THE EXPERIMENTAL STUDY ON DIFFERENTIAL FLOCCULATION OF CLAY MINERALS
—AN APPLICATION OF ITS RESULT TO RECENT SEDIMENTS IN ISHIKARI BAY—

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INTRODUCTION

A series of investigations by Whitehouse and his cooperators (Whitehouse et al., 1960) have offered available sedimentological data on differential flocculation only under monomineralic dispersed system. But it seems uncertain whether their results exactly reflect natural condition under polymineralic dispersed system. For understanding the clay mineral distribution in natural sediments, it is advisable to make the experiments on polymineralic dispersed system.

Through the investigation of bottom sediments of Ishikari Bay, the author (Shiozawa, 1969) inferred that its clay mineral distribution was due mainly to be influenced by differential flocculation during sedimentation. To ascertain this inference, he makes an experiment on sedimentation of clay minerals under a certain condition.

I wish to express hearty thanks to Professor Yasuo Sasa of Hokkaido University at Sapporo and also to Assistant Professor Toshimasa Tanai of same university for their valuable advices in preparing this paper. The author is indebted to Dr. Toru Kuwabara, Meijo University at Nagoya for attracting his attention to this problem. Several fruitful discussion with Mr. Tsutomu Kondo and Mr. Hiroshi Watanabe are gratefully acknowledged.

EXPERIMENTAL METHOD

The clay minerals in Ishikari Bay are composed of montmorillonite, chlorite and illite. Whitehouse et al. (1960) described that these three clay minerals have different behavior in differential flocculation as chlorinity increases.
Montmorillonite (from Kunimine Mine)*, chlorite (from Wanibuchi Mine)* and sericite** (from Murakami Mine)* are chosen as materials of the experiment. The experimental method is as follows:

1. Clay minerals are well dispersed in distilled water, and are sized with less than $2\mu$.

2. The samples ($<2\mu$) of montmorillonite, chlorite and sericite are mixed with the equal ratio, and are diluted by distilled water to become the total weight of $0.3\ g/l$, $0.6\ g/l$ and $1.2\ g/l$ respectively. Each sample is divided into 11 beakers of 100 cc.

3. NaCl is added in 10 beakers to become $0.5$, $1$, $2$, $3$, $4$, $7$, $10$, $13$, $16$ and $18$ chlorinity ($\%$) respectively, and the remaining one beaker retains under fresh water situation.

4. Each sample of 11 beakers is well mixed. The upper suspension (30 cc) of each beaker is taken by siphon after 30 minutes' standing (B), and also after 18 hours' standing (C).

5. Two siphoned samples (B and C) and remaining part (A)** are centrifugalized at 2500-3000 rev/min. for 30 minutes. Then, settled fractions are orientated on glass plates.

6. The samples treated by ethylene glycol are X-rayed. The relative abundance**** of clay mineral composition is computed from the peak height, and is averaged from three measurements.

**EXPERIMENTAL RESULTS**

Clay mineral composition in three cases of clay concentration are different in the relative abundance with change of chlorinity as shown in figures, la, 1b and 1c.

The case of $0.3\ g/l$ clay concentration (Fig. 1a): Montmorillonite ranges from 30 to 60% in A, from 35 to 46% in B and from 48 to 52% in C. Chlorite is contained with 23-46% in A, with 29-40% in B and with 24-28% in C. The ranges of sericite are 16-25, 22-27 and 22-26% respectively. When each clay mineral quantity of A, B and C at each chlorinity are compared (Fig. 2), it is found that montmorillonite is generally most abundantly contained in C and

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* The author is grateful to Dr. Koichi Aoyagi (Japan Petroleum Development Corporation) for providing the samples.

** As the standard sample of illite is not at near hand, the author used sericite which is closely similar to illite in mineralogical character.

*** The reason which measures A is to estimate any error due to the mixture of three clay minerals as compared with B and C. As a result, clay mineral composition under chlorinity of more than $2\%$ is generally similar to that of starting material.

