Origin and Accumulation of Aluminosilicates in the Ocean[1]

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Abstract

The basic assumptions used by B. Kullenberg in his attempt to calculate the probable magnitude of the variations of the rate of accumulation of clay appear unrealistic in the light of present knowledge, and consequently the results are hardly applicable. His assumptions imply that the sizes of the clay particles now observed in samples from the ocean floor have remained essentially unchanged during transport and deposition. Most probably, however, the marine clays represent the end product of precipitation and coarsening processes, the initial particles partly being of ionic and molecular size. Changes in the rate of deposition of aluminosilicates in eupelagic areas are rather determined by physico-chemical properties of sea water than by changes in the influx to the ocean. Such changes are supposed to be practically equalled out in the neritic and hemipelagic environment.

In a recent paper (1953), B. KULLENBERG has made an interesting attempt to estimate the maximum concentration of inorganic particles suspended in the open ocean. Kullenberg's calculation is based on the assumption that the approximate size distribution of the suspended mineral matter can be derived from the size distribution of the pelagic clay sediments. Knowing the effect of size and concentration of suspended particles on the scattering of light, Kullenberg uses measurements of the latter property, and arrives at an oceanic maximum concentration of $56 \cdot 10^{-6}$ g of solid matter per liter, or $21 \cdot 10^{-3}$ g in a column of 1 cm^2 cross section at average oceanic depth. Pointing to the fact that this amount is deposited in less than 300 years over a surface of 1 cm^2 in the calcareous part of the eupelagic area of the East Equatorial Pacific, Kullenberg demonstrates in an elegant way, that, provided his assumptions are valid and complete, the amount of fine terrigenous matter present in the sea is probably insufficient to act as a buffer against variations of supply during a major climatic cycle. He further claims that these variations were probably considerable, and that consequently changes in the rate of accumulation of terrigenous matter during the Pleistocene cannot be neglected, even in pelagic areas far away from the source of supply and characterized by great regional uniformity of this rate. Therefore, it does not appear feasible to Kullenberg to base an estimate of geological time in pelagic sequences on the assumption of a constant rate of accumulation of clay in eupelagic areas.

These conclusions are contradictory to those which can be drawn from the composition of Pleistocene eupelagic clay sediments as a

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function of time. The main constituents of these sediments are solid phases, formed in the ocean (marine hydrogenous matter, GOLDBERG 1954), further solids originating in the supramarine part of the hydrosphere and transported to the sea in suspension, and finally solid phases formed in the lithosphere (lithogenous matter, ibid.), and represented by igneous minerals such as finely divided quartz. Biogenous matter is of subordinate importance in the case of most pelagic clays.

If the rate of accumulation of any of the main constituents changes considerably, as supposed by Kullenberg, this will certainly be reflected by a corresponding change in their proportios in the sediment. The probability of simultaneous changes in the rates of accumulation of all phases, such that changes in the relative proportions were cancelled out, is exceedingly small. It ought therefore to be relatively easy to trace changes in the rate of accumulation of one phase or another by variation with time of the composition of the sediment. Such changes are, indeed, frequently recognized in shelf and hemipelagic deposits. Extensive rate changes in space and time also seem to be normal features of most pelagic sediment sequences in topographically irregular areas, and in environments with a considerable influx of turbidity currents (STETSON and SMITH 1938, PHLEGER 1951, ARRHENIUS 1952, ch. 2.39—2.48, RIEDEL 1952, CORRENS 1954). Under certain conditions, however, the changes in space and time of the rate of non-biogenous accumulation appear to be lowered to a small fraction of the rate value. These conditions seemingly are fulfilled in the eupelagic area of the East Equatorial Pacific (Arrhenius, l.c. fig. 1.0). Here the thickness of the Pleistocene strata (corrected for biogenous matter in the calcareous facies) is strikingly uniform, and the Pleistocene clay deposits so far investigated are characterized by considerable homogeneity with regard to the relative proportions of the inorganic components, thus indicating that no drastic changes in the rate of accumulation of single components took place in this area during Pleistocene time. A quantitative study of these conditions is being carried out at the present time, using the sediment cores collected from the East Equatorial Pacific during the Scripps Institution CAPRICORN Expedition of 1952—1953.

