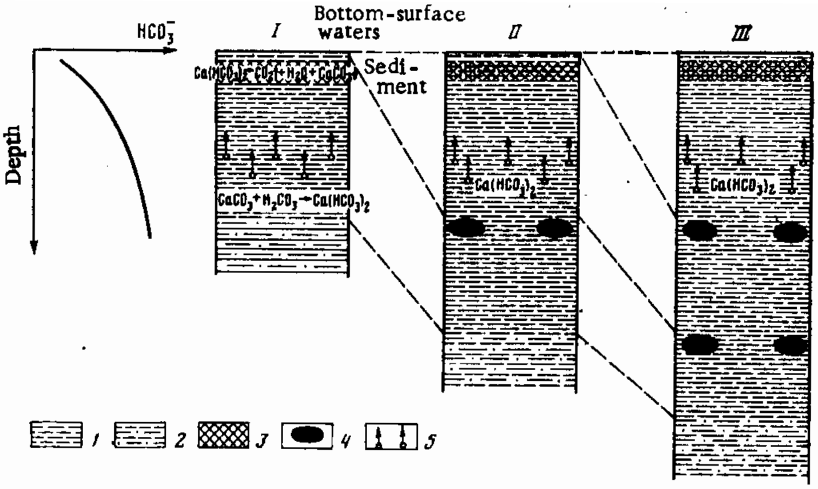

Fig. 5. Development of a rhythmic concretion horizon: 1) argillaceous sediments enriched in organic matter; 2) clayey silts; 3) layer of diagenetic accumulation of $CaCO_3$; 4) developed carbonate concretions; 5) direction of Ca bicarbonate diffusion.

the carbonate content in sediment, and the degree of its homogeneity, and perhaps some others.

To start with, it is significant that rhythm of the Chokrakian-Karaganian deposits is associated with black claystone horizons with a high OM content (C_{org}, 3-10%). This considerable content of OM is responsible for the high intensity of diagenetic reworking of sediments by virtue of its critical role in reduction processes. As another effect of these processes, a carbon dioxide regime favorable for the origin of diagenetic stringers is set up in oozes. Thus, enrichment of sediment in OM evidently is a prerequisite for development of diagenetic rhythmicity.

The rate of sedimentation has a similar effect on the progress of diagenetic processes. We know that the lower the sedimentation rate, the more intense is sulfate-ion diffusion from bottom-surface waters to oozes (Strakhov et al., 1959; Berner, 1964). In its turn, the intensity of reduction processes depends to a considerable extent on the amount of SO_4^{2-}. For this reason a low sedimentation rate should be regarded as favorable for rhythm development. This point is supported by the fact that sedimentation rates were the lowest for calcite-concretion-carrying black claystones, as determined by comparative analysis of various Chokrakian-Karaganian rocks.

It should also be noted that, at high sedimentation rates, the rate of bicarbonate diffusion in oozes may become lower than that of thickening of the sedimentary layer. In that event, bicarbonates from deeper parts of ooze would not have the time to reach the near-surface parts of sediments, and a diagenetic "cumulative layer" would not develop.

The black claystone horizons are distinguished by an almost total absence of sandy silt, which also contributed to developments of rhythms. As a matter of fact, the presence of a coarser material in clays would disturb this process, because CO_2 removal through these intercalations would modify its regime. Therefore, another prerequisite for a successful development of rhythm is a consistent accumulation of a homogeneous argillaceous sequence.

As long as development of concretion stringers entails a mobilization of carbonate substance from the entire volume of sediments, this process should have affected the change in carbonate content of claystones. The more intense the process, the less the amount of primary carbonate left behind in the rock. Indeed, a reverse relationship has been observed between C_{org} and carbonate contents of claystones: those with a considerable C_{org} content (up to 10%) are almost carbonate-free. This is well illustrated in Fig. 1, which shows a segment of the lithological and geochemical Chokrakian section along the Elistanzha River. Inasmuch as carbonate material of sediments was strongly redistributed, the resulting carbonate content does not represent the original situation. However, we have not encountered any rhythmic horizons with a carbonate content in claystones over 15-20%.

We see then that the process of diagenetic stratification is controlled by many factors, i.e., it is the function of several arguments. Variations in the latter determine the significant difference between rhythms in different parts of sections.

Many structural details of concretion horizons from the Chokrakian-Karaganian deposits are consistent with the described mechanism of rhythm development. Namely, direct relationship between the size of concretions and the spacing of concretion horizons (in the absence of appreciable increase in spacing of concretions within the layer), is better understood. Indeed, the greater volume of sediment out of which carbonate was mobilized (i.e., as spacing of layers increases), the greater is the size of concretions (Figs. 2 and 3). The calcite concretions have never been observed in the base of black claystones owing to the necessity for reworking a definite volume of sediments that would produce enough material for the concretion layer. It should be noted, however, that reasons for the considerable fluctuation in the spacing of diagnetic layers are not clear, as yet. An answer to this question requires additional special study on a greater number of objects.

Rhythmic structure of horizons in the Chokrakian-Karaganian deposits is typical primarily of early diagenetic calcite nodules. The reason is that the rhythm-producing process is most active at the early diagenesis stage, in the active zone of sediment, about 1.5 m thick (Strakhov, 1976), with the highest gradient of alkali reserve. Inasmuch as spacing of calcite concretion layers is 10-30 cm, as a rule, and the black siltstones compact in diagenesis by a factor of 4-5 (Gavrilov, 1977), this spacing in loose oozes was 0.5-1.5 m. A loose character and high water content of oozes are necessary also for a successful diffusion of bicarbonates in bottom-surface waters.

