MINERALOGICAL PROBLEMS OF
INTERMEDIATE CLAY MINERALS

by

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ABSTRACT

On the basis of mineralogical studies on many kinds of clay minerals found in Japan, the writers attach great importance to subtle variations in clay minerals and discuss them in the light of the concept of intermediate minerals. An intermediate mineral behaves partly as one mineral (say A) with certain treatments, and as mineral B under other conditions. There are two types of intermediate minerals: the deviation type and the mixed-layer type. The deviation type is homogeneous enough in its structure that we can describe it as composed of a combination of clearly different layer groups. The mixed-layer type has an inter-stratified structure of two or more kinds of layers. Furthermore it is suggested that each component layer of the mixed-layer type, in general, shows the properties of the deviation type. As an example of a mineral that can be discussed in light of the intermediate mineral concept, the writers describe the properties of very complex mixed-layer minerals related to mica clay minerals associated with epithermal ore deposits in Japan. Normally the mixed-layer minerals are found where there has been successive attack under different conditions of chemical environment or in an area that is transitional between two different chemical environments.

Intermediate minerals in general are considered to be a mineral state (mineral configuration) modified in various degrees from an original mineral in response to successive changes of environmental conditions. The above viewpoints are supported by study of many clay specimens collected from alteration zones of epithermal ore deposits in Japan.

It is considered that formation of intermediate minerals may be originated because of a latent defect structure in the original mineral. Polar character that is due to unequal distribution or ratio of the tetrahedral cations in a silicate layer may be favorable for the formation of the regular mixed-layer structure. Finally, intermediate minerals may be arranged according to the following scheme: Mineral A—deviation type of mineral A—mixed-layer mineral A-B—deviation type of mineral B—mineral B.

INTRODUCTION

It is well known that clay minerals identified as the same species show slightly different properties from individual to individual on close examination. Subtle variations in properties of individual samples may be

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termed "individuality of clay minerals." We frequently find minerals that have noticeable individuality and they can be called intermediate or hybrid clay minerals. They behave as mineral A with some treatments and as mineral B with other treatments. Swelling chlorite is a common example (Stephen and MacEwan, 1951), as are intermediate minerals of chlorite–vermiculite–montmorillonite (Brown, 1953; Hathaway, 1955; Tamura, 1958; Walker, 1957, 1958).

Here the writers will extend their discussion by classifying the intermediate mineral in two groups: "the deviation type" and "the mixed-layer type." The former is a mineral having some properties like those of another mineral, but its structure is homogeneous enough that we can identify it as composed of clearly different kinds of layer groups. The latter has an interstratified structure of two or more kinds of layers that are grouped into the random and regular types (Sudo, 1959). The regular type is a discrete mineral. Nonetheless, in light of the mode of occurrence, it frequently is suggested that all these types — deviation, random and regular — are intimately related in their genesis. In other words, they are considered to represent mineral states formed in the course of alteration of an original mineral. Hence it may be significant to deal with them in the intermediate mineral concept. Considerable information that allows discussion of these minerals from the standpoint of intermediate or hybrid states has been accumulated in Japan. The minerals are discussed under three headings: (1) recent mineralogical data on hydrous complexes of mica clay minerals; (2) the mode of occurrence of some mixed-layer minerals associated with epithermal ore deposits; and (3) genetic consideration.

ACKNOWLEDGMENTS

HYDROUS COMPLEXES OF MICA CLAY MINERALS

Mica clay minerals commonly are found in Japanese diaspore–pyrophyllite deposits where they occur as mixed-layer minerals that could be called interstratified illite–montmorillonite or illite–vermiculite. Close examination, however, shows that their properties vary considerably.