The relative uniformity of the rate of non-biogenous accumulation in the east eupelagic area of the Pacific Ocean may partly be explained by the large distance to the continents, the absence of islands, the smooth, rolling bottom topography, the low seismicity, and the presence further to the east of the East Pacific Rise, acting as a barrier to turbidity currents, released on the shelf slope. Even in the predominantly eupelagic parts of the East Equatorial Pacific, local depositional disturbances are found on topographic highs, where erosion sometimes occurs, and close to these localities, where the eroded material contributes to an abnormally high rate of accumulation (ARRHENIUS 1952, ch. 2.53). These effects appear, however, to be of only local importance, probably because the eroded, coagulated sediment in suspension forms aggregates which settle out again quickly enough to prevent transport over more than a few nautical miles.

The apparent disagreement between the observed evidence of low variability in Pleistocene time of the rate of non-biogenous accumulation in the east eupelagic area, on one hand, and Kullenberg's arguments on the other, still remains to be explained. To accomplish this we shall scrutinize the assumptions, on which Kullenberg has based his reasoning. The sedimentation model used by most earlier workers, including the present author (ARRHENIUS 1952) and KULLENBERG (1953) implies that the clay particles, observed in the eupelagic deposits, were transported to the site of deposition from the continental source without any essential changes in size and internal structure. Kullenberg, in accordance herewith, uses the grain size distribution of a recent pelagic clay to compute the size distribution of particles suspended in the ocean. A serious objection against this procedure arises from the fact that the mineral grains have to a large extent been cemented to aggregates, by hydrous oxides of manganese and iron. Many minerals further appear to have undergone secondary enlargement after deposition. This makes it highly doubtful whether the size distribution quoted by Kullenberg is in any way representative of the size distribution of the grains, even at the time when they crossed the water-sediment interface. Furthermore, the static model applied, which postulates an essentially unchanged size and internal structure

of the particles from the moment of suspension to the moment of arrival to the sediment interface appears to be unrealistic in the light of recent investigations. CORRENS and v. ENGELHARDT (1938) have demonstrated that weathering proceeds by the breakdown of the parent mineral to ionic solutions and that the secondary minerals are reaction products of such solutions. A large fraction of the aluminum and silica, dissolved from continental rocks, is precipitated in the continental part of the hydrosphere or in the coastal areas of the ocean, but considerable amounts are carried in solution, even in the open ocean, and must be taken into account as a source of pelagic clay minerals. Dissolved silica is present in the sea in comparatively high concentration, and provides a steady source of reactive silicate ions. Analyses of the aluminum of sea water range between 3 and $2400 \cdot 10^{-6}$ g/l, the very high values reported from coastal waters (THOMPSON and ROBINSON, 1932; HAENDLER and THOMPSON, 1939; KALLE, unpubl., quoted by WATTENBERG, 1943; ISHIBASHI and FUJINAGA, 1951; SIMONS, MONAGHAN and TAGGART, 1953). For the sake of discussion we shall adopt a tentative figure for the open Pacific, and choose the conservative value of $10 \cdot 10^{-6}$ g/l Al. In addition to the dissolved aluminum a certain amount is present in particulate form, presumably as aluminosilicates. This amount is probably several times the mass in ionic solution. A concentration of particulate aluminum three times the concentration of dissolved aluminum is certainly a conservative estimate. The total amount of aluminum may thus be of the order of $40 \cdot 10^{-6}$ g/l. Although this figure may be far off from the true concentration, it is probably not too high, and it may be justified to use it for minimum computations. The concentration value used corresponds to $18 \cdot 10^{-3}$ g Al or $35 \cdot 10^{-3}$ g Al_2O_3 in a column of 1 cm^2 cross section at average depth, 4600 m, in the equatorial east eupelagic area of the Pacific. The mean concentration of Al_2O_3 in the eupelagic clay is 19 % by weight at 110° C and 17 % at the temperature and moisture conditions adopted in the work of the Swedish Deep Sea Expedition. Thus $18 \cdot 10^{-3}$ g Al will ultimately produce $206 \cdot 10^{-3}$ g of clay, i.e. ten times more than Kullenberg's estimate. With a rate of accumulation of $73 \cdot 10^{-3}$ g of clay per cm^2 in 1000 years (ARRHENIUS 1952, § 1. 2. 10) the period of turnover is at least 3000 years.

The aluminum bearing particles presumably have a particle size range from a few units of 10^{-8} cm to the order of magnitude 10^{-4} cm. Below the particle size 10^{-5} cm (MECKLENBURG, 1915) or $8 \cdot 10^{-5}$ cm (BECHHOLD and HEBLER, 1922) the scattering entirely follows Rayleigh's law, and the intensity of the scattered light of the Tyndall beam is thus a function of the third power of the diameter of the particles, the mass concentration of the solid phase being kept constant. Tyndall measurements, used as a basis for the determination of mass concentration, thus give far too low values, if Kullenberg's above mentioned assumption is applied with regard to the size distribution of inorganic suspended particles.

