LIESEGANG'S STRATIFICATION DEVELOPED IN THE DIATOMACEOUS GYTTIA FROM LAKE HARUNA, AND PROBLEMS RELATED TO IT.

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Deposits were sampled from Lake Haruna by S. Yoshimura in June, 1932. They were charged in several glass tubes and kept in his laboratory with cork lids. In the course of one year, a series of reddish brown stripes developed in one of these tubes along the glass wall from the surface towards the bottom (Fig. 1). At a glance, they remind of Liesegang's stratification. After the statement of Yoshimura, the stratification had been developed to some extent in March 1933 and it seems to have grown in number downwards thereafter. The author confirmed that this was actually Liesegang's stratification by the measurement of the distance between two succeeding stripes and by the determination of their chemical composition.

The results of the measurement of the distances between succeeding stripes are given in Table 1. In the upper part, the stripes are so densely crowded that they massed into an evenly reddish brown zone and individuals are not able to be discriminated. This part is followed by a series of 16

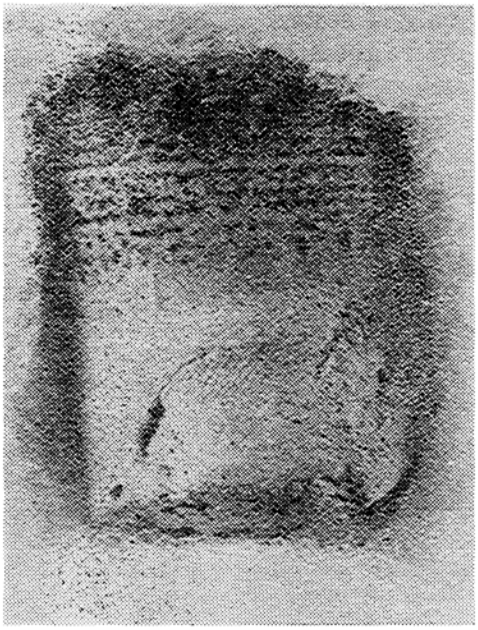


Fig. 1.

distinct stripes. The distance between two consecutive stripes grows as the stripes go downwards. This is what is observed in typical Liesegang's stratification. But there are two irregularities: One lies in that the distance, which grows downwards to the 7th stripes in the section (a), and to the 8th in the section (b), is abruptly somewhat shortened at the succeeding one or two intervals while it continues to grow larger again. The cause of this irregularity is not certain, but it might be attributed to some change of the surrounding condition in the course of the development. The second irregularity is the development of the

Table 1.

	Section a		Section b	
No. of stripe	Depth mm.	Dist. betw. consec. str.	Depth mm.	Dist. betw. consec. str.
I	3.3			
II	3.8	0.5		
III	4.2	0.4		
IV	4.6	0.4	5.0	
V	5.0	0.4	5.4	0.4
VI	5.5	0.5	5.9	0.5
VII	6.1	0.6	6.4	0.5
VIII	6.6	0.5	7.0	0.6
IX	7.0	0.4	7.4	0.4
X	7.4	0.4	7.8	0.4
XI	7.9	0.5	8.4	0.6
XII			8.7	0.3
XIII	8.5	0.6	9.0	0.3 (0.6)
XIV	9.2	0.7	9.7	0.7
XV			10.2	0.5
XVI	9.9	0.7	10.5	0.3 (0.8)

12th and 15th stripes which appear only in section (b), and disappear on the way from the section (b) to (a). Were these two stripes not present, the distance between two succeeding stripes would grow in (b) as regularly as in (a). These two irregular stripes might be independent in their origin of the other ones and they might have been developed secondarily after the completion of the main series. This is what is the case very often in actual Liesegang's stratification. However, as we know nothing about the sequence of the formation of the stripes, this way of interpretation cannot positively be sustained.

As to the comparison of the chemical composition at different parts of the sample, the author performed at first a complete analysis of the lake deposits, results of which are given in Table 2. Then the determination of the content of iron was carried out in three different parts of the sample i.e. in the reddish brown stripes, in the intermediate grey layer, and in the

Table 2.

Chemical composition of the deposits dried at 110°C.

Loss of ignition	16.97%
SiO_2	62.90
Al_2O_3 } Fe_2O_3 }	15.12
(Fe_2O_3)	(3.36)*
Mn_2O_5	0.91
CaO	2.64
MgO	0.03
(P_2O_3)	(0.40)*
	98.97

* determined colorimetrically

Table 3.