**** The relative abundance shows the intensity ratio of each basal reflection which reflects the real proportion of each clay mineral.
Fig. 1. Influence of chlorinity variations upon the relative abundance of clay minerals in three parts. (a) In the case of 0.3 g/l clay concentration. (b) In the case of 0.6 g/l clay concentration. (c) In the case of 1.2 g/l clay concentration. B: The upper suspension after 30 minutes' standing. C: The upper suspension after 18 hours' standing. A: Remaining part.
Fig. 2. Influence of clay concentration variations upon the relative abundance of clay minerals in three parts at each chlorinity. A, B and C are the same in Fig. 1.

most scarcely in A (maximum difference between the relative abundance of montmorillonite in A and in C is 19%), and that chlorite is generally most abundant in A and most scarce in C (maximum difference is 19%). In chlorinity of more than 10%, the particles are not deposited before 18 hours' standing with volume which is X-rayed.

The case of 0.6 g/l clay concentration (Fig. 1b): Montmorillonite ranges from 25 to 61% in A, from 35 to 52% in B and from 41 to 78% in C. Chlorite is contained with 24-51% in A, with 27-40% in B and with 10-32% in C. The ranges of sericite are 14-25, 20-24 and 12-26% respectively. In chlorinity of more than 2%, montmorillonite is generally most abundant in C and most scarce in A (maximum difference is 48%), but chlorite is generally most abundant in A and most scarce in C (maximum difference is 36%). The X-ray data in C can not be taken in chlorinity of more than 10%.

The case of 1.2 g/l clay concentration (Fig. 1c): Montmorillonite ranges from 25 to 60% in A, from 31 to 57% in B and from 56 to 91% in C. Chlorite is contained with 24-50% in A, with 26-44% in B and with 5-24% in C. The ranges of sericite are 15-24, 16-25 and 3-20% respectively. In chlorinity of more than 2%, montmorillonite is abundant in C and scarce in A (maximum difference is 65%), and chlorite is most abundant in A and scarce in C (maximum difference is 44%). The X-ray data in C can not be taken in 16 and 18% chlorinity.

Comparing the relative abundance of each clay mineral in A, B and C (Fig.
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2), montmorillonite is generally most abundant in C and most scarce in A, and chlorite is generally most abundant in A and most scarce in C under three clay concentration. The difference between the relative abundance of each clay mineral in A and in B is commonly far smaller than that between those in B and in C. The relative abundance of montmorillonite becomes larger in suspension, and chlorite becomes less at chlorinity of more than 4% as standing time increases. Differential flocculation between montmorillonite and chlorite becomes more effective as clay concentration and chlorinity increase. Sericite is similar in its flocculation to chlorite, but is, in general, less distinctly effective in differential flocculation.

The experimental results are summarized as follows. Montmorillonite remains more abundant in C than in B, compared with chlorite and sericite. Differential flocculation between montmorillonite and chlorite is more evidently found as chlorinity and clay concentration increase.

**DISCUSSION**

Differential flocculation between montmorillonite and chlorite* occurs more evidently in C at a high chlorinity: in suspension after 18 hours' standing, montmorillonite remains abundantly and chlorite remains scarcely. The stability of clay colloids is due mostly to the interaction between the van der Waals attractive force and the double layer repulsive force. Due to the compression of double layer at increasing electrolyte concentration, the range and the strength of the repulsion are considerably reduced as shown in Fig. 3. Experiments in monomineralic dispersed system reveal the following facts: the diffuse double layer of montmorillonite is less easily compressed than that of chlorite as chlorinity increases, and that the energy barrier between two montmorillonites may exist even at a high electrolyte concentration (Whitehouse et al., 1960; Sakamoto, 1967). Montmorillonite is smaller in initial particle size than chlorite. The relative abundance of montmorillonite in C, therefore, is larger than in A or B, and differential flocculation between montmorillonite and chlorite occurs more distinctly with increasing chlorinity. The inference above mentioned is done about the interaction between same minerals. How is the interaction between different minerals?