About 100 samples of mixed-layer minerals were examined (by Shimoda) from the diaspore–pyrophyllite deposits of the Gotō mine, Nagasaki Prefecture, and of the Yonago, Honami, and Misawa mines, Nagono Pre-

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fecture. Hydrous complexes of mica clay minerals form veinlets in those parts of the alteration zones where pyrophyllite or both pyrophyllite and diaspore are most abundant in these mines. However, they are chiefly associated with pyrophyllite. The Yonago mine is typical of these deposits, and detailed studies (including quantitative estimates of the amounts of diaspore, pyrophyllite, quartz, and kaolinite) were made.

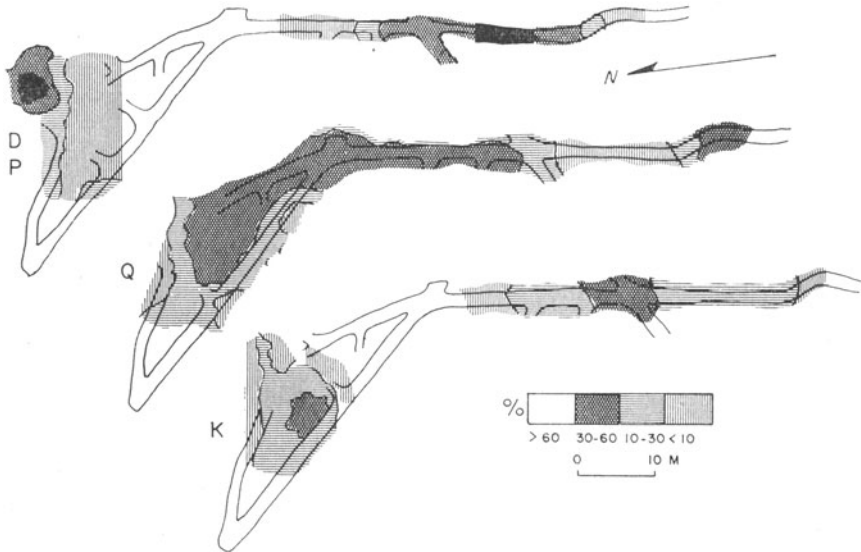The mineral distribution in the Yonago mine is complicated (Fig.1),

FIGURE 1.—Mineral distribution maps of the Yonago mine, Nagano Prefecture.
D and P: Distribution of diaspore and pyrophyllite; amounts are represented
as their total percentage. Q: Distribution of quartz. K: Distribution of kaolinite.
After Shimoda.

but kaolinite, and diaspore and pyrophyllite are most abundant in restricted areas of the mine. The mica clay minerals occupy veinlets within the areas rich in diaspore and pyrophyllite as well as those areas rich in kaolinite. In addition, a montmorillonite–aluminan chlorite mixed-layer clay occurs in those areas enriched in quartz. About 100 specimens of hydrous complexes of mica clay minerals were examined and compared under fixed conditions of treatment by taking powdered test samples from different portions of each hand specimen. The properties of these specimens are compared in Table 1; the experimental conditions are given in the footnotes. The important points are discussed in the following paragraph.

Generally speaking, these minerals can be grouped into random and regular types; the former shows a broad 10–15 Å reflection and the latter

shows a strong, sharp 24–27 Å reflection. The random type from the Gotō mine shows a broad 10–15 Å reflection, which was replaced by a 10 Å reflection after heating at 300 °C; this 10 Å reflection persisted up to 900 °C. Treatment with ethylene glycol, glycerol, and water did not noticeably affect the X-ray reflections. Treatment with 1 N KOH solution caused the 10–15 Å reflection to be replaced by a sharp 10 Å reflection.