In order to arrive at a maximum figure for the concentration of the solid phase, Kullenberg allows the entire scattering observed to be regarded as due to inorganic particles. Considering the probably very small dimensions of most of these particles and the resulting weakness of the Tyndall effect, however, only a small fraction of the total scattering needs to be ascribed to inorganic matter, the main part of the Tyndall effect probably being due to plankton and organic detritus.

The mechanism of precipitation of aluminum in the sea has not yet been experimentally studied, but as the concentration in the ocean appears to be far below the solubility of aluminum hydroxide, it is believed that the primary solid phase consists of an aluminosilicate sol, which is progressively turning coarser by condensation and coagulation, and thereby settles out.

The concept of a marine origin of clay minerals is not a new one, but as far as the present author is aware, it has not been previously published or discussed in detail. Dr Josef Eklund at the Geological Survey of Sweden mentioned the idea in the early 1940's and the possibility of similar processes has recently been pointed out also by Dr George Bien at the Scripps Institution of Oceanography. The concept is in agreement with the results of GRIM, DIETZ, and BRADLEY (1949) on the properties of Pacific clay minerals. The formation of clay minerals in the marine environment has been demonstrated by NORIN's (1953) finding of authigenic illitic

mica in sediments from the Tyrrhenian Sea. The mineral is confined to coarse-grained strata, where the water can circulate readily, and Norin points out that the authigenic illite is not derived from the detrital minerals, which are perfectly fresh, and that there is no relationship between the composition of the authigenic mineral and that of the surrounding detritus.

Even if the period of turnover of non-biogenous matter in the eupelagic area of the Pacific Ocean is 3000 years or a low number multiple of this value, instead of Kullenberg's value 300 years, this period is still short in comparison with a major climatic cycle. Following Kullenberg's reasoning there would under such circumstances be a close relationship between the rate of accumulation of clay in the eupelagic environment and the considerable changes, which he postulates in the rate of influx of source material of eupelagic clay. First, however, if the source material or a great part of it prevails in dissolved form, there is no need to assume large variations in the influx of such material to the ocean during the Pleistocene. Second, even large variations in the total influx of the reactive components may have a negligibly small effect on the concentration of these components in an advanced state of the reaction, i.e., after the lapse of such a time that the water mass in question has been transported far away from a coastal area. In a second order reaction, where, for the sake of simplicity, both reactants are regarded as identical, and enter the reaction in the concentration A_0, the concentration a' found after a time t is expressed by

$$a' = \frac{A_0}{1+ktA_0},$$

where k under given conditions is a constant.

If the initial concentration were different from A_0 by a factor n, the concentration a'' at the time t would be

$$a'' = \frac{nA_0}{1+ktnA_0}$$

and thus the ratio between concentrations under these two conditions is:

$$\frac{a'}{a''} = \frac{\frac{1}{n}+ktA_0}{1+ktA_0} \qquad \lim_{t\to\infty}\frac{a'}{a''} = 1$$