There are numerous indications that calcite concretions developed precisely in the uppermost horizons of sediments. Later on, siderite developed on these concretions in some of the compacted horizons, to form zoned nodules. Significantly, siderite of these horizons did not produce independent nodules but concentrated about the calcite cores developed at different stages of diagenesis. However, differentiation of carbonate and argillaceous substances, in early diagenesis, was not effective enough to be expressed in chains of concretions or intercalations within the developed rock. Diagenetic stratification was expressed also in the emergence of slightly carbonate layers. In any event, inhomogeneity of the sediments was high enough to control the redistribution of authigenous components of ooze at the later stages of diagenesis. If there was a subsequent development of carbonates, such as $FeCO_3$, in the sediments, they concentrated, as in the development of zoned concretions, in stringers enriched in $CaCO_3$ and were deposited about them.

Another point to be considered is that stringers enriched in carbonate material could have played the role of peculiar geochemical filters. In consequence of higher pH of these stringers, carbonates dissolved in water squeezed out in compaction were deposited here and raised their content in the stringers, thereby contributing to differentiation of the sediment into two phases.

Thus, lithological inhomogeneity, originated in sediments at early stages of diagenesis, intensified with time.

It has been repeatedly observed in the Chokrakian-Karaganian deposits that the chains of concretions change along the trend to a continuous thin (2-4 cm) layer traceable for hundreds of meters. These layers undoubtedly are diagenetic. The critical factor of carbonate concentrations in nodules or in a layer evidently is the amount of mobilized carbonate substance: a continuous layer is developed at high concentrations. As seen in the section, these layers can be mistaken for the original sedimentary beds. The criteria of their diagenetic origin evidently are their lateral inconsistency (hundreds of meters; less commonly a few kilometers); the presence of a considerable amount of definitely diagenetic minerals (siderite); and the absence of definitive sedimentary features (evidence of life activity, turbidity, submarine slumps, etc.).

The hypothesis of diagenetic stratification explains some of the structural features of concretion layers. For example, their splitting in two branches along the trend, as observed by some investigators (Vital, 1959, and others). Obviously, such a phenomenon cannot be the effect of sedimentation. On the other hand, the mechanism of diagenetic stratification is quite capable of producing a split-up layer. This can take place at ostensibly insignificant lateral changes in the character of sediment: variations in the content of carbonate material, organic matter, and silt. All these factors (and possibly others) affect the course of diagenetic transformations and can accelerate or slow down the stratification process, as compared with the adjoining areas. As a result, either one or two carbonate stringers may develop in different segments of one and the same layer. The second alternative is seen in section as a split-up concretion layer. [Translator's Note: The split-up effect may just as well be achieved in sedimentation.]

The diagenetic rhythms in terrigenous sediment evidently are not uncommon. Rhythmic stratification is illustrated by siderite accumulations in the Lower and Middle Jurassic rocks of Daghestan. Here, argillaceous horizons, ten of meters thick, contain numerous nodular to continuous siderite stringers, 2-3 cm thick, spaced 5-15 cm. These stringers extend for hundreds of meters without appreciable changes. Inasmuch as they consist mainly of siderite, a typical diagenetic mineral, there is no reason for ascribing to them a sedimentary origin. On the other hand, every structural detail of this rock sequence can be explained on the assumption of its diagenetic origin.

A. Hallam (1964) cites interesting data bearing on a diagenetic development of carbonate stringers in Liassic deposits of England. He noticed that the thicker the section, the more numerous are the calcareous layers it contains. The disappearance of some of the calcareous layers in the thinner sections cannot be the result of nondeposition: there are reliable paleontological data indicative of synchronism of the correlated sections. In this instance, the observed orderly cyclic sequence is wholly determined by a secondary redistribution of substance in the sedimentary section. In the opinion of Daff et al. (1971), the "rhythmic differentiation" hypothesis removes difficulties of interpreting the numerous minor but telling lithological changes in rocks throughout the section, in terms of sedimentation.

The diagenetic mechanism of carbonate rhythm implies that the critical factor of such stratification is vertical changes in HCO_3^- concentration in ooze waters. However, this is not true of all the hydrochemical types of ooze waters in present sediments. For example, HCO_3^- distribution is uniform in chloride—soda—calcium waters. Consequently, no carbonate stringers can be developed here. Even at a consistent rise of HCO_3^- content in ooze waters, with depth, diagenetic stratification does not necessarily take place, except at a certain difference in concentration. The alkali gradient is a variable dependent on a variety of factors. In the instance of present sediments, behavior of HCO_3^- in ooze waters varies appreciably (Sea of Okhotsk; Shishkina, 1972). In some areas, HCO_3^- concentration rises greatly with depth; in other areas, this increase is comparatively slight. It is therefore not surprising that, in sections of ancient deposits, even an insignificant variation in the character of component rocks lead to an appearance or disappearance of diagenetic carbonate (concretion) stringers.

The process of diagenetic rhythm development evidently is taking place in sediments of some of the present basins.

We believe that the reality of this mechanism would be substantiated by further study of sediments. However, positive results would require that investigations be carried out on suitable objects (reduced sediments; consistency of sedimentation, i.e., a comparatively uniform rock sequence precluding a sedimentary accumulation of carbonate stringers). Secondly, a comprehensive study of sediments and ooze water is necessary. Finally, the testing should be highly detailed in order to identify variations in carbonate content not only within segments of the section, but throughout its entire length.

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