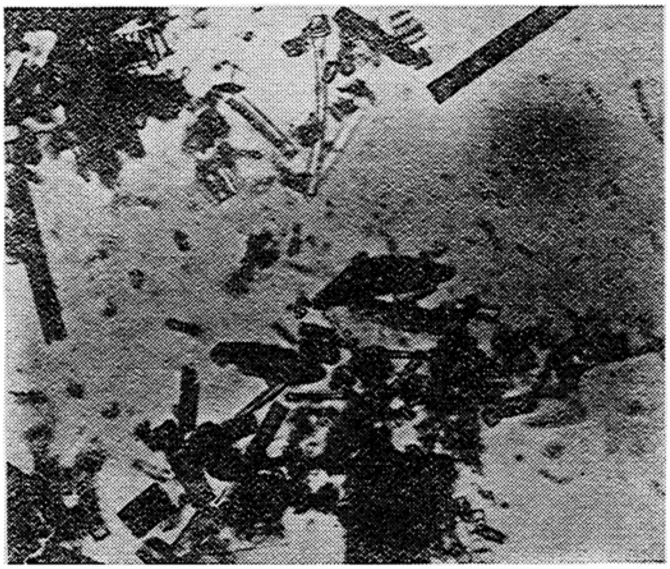
Distribution of iron in the material dried at 110°C.

	Fe_2O_3
Stripe	10.6%
Intermediate layer	5.6%
Lowest portion with no stripe	1.3%

The iron content was determined colorimetrically

lowest part where the stratification did not occur, the results of which are given in Table 3. The iron content is 10.6 per cent. in the stripe, 5.6 per cent. in the intermediate layer, and only 1.3 per cent. in the lowest part without stripes, while 3.36 per cent. in the complete anaysis, this value lying within the above three. From above analyses, it is obvious that the stripes are mainly composed of iron, which was precipitated presumably in the form of its hydroxide by the reaction between ferrous ion (which was in dissolved state beforehand in the capillary water of the deposits), and the aerial oxygen (which diffused in from the opening of the tube).

The peculiarity of the author's sample lies in that the formation of stripes is due to the oxidation by dissolved gas and in that the medium, in which the reaction occurred, is silicious deposits. In fact, as shown in



Microscopic photograph of the diatomaceous gyttia from Lake Haruna.

Fig. 2.

Fig. 2, the deposits are a typical diatomaceous gyttia with little contamination, and it seems by its highly developed capillarity to make the diffusion of dissolved gas and ion easy.

As to the mechanism of the development of the stratification little can be told because of the shortage of the facts observed. But taking in consideration that the medium is neutral in reaction and that there is little phosphate, it is probable that at least the greater part of the oxidized iron was coagulated as hydroxide and not as phosphate as it might be the case when the phosphate content were rich.

Now some geological and limnological problems, which are closely related to the stratification dealt above, will be depicted.

1) It is not rare to find examples of a geological specimen which bears a stratification resembling exactly that of Liesegang. But many cases of such a stratification are not accepted as true Liesegang's stratification. They are, except a few examples of igneous rocks such as some species of agate or malachite, mainly developed through the periodic alternation of

sedimenting materials of different natures (such being often the case in examples of sedimentary rocks).

Now in spite of this general scheme, there is one example of sandstone from Münzenberg whose stratification was interpreted as true Liesegang's one by Liesegang(1) himself in 1914 with the following description : "Verschiedene Anzeichen deuten darauf hin, dass es (Eisenhydroxyd, das verschieden dehydriert) vorher einmal in anderer chemischen Verbindung in gleichmässiger Verteilung darin (im Sandboden) vorhanden· war. Eine Zeitlang war diese Zone durch überlagernde andere Schichte der Einwirkung der Atmosphärilien entzogen. ...... Als durch spätere geologische Vorgänge die überlagernden Schichten wieder abgetragen wurden, drangen Sauerstoff, ... von der freien Oberfläche ...... Dabei wurde das Eisen intermediär gelöst ; entweder als Ferrosulfat oder als Eisenbikarbonat. Das nachdringende Ueberschuss der Atmosphärilien verwandelte letztere wieder in unlösliches Eisenhydroxyd." Now when we compare this course of formation of the stratification in Liesegang's sandstone, which is practically based upon his speculation, with that of the example from Lake Haruna, which was established actually half in vitro, both agree in their general scheme, while there is an important difference in nature that, even if the author's example be compacted, it would turn out into a clay-slate-like specimen and not into a sandstone. Anyhow, this agreement may be accepted to be an evidence which strengthens the conviction that true Liesegang's stratification can be formed in natural sedimentary rocks.

2) The secend question deals with stratifications which are *to be* found in lake deposits.

After the current opinions, there are two kinds of ways in which a stratification is developed in lake deposits. One is that in which changes of surrounding geological or climatic conditions in a long duration bring forth corresponding changes in the nature of sedimenting materials, and thus a vertical stratification is developed in deposits. The other is that in which the seasonal variation of planctic lives in the lake causes a corresponding variation of sedimenting materials and a vertical stratification is produced, where the portion between two succeeding layers of the same nature corresponds to one year sedimentation. The first example of the stratification of the latter type was given by F. Nipkow(2) in 1920 in the deposits of Lake Zürich, which provoked the interest of limnologists with the result that nowadays it is a prevailing tendency to attribute every fine stratification met with to the latter type without enough inspection.

(1) R Liesegang, *Kolloid-Z.*, **16** (1914), 21-22.

(2) F. Nipkow, *Zeitschrift für Hydrologie*, **4** (1927), 107-143.