Montmorillonite has a relatively thick double layer at a high electrolyte concentration. Chlorite has a thin double layer at a comparatively low electrolyte concentration. The mutual flocculation in montmorillonites, there-

* The change of relative abundance of sericite as increasing chlorinity is roughly similar to that of chlorite. The term of chlorite which is used in this discussion, therefore, implies sericite.
Fig. 3. Repulsive and attractive energy as a function of particle separation at three electrolyte concentrations. \( V_A \): Attractive energy, \( V_R \): Repulsive energy.

The author examined the following two problems; they must be considered when he applied his results to the deposition of clay minerals in marine environment.

(1) The effects of electrolytes excluding NaCl

The ratio between the flocculation values for the monovalent and divalent cation is commonly of the order of 50-100 for a hydrophobic sols (Schulze-Hardy rule). This ratio shows unusually an order of 5 for Na- and Ca-montmorillonite sols (Olphen, 1963). Of many kinds of electrolyte contained in saline water, NaCl generally occupies about 80% of their total volume. Therefore, an experiment using NaCl as an electrolyte may be closely similar to those in saline water system.

(2) The effects of suspended particles except clay minerals

Along with positive colloids, negative ones are common in nature. The former occur usually less abundantly in nature, and represented by metallic (Al, Fe, etc.) oxides and hydroxides. The latter occur usually more in nature, and are represented by clay minerals and most of organic colloids. The colloids with different charge easily flocculate, while those with same charge interfere each other. Because organic colloids abundantly contained show characteristic properties for clay colloids, it is necessary for the application of the experimental results to examine them. There are many kinds of organic colloids, and therefore, is more difficult than in chlorites. Though montmorillonite is different in the double layer repulsion from chlorite at a certain chlorinity, coagulation value between montmorillonite and chlorite may be generally smaller than that between montmorillonites, and larger than between chlorites.

The relationship of differential flocculation with chlorinity change can be well explained by the experimental results of monomineralic dispersed system, but the fact that differential flocculation is more evidently effective as clay concentration increases, may be not explained. This fact is left unsolved.
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the author cannot fully explain their effects on clay colloids. As an example, the interaction between sodium-carboxymethylcellulose and sodium bentonite is shown in Fig. 4. When very small amount of Na-carboxymethylcellulose is added into suspension, salt tolerance of Na-bentonite considerably increases. This effect is called sensitizing action. A further addition of Na-carboxymethylcellulose, however, protects Na-bentonite; this effect is called protective action. The sensitizing and protective action are commonly found in the interaction between hydrophilic and hydrophobic colloids. As there are little known regarding to the effects of organic colloids for clay minerals in saline water, it is an important problem to be solved in future.

Fig. 4. Protective and sensitizing action of a polyelectrolyte (Na-carboxymethylcellulose) on a sodium bentonite suspension (Olphen, 1963)
AN APPLICATION OF THE EXPERIMENTAL RESULTS FOR UNDERSTANDING OF CLAY MINERAL DISTRIBUTION IN ISHIKARI BAY

It is necessary for the application of the author's experiment to satisfy a certain condition: for instance, clay minerals in surfacial sediments are recent in origin, and are supplied from one source area. These conditions seems to be satisfied in Ishikari Bay (Shiozawa, 1969). The clay minerals in Ishikari Bay are composed of montmorillonite, chlorite and illite. As shown in Fig. 5, montmorillonite is rich offshore, while chlorite is rich inshore. Illite shows little difference in relative abundance in Ishikari Bay. Their distribution appears due to differential flocculation, and not to be diagenesis and current sorting (Shiozawa, 1969).

To compared the data of Ishikari Bay with the experimental results, Ishikari Bay is divided into 3 areas: prodelta and its neighbours (P area), most of inner neritic zone (N area) and most of further offshore (O area). The average clay mineral composition of 3 areas and the suspension in Ishirakri River are shown below.