The regular types closely resemble one another, but on careful examination they can be distinguished from each other and arranged as follows: (1) Gotō, (2) Yonago, and (3) Honami and Misawa. The Gotō material shows a sharp, strong 25.3 Å reflection; the spacing does not show noticeable variations even from several different parts of a hand specimen. This reflection was replaced by a 24.5 Å reflection after heating at 300 °C, and at 500 °C by a 19.6 Å reflection which was persistent up to 900 °C. A rehydration effect was observed even after heating at 500 °C and exposure to room air; *i.e.* a tailed reflection appeared on the low-angle side of the 19.6 Å peak. Treatment with ethylene glycol, glycerol, and water caused expansions of about 1 Å, 2 Å, and 3 Å, respectively. Treatment with 1 N KOH solution caused the 25.3 Å reflection to be replaced by a 22. 7 Å reflection.

The Yonago material (Table 2) shows a sharp, strong reflection between 24 and 27 Å; the spacing is variable in different parts of a hand specimen but has an average value of 26.1 ± 1 Å. It is noteworthy that the reflection is skewed (or tailed) toward the low-angle side. The 26.1 Å reflection is just visible up to 500–700 °C but is replaced by a weak 19.6 Å reflection at 900 °C. A 10.3 Å reflection appeared at 300 °C and became stronger progressively on raising the temperature and was persistent up to 900 °C. Treatment with ethylene glycol gave variable results; it did not give expansion in some specimens whereas a definite expansion to a 28 Å spacing occurred in some others. Treatment with water always caused the 26 Å reflection to be replaced by a 29.2 ± 1 Å reflection. A rehydration effect was observed after heating at 700 °C followed by standing at room temperature – a tailed reflection appeared toward the low-angle side of the 10 Å reflection.

The Honami and Misawa materials (Table 3) show a 25–27 Å reflection that is tailed toward the low-angle side and varies even in several different parts of a small hand specimen as in the case of the Yonago material. The 25–27 Å reflection was easily and completely replaced by a 22 Å reflection after heating at 300 °C and by a 10 Å reflection after heating at 500 °C. The 10 Å reflection was persistent up to 800–900 °C. Treatment with ethylene glycol did not show clear expansion. Treatments with glycerol and with water usually caused expansion: 2 Å with organic reagents, and about 3 Å with water. Treatment with 1 N KOH solution for 1–3 hr caused the 26 Å reflection to be replaced by a 22 Å reflection.

TABLE 1.—HYDROUS COMPLEXES OF MICA CLAY MINERALS

	Gotō	Gotō	Yonago	Honami	Misawa	Misawa
Largest spacing shown by X-ray powder reflections[1]	10–15 Å	25.3 Å	24–27 Å	26–27 Å	25.2 Å	26 Å
Color	Brown	White	White	Brown	Blue	White
Mode of occurrence	Vein-shaped mass	Vein-shaped mass	Vein-shaped mass	Vein-shaped mass	Vein-shaped mass	Vein-shaped mass
Associated minerals	Pyrophyllite, kaolinite, illite	Pyrophyllite quartz	Pyrophyllite, diaspore	Pyrophyllite	Pyrophyllite, illite	Pyrophyllite
Room temp.	10–15 Å broad	25.3 Å sharp	24–27 Å variable; tailed reflection; 26.1 ± 1 Å mean value	26–27 Å variable; tailed reflection	25.2 Å variable; tailed reflection	26 Å variable; tailed reflection
Effects of heat[2] 300 °C	10–15 Å → 10 Å	25.3 Å → 24.5 Å 12.5 Å → 11.1 Å	26 Å, just visible; 13 Å → 12.3 Å	26–27 Å → 9.94 Å	25.2 → 22 Å	26 Å → 10 Å broad
500 °C	10 Å	24.5 Å → 19.6 Å 11.1 Å → 9.8 Å	26 Å, just visible; 12.3 → 10 Å tailed reflection[5]	10 Å	10 Å	10 Å
700 °C	10 Å	19.6 Å 9.8 Å	26 Å; 10 Å, tailed reflection	10 Å	10 Å	10 Å