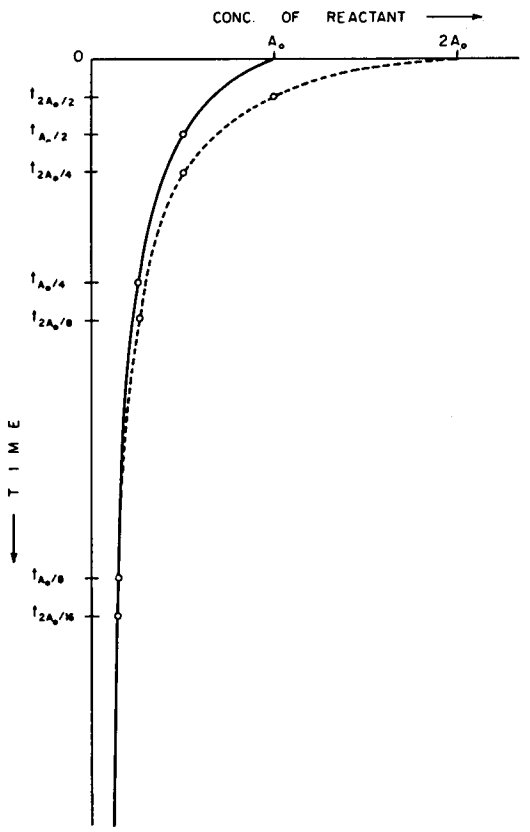

Fig. 1. Concentration as a function of time in a second order reaction. To simplify the example the reactants are regarded as identical. In the cases shown, the initial concentrations differ by a factor of two. The diagram illustrates the fact that the initial difference in concentration decreases rapidly with time, and that in an advanced state of the reaction the concentrations are practically equal in both cases. At a varying influx in the sea of suspended colloids or of dissolved thalassoxenic solids, large variations in the rate of precipitation can thus be expected in the coastal areas, close to river mouths, and negligible variations after a certain time of travel of the water mass containing the reacting system. Eupelagic conditions require that the uniformity of precipitation should be accompanied by uniformity of accumulation of the solid phase in question on the ocean floor.

$t_{A_0/2}$ indicates the first, $t_{A_0/4}$ the second, etc. half life of the reactants, in the case where the original concentration was A_0. $t_{2A_0/2}$, etc. are corresponding symbols for the case of the original concentration $2A_0$.

It is evident that the initial deviation of the ratio from unity is rapidly decreasing with increasing time and thus that differences in the initial concentration are practically eliminated in an early stage of the reaction. This is graphically illustrated in fig. 1. The rapidity

of the elimination of these differences is still greater if the reaction is of higher order, which may very well be the case.

Similar relationships hold true also for the coagulation of particulate matter, which has been demonstrated by V. SMOLUCHOWSKI (1917) to be a second order reaction. Even if a considerable amount of the eupelagic clay is of supramarine origin it is thus possible to account for eupelagic uniformity of the rate of accumulation of clay, occurring togetner with large variations in the influx to the ocean. The main factor determining the eupelagic rate of accumulation of aluminosilicates appears to be the magnitude k, which is determined by the physico-chemical properties of sea water, and therefore probably subject to comparatively small fluctuations during the Pleistocene period.

This kinetic model is a deliberately oversimplified representation of the real conditions. The precipitation, condensation, and coagulation reactions in the ocean are most certainly much more complicated and heterogeneous than a simple second order reaction. However, such a simplified model appears to be useful and significant as long as the discussion is restricted to the question whether a buffer mechanism for the pelagic rate of precipitation can or cannot exist in the ocean.

It should further be pointed out that iron, titanium and zirconium on one hand, and the aluminosilicates on the other, appear to have different cycles in the sea (LEWIS and GOLDBERG, 1954, ARRHENIUS and BLOMQVIST, 1954). Although the uniformity of the titanium content of the eupelagic clay furnishes additional evidence of uniformity of the rate of accumulation of these two components, the validity of the use of titanium for dating purposes is obviously not directly connected to the question of the rate of accumulation of clay minerals.

The estimation of geological time from accumulated mass involves the approximation of a constant rate of accumulation. The error of age determination may largely be determined by deviation of this approximation from true conditions. Our knowledge of the average magnitude and the variance of this error is at present limited to the order of magnitude, and further studies of these factors are needed. Keeping in mind actual limitations of the method, it can, however, be used for the approximation of time factors and rate processes in the area and time interval in question. Although far from perfected, the procedure appears more reliable than previously available dating methods for the Pleistocene, which place the duration of this period between the probable limits 0.6 and 2 million years.

As some confusion appears to have arisen (BROTZEN, 1953) with regard to the significance of the uniformity in space and time of the rate of non-biogenous accumulation, it should be stressed again that the conclusions drawn by the present author apply only to the area and the time-rock units, where the indicative observations have been made, i.e., to the Pleistocene strata of the east eupelagic area of the Equatorial Pacific, and in a strict sense only to the cores from which the observations in question were derived. Large areas have been investigated (ARRHENIUS, 1952) where no such uniformity was found. It is therefore erroneous to regard the concept of uniformity of the rate in question as suggested for the entire ocean bottom.

From what has been said above, it is concluded that the indications of Pleistocene uniformity of the rate of accumulation of non-biogenous matter, observed, and so far observed only in the equatorial east eupelagic area of the Pacific Ocean, are in agreement with what is so far known and what can safely be postulated with regard to the mechanism of formation of pelagic deposits. Kullenberg's criticism deals with an improbable model of petrogenesis and does not take into consideration the reaction kinetics of the process of formation of marine sediments. Although it is an interesting and elegant attempt to treat one aspect of marine sedimentation, it does not, for the reasons given, apply to the pelagic environment.

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