Now the author points out other two possible ways in which a stratification can be developed. One is that in which true Liesegang's stratification is developed. Could changes take place in the actual bottom of a lake, as they did in vitro, it is very promising to find Liesegang's stratification in lake deposits. And a lake bears very often the conditions, which favour such changes to take place. For instance, in a large number of lakes in temperate zone, the period of circulation alternates with that of stagnation. In the latter period, which occurs from spring to summer, a high reduction potential is developed in the bottom layer, because of the limited supply of oxygen, and the ferric iron in deposits is easily reduced to diffusible ferrous one. Now the period of circulation, which occurs from autumn to winter, succeeds, in which the surface water, rich in oxygen gets to the bottom and oxygen may diffuse from the surface of the reduced deposits, as it did in the glass tube. Thus the bottom of some lakes bears conditions, which favour the development of true Liesegang's stratification, and this is why the author claims Liesegang's stratification as the third possible type of stratifications in lake deposits.

The fourth stratification type of lake deposits is also thinkable. Such a view is based upon the above observation that the diffusible iron is heavily adsorbed on the surface of the deposited one and the iron, which was evenly distributed beforehand, is now concentrated locally at a particular point, where it is precipitated by oxidation (see Table 3).

Thus, in the period of circulation, as the iron, present on the deposits surface, is oxidized and precipitated there, ferrous iron moves by diffusion from deeper layer towards the surface to be accumulated there.

In consequence, be such a sequence of changes regularly repeated, it is highly possible that an annual stratification is developed in which layers rich and poor in iron alternate and to which the author gives the name "the fourth possible type of stratification in deposits".

Finally it must be remarked also that there exist moments which act negatively upon the formation of these stratifications or act destructively upon the stratifications once developed. As an example of the former moment, the so-called "Mikroschichtung" may be mentioned, and as that of the latter the movement of some of benthoic animals in the deposits. Such circumstances might be given as the answer why it is not so easy to find examples of the stratifications discussed above.

3) The final problem is related to the redissolution of precipitated iron. As to its fate, iron differs from other elements in lake deposits in that it is favoured to be accumulated upon the surface of deposits as stated above.

There is another important difference between them. The iron, which is accumulated upon the surface as mentioned above, tends to be reduced into soluble state in the next period of stagnaticn, and its considerable portion, at least, may go into solution in the overlying water to be carried back to the main water due to current in the subsequent period of circulation. Thus a well-schemed cycle of iron is developed in a lake (Fig. 3).

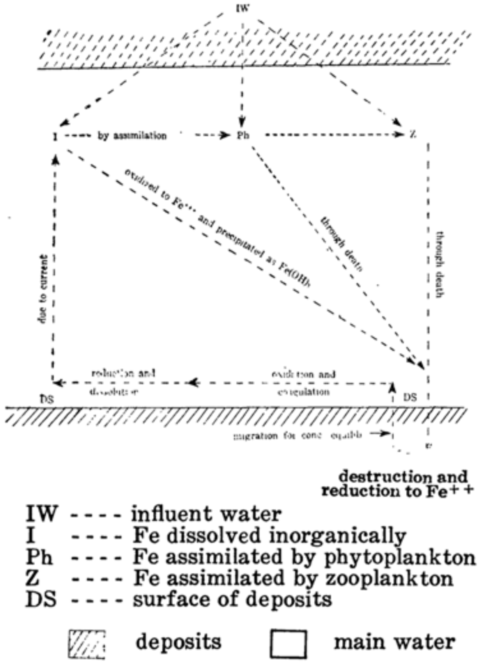


Fig. 3.

It is generally accepted that influent waters are the main supply of nourishment for lives in a lake. As to iron, however, as it is evident from its cycle established above, it can not be forgotten that deposits play an important rôle as another source of its supply. The iron, carried continuously in a lake by influent waters, may be once separated as deposits from hydrosphere, but its considerable portion is carried back into the water bosom through redissolution. Thus it results in that the content of iron in lake water becomes larger and larger as ages elapse.

Such a view that deposits are an important supply of iron to the lake water, was already advocated by many authors. Really S. Yoshimura[(3)] observed that the tropholytic zone of pond Takasukanuma increases in content of iron much towards the beginning of the period of circulation. This increase can be interpreted only by supposing that its main source lies in bottom deposits, because the computed amount of iron, carried in by influent water, does not suffice for the large amount observed.

Thus above reasoning of the author is hoped to be accepted as *one* concrete support for the view of these predecessors regarding the source of iron in lake waters.

Summary.

(1) An example of Liesegang's stratification of ferric hydroxide is given, which was formed half experimentally in the medium of diatomaceous gyttia from Lake Haruna.

(3) S. Yoshimura, *Jap. J. Geol. & Geogr.*, **8** (1931), 269–279.

(2) An evidence is given which strengthens the conviction that true Liesegang's stratifications can be found in natural sedimentary rocks.

(3) It is pointed out that there are two kinds of ways possible, besides those hitherto established, in which stratifications are developed in lake deposits.

(4) The cycle of iron in a lake is dealt, and a reasoning is given, which supports the view that a considerable portion of the deposited iron is redissolved and is carried back to the main water.

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