900 °C	10 Å	19.6 Å 9.8 Å	26 Å → 19 Å; 10 Å, tailed reflection	10 Å	10 Å	x
1000 °C	x[6]	x	x	x	x	x
Ethylene glycol[3]	No effect	25.3 Å → 26.5 Å	no effect or 26 Å → 28 Å	no effect	25.2 Å → 27 Å	26 Å → 27 Å
Glycerol	No effect	25.3 Å → 28.5 Å (2 Å expansion)		26 Å → 27.9 Å (2 Å expansion)	25.2 Å → 27 Å (2 Å expansion)	26 Å → 28 Å (broad)
Water	No effect	25.3 Å → 28.8 Å (3 Å expansion)	26 Å → 29.2 Å	26 Å → 28.7 Å (3 Å expansion)	25.3 Å → 28 Å (3 Å expansion)	26 Å → 29 Å (3 Å expansion)
1N KOH[4]	10 Å (1 hr)	25.3 Å → 22.7 Å (1–9 hr)		26 Å → 22 Å (1–3 hr)		

[1] This table shows mostly the effects of heat and other treatments on the largest spacing shown on X-ray powder reflections. About 1 g of each specimen was pulverized in an agate mortar, packed into an aluminum holder, and radiated with X-rays.

[2] Test powders were heated at the designated temperature for 1 hr and irradiated with X-rays immediately after cooling by exposure at room temperature.

[3] Treatment with ethylene glycol, glycerol, or water: test powders packed into holders were immersed in these materials and set aside for 30 min; extruded portions were then cut off to make a smooth, flat surface.

[4] Test powders were immersed in this solution at room temperature, and supernatant liquid was removed; powders were washed with distilled water and dried at room temperature. KOH treatment for 1 hr gave the effect described in the table. Treatment for a longer time did not produce additional changes.

[5] Tailed reflections that appeared in heated specimens are considered to be due mostly to rehydration. In the Gotō material (25.3 Å type), the 11.1 Å peak was gradually replaced by a 12.5 Å reflection when the specimen was heated at 300 °C and allowed to remain in contact with room air for several hours. Furthermore a tail appeared on the low-angle side of the 19.6 Å reflection when the specimen was heated at 500 °C and allowed to remain in contact with room air for several hours. Rehydration effects were not observed in the specimen heated at 700 °C.

[6] x: Powder reflections of the clay minerals have been completely destroyed.

Mineralogical behavior of these regularly interstratified specimens can be summarized as follows:

(1) The long spacing of the Gotō mineral does not show noticeable variation from sample to sample, whereas the spacings of the other minerals vary considerably in different parts of a hand specimen and show a tailed reflection on the low-angle side of the principal spacing.

(2) On heating, the Gotō mineral shows 19.6 Å and 9.8 Å reflections whereas the other minerals show a 10 Å reflection and its higher order reflections agreeing with those of mica clay minerals.

(3) A rehydration effect can be observed in all these minerals after heating to 500–700 °C.

(4) Treatment with water caused expansion of about 3 Å in all of them.

(5) Treatment with 1 N KOH solution at room temperature caused the long spacing to be replaced by a 22 Å reflection.

(6) Treatment with ethylene glycol or glycerol usually caused expansion of 2 Å, but the results obtained are not universal. The Gotō mineral usually gave a 1 Å expansion with ethylene glycol, but a 2 Å expansion with glycerol. The Honami and some samples of Yonago minerals did not show expansion on treatment with ethylene glycol, but they did expand on treatment with glycerol.

Thus we note that slight variations are shown by different parts of a hand specimen, particularly in the long spacing and its behavior on treatment with ethylene glycol. But we could find no correlative relationship in these behaviors. Among many X-ray data, two examples are given in Tables 2 and 3. Three chemical analyses are given in Table 4. Inasmuch as it was difficult to make complete chemical analysis of each part of a hand sample, each analysis gives the mean chemical composition of powders obtained by pulverizing and mixing a hand specimen (about 100 g). The samples analyzed chemically were tested by X-ray and it was found that they were pure with respect to the mixed-layer minerals under consideration.