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<th>Mont.</th>
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<tr>
<td>P area</td>
<td>19.5</td>
<td>25.5</td>
<td>55</td>
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<tr>
<td>N area</td>
<td>27.5</td>
<td>25.5</td>
<td>47</td>
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<tr>
<td>O area</td>
<td>38.5</td>
<td>23.5</td>
<td>38</td>
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<tr>
<td>River suspension</td>
<td>20</td>
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Fig. 5. Areal distribution of clay minerals in Ishikari Bay
P : Prodelta and its neighbours,  N : Most of inner neritic zone,  O : Most of further offshore.
When the clay minerals of Ishikari River-suspended load come in contact with saline water, their suspension stability decreases. It is known from the experimental results that the flocculation of each clay mineral at a very low chlorinity (less than about 2°/o) is different from that at a higher chlorinity. The flocculation of clay mineral at a low chlorinity is not important to understand the clay mineral distribution of Ishikari Bay, because the chlorinity even in P area is similar to that of offshore water. Clay minerals is little different in composition between river-suspended load and sediments in P area. The resemblance in composition is evidently inferred from the fact that clay minerals in B is similar in their relative abundance to those in A. Clay minerals deposited soon after river suspension comes in contact with sea water, may be little influenced by the differential flocculation.

The clay minerals in N area contain more abundant montmorillonite and less chlorite than in P area. In O area montmorillonite is most abundant, and chlorite is most scarcely contained. The ratio of montmorillonite to chlorite becomes larger in the ascending order: P, N and O area. Such relative abundance can be explained by the fact that montmorillonite is more abundant in C than in B, and chlorite is less in C than in B: the ratio of montmorillonite to chlorite in suspension becomes larger with time required since the experiment began. The ratio of montmorillonite to chlorite in suspensions and in sediments, may changes as shown schematically in Fig. 6. The ratio in sediment I (7:8) is similar to that in river-load (1:1), and the ratio in suspensions and sediments becomes larger in the ascending order: I, II and III. As illite is little different in its relative abundance in Ishikari Bay, the author leaves it out of consideration.

As discussed above, areal distribution of clay minerals in Ishikari Bay can be well explained by the experimental results of polymineralic dispersed system. This seems to support the author's interpretation (Shiozawa, 1969): the clay mineral distribution of Ishikari Bay appears due mainly to differential flocculation.
CONCLUSION

The experiment on differential flocculation of clay minerals was performed in the polymineralic dispersed system (montmorillonite: chlorite: sericite=1:1:1). Montmorillonite remains more abundantly in the upper suspension after 18 hours' standing than those after 30 minutes' standing at chlorinity of more than 2‰, while chlorite and sericite are less. Differential flocculation occurs more effectively as chlorinity and clay concentration increase. Differential flocculation as increasing chlorinity in the polymineralic dispersed system can be explained by the difference of double layer compression of each clay mineral in the monomineralic dispersed system.

The experimental results are well explicable for areal distribution of clay mineral composition in Ishikari Bay. This seems to support the author's interpretation (Shiozawa, 1969): the clay mineral distribution of Ishikari Bay appears mainly due to differential flocculation.

REFERENCES


粘土鉱物の分凝作用に関する実験——石狩湾現世堆積物への応用——
塩沢孝之

摘 要

筆者は石狩湾堆積物中の粘土鉱物組成を調べ、その分布を規制している主な要因が分凝作用であろうと推論した（塩沢，投稿中）。その推論を確かめるべく、湾の主要構成粘土鉱物のモンモリロナイト・クローライト・イライド（代わりにセリサイト）からなる分散系で分凝作用に関するある種の実験を行なった。

それによると、モンモリロナイトは懸濁液保存装置後の時間経過に伴って、懸濁液中で相対的に混雑し、クローライト（セリサイトもほぼ同じ）は逆に減少することが明らかになった。この分凝作用は一般に塩分濃度と分散系中の粘土鉱物濃度の増加にともなって顕著になる。この結果は、Whitehouse ら（1960）の単一鉱物の分散系で行った実験結果からほぼ説明される。今回の実験結果は、石狩湾に関する筆者の推論が正しいであろうことを裏づけた。

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