There is no doubt that complex solvation behavior depends on the interlayer ion population. However, the dependency is not clear, because these natural samples are unsaturated with respect to Na, K, and Ca ions. The chemical analyses are thought to show only their mean chemical behavior. Nonetheless the Gotō mineral in general contains more Na as well as total Na, K, and Ca than the other mixed-layer minerals. It seems that expansion due to ethylene glycol tends to be interrupted somewhat by the interlayer population of Na and K ions.

Assuming that the number of ions in tetrahedral and octahedral layers is 12, the number of ions of Na, K, and Ca is as follows:

Gotō: Na, 0.50; K, 0.20; Ca, 0.14; total, 0.84.
Yonago: Na, 0.10; K, 0.51; Ca, 0.08; total, 0.69.
Honami: Na, 0.23; K, 0.42; Ca, 0.01; total, 0.66.

TABLE 2.—X-RAY DATA FOR HYDROUS MICA COMPLEX FROM THE GOTŌ MINE
(UNHEATED AND HEATED SPECIMENS)
(CuK$_\alpha$: 1.5418 Å)

20 °C		300 °C		500 °C		700 °C		900 °C		1000 °C	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
26.0	VS										
		24.5	8SB								
				20.5	5B	19.6	4S	19.6	3SB		
12.5	69VS										
		11.1	13SB								
				9.83	24VS	9.83	23VS	9.83	7S		
9.21	21VS	9.31	11S	9.31	11VS	9.31	7S	9.21	5S		
8.51	3B										
				6.61	3B	6.42	3B				
										5.50	6SB
5.01	20VS	4.98	10S								
				4.85	16S	4.85	17VS	4.87	8S		
4.62	15VS	4.60	4S	4.85	16S	4.85	17VS	4.87	8S		
4.44	13S	4.44	16S	4.51	28VS	4.46	32VS	4.44	15S		
								4.23	8S		
3.99	2VS										
3.93						3.90	5SB				
3.56	3SB	3.53	3VB								
										3.44	11S
3.35	1	3.56	4B	3.35	13S			3.39	5SB		
3.31	3SB										
3.13	21S	3.13	13S	3.23	33VS	3.24	34VS	3.25	17VS		
										3.14	5S
3.07	31VS	3.07	12VS	3.08	13VS	3.11	16VS	3.11	14VS		
										2.90	4SB
						2.84	3B	2.88	3SB		
						2.77	2	2.71	2B	2.72	5SB
2.56	4SB	2.56	11S	2.57	7SB	2.57	7SB	2.59	4SB		
								2.54	6S	2.56	5S
								2.46	3SB		
2.43	2B	2.42	3B	2.43	4B	2.44	4SB	2.43	3SB		
2.30	2S	2.30	2S					2.31	2B		
				2.25	3SB	2.21	3	2.20	4S	2.22	7S
				2.18	2B			2.17	2		
		2.14	3B	2.15	3S			2.12	3S	2.14	3SB
1.93	2B					1.95	3VB				
1.84	3SB			1.84	3S						
				1.82	2SB						
						1.71	2				
						1.68	2VB	1.68	2VB		
		1.65	2VB								
						1.66	3S				
								1.61	2	1.61	3SB
								1.60	2		

(Table 2 continued)

20 °C		300 °C		500 °C		700 °C		900 °C		1000 °C	
$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I
								1.58	1		
								1.55	1		
										1.53	4 SB
1.49	5 S	1.49	7 S	1.50	3 VB	1.50	3 B	1.52	3 SB		
										1.45	2 SB
								1.40	2 VB	1.41	2 VB

VS: Very Strong. S: Strong. B: Broad.

TABLE 3.— X-RAY DATA FOR HYDROUS MICA COMPLEX FROM THE
HONAMI MINE (UNHEATED AND HEATED SPECIMENS)
(Cu K_α: 1.5418 Å)

20 °C		300 °C		500 °C		700 °C		900 °C		1000 °C	
$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I	$d(\text{Å})$	I
26.8	36 VS										
12.6	36 VS										
		9.94	12 S	9.98	10 S	10.0	8 S	10.0	11 S	9.94	6 S
9.21	3 VS										
5.07	12 S	4.87	7 BS	4.90	6 BS	4.95	7 S	4.95	8 S	4.95	5 S
4.48	10 VS	4.46	16 VS	4.46	18 VS	4.48	26 VS	4.48	29 VS	4.46	21 VS
										4.09	3 BS
										3.74	3 VS
										3.63	2 S
3.52	7 VS	3.50	4 S	3.50	3 S	3.50	4 S	3.50	3 S	3.50	3 S
3.19	11 SB	3.24	8 BS	3.25	10 BS	3.27	12 S	3.27	15 S	3.33	8 B
										3.11	2 VB
2.56	6 SB	2.56	8 S	2.57	7 S	2.57	6 BS	2.57	5 BS	2.57	4 B
2.48	2 B										
2.44	2 B			2.42	2 VB						
2.38	3 B										
1.99	2 B										
1.86	3 B										
1.48	5 B			1.49	3 VB						

VS: Very Strong. S: Strong. B: Broad.

Although reliability is not expected to be good, because we could not obtain enough reflections, X-ray patterns of these specimens were analyzed by the Fourier transform method proposed by MacEwan (1956). For the Gotō mineral, the 15.5 Å and 9.8 Å peaks were obtained from untreated samples, the 17.3 Å peak was obtained by glycerol treatment, the 19 Å peak was obtained by water treatment, and the 12.5 Å peak was obtained

by KOH treatment. For the Yonago, Honami and Misawa minerals, three peaks at about 10 Å, 13 Å, and 16 Å were obtained in untreated samples, but in the treated samples the same results were obtained as with Gotō material; the peak of 17–18 Å was obtained by glycerol treatment, 19 Å by water, and 12–13 Å by KOH treatment.

In the light of the present data, the Gotō material is nearest to allevardite (Caillère, Mathieu-Sicaud, and Hénin, 1950) analyzed by Brindley (1956), but it is doubtful that the present specimen is as simple as a structure made up of potassium ions and a double layer of water molecules without exchangeable cations occupying the interlayer positions.

Other minerals seem to be composed of a more complex stacking of layers, suggested particularly by a tailed 24–27 Å reflection.

The following model for such a complex mixed-layer structure is proposed here: In a mica clay mineral and its hydrated states, several kinds of layers can be considered: (A) a 10 Å layer of mica clay mineral, (B) a 12.5 Å layer obtained when potassium ions are replaced completely by a single layer of water molecules, and (C) a 15.2 Å layer obtained if potassium ions are completely replaced by a double layer of water molecules. These

TABLE 4.—CHEMICAL COMPOSITION OF HYDROUS COMPLEXES
OF MICA CLAY MINERALS

	(1)	(2)	(3)
SiO_2	44.80%	43.17%	45.44%
TiO_2		0.51	1.54
Al_2O_3	33.88	33.54	33.37
Fe_2O_3		0.26	
FeO	0.39	0.13	0.26
CaO	0.97	0.52	0.06
MgO	1.24	0.65	1.10
Na_2O	1.88	0.38	0.65
K_2O	1.13	2.84	1.96
H_2O (+)	6.91	7.75	7.48
H_2O (−)	8.13	10.48	7.40
S			0.14
P_2O_5	none	tr.	
Total	99.33	100.23	99.40

(1) Hydrous complex of mica clay mineral from the Gotō mine, Nagasaki Prefecture (Analyst: S. Shimoda),
$(Na_{0.50} \cdot K_{0.20} \cdot Ca_{0.14}) \cdot (Al_{3.67} \cdot Fe_{0.01} \cdot Mg_{0.32}) \cdot (Si_{6.18} \cdot Al_{1.82} \cdot O_{18.41} \cdot (OH)_{6.40}$.

(2) Hydrous complex of mica clay mineral from the Yonago mine (diaspore–pyrophyllite), Nagano Prefecture (Analyst: S. Shimoda),
$(Na_{0.10} \cdot K_{0.51} \cdot Ca_{0.08}) \cdot (Al_{3.83} \cdot Fe_{0.02}^{III} \cdot Fe_{0.01}^{II} \cdot Mg_{0.14}) \cdot (Si_{6.21} \cdot Al_{1.79}) \cdot O_{17.74}(OH) \cdot {}_{7.34}$.

(3) Hydrous complex of mica clay mineral from Honami mine, Nagano Prefecture (Analyst: S. Shimoda),
$(Na_{0.23} \cdot K_{0.42} \cdot Ca_{0.01}) \cdot (Al_{3.75} \cdot Fe_{0.03}^{II} \cdot Mg_{0.22}) \cdot (Si_{6.30} \cdot Al_{1.70}) \cdot O_{17.92} \cdot (OH)_{6.91}$.

three layers are ideal ones. Intermediate states in which potassium ions are still associated with water layers also are possible. Inasmuch as the number of potassium ions associated with water layers are small, the fluctuation of these cell heights may be small, and the principal cell heights would be grouped around 10 Å, 13 Å, and 16 Å. Various combinations of these three kinds of layers were considered, and finally it was shown that the structure of a random stacking of layers of 25.1 Å $(A + C)$ and 27.6 Å $(B + C)$ in equal proportions gave the calculated intensity values nearest to the mean observed ones. Actually it is appropriately considered that small numbers of potassium ions are still preserved even in B and C layers, because, as shown above, the X-ray powder reflections of mica clay minerals are revealed in the reflections of the fired products (Yonago, Table 1).

Furthermore, the long spacings show slight fluctuations even in small parts of specimens; hence the way the layers are stacked varies somewhat. The variation of the proportions of the different layers may be one of the important causes of this fluctuation. It is difficult to estimate the interlayer population of these three kinds of lattices, but it is natural to consider that interlayer population decreases in the order of $A - B - C$. The above model is only to show an average configuration.

It is also difficult to evaluate the expansion behavior of A, B, and C layers. It is natural to consider that, usually, A is nonexpandable and C is expandable and its maximum degree of expansion is attained in the experimental conditions applied. But the expansion behavior of the B layer is difficult to predict. It is thought that it may expand by the uptake of a single layer of ethylene glycol, or expand to the same degree as the C layer, or to a lesser degree than the C layer, thereby taking up fewer layers of water molecules than the C layer. However, the expansion behavior of the B layer also depends upon experimental conditions such as time.

Under the experimental conditions of treatment with organic materials, water, or inorganic solutions, we usually obtained strong reflections with the tailed expanded spacings, and particular reflections did not become broad or split into doublets. This fact may suggest that the height of the expanded B layer still remains at a fixed value smaller than that of the expanded C layer. The fundamental scheme of structure after expansion may be expressed as the same manner of stacking of three kinds of layers; in this case nonexpandable A layers, expandable C layers, and B layers having a cell height intermediate to those of the A and C layers.

From the above considerations we would expect that the expansion behavior of the Yonago, Misawa, and Honami minerals should be similar to that of the Gotō material (Table 1).

With KOH treatment, it is possible that the C layer partly contracted to 12 Å and the B layer to 10 Å. In our model with random stacking of $(A + C)$ and $(B + C)$ layers, the C layer is partly associated with the A

layer and partly with the B layer. The C layers themselves even may be slightly different from each other in interlayer population and expansion behavior. Furthermore, it is possible that the C layer associated with the A layer is slightly different from that associated with the B layer.

It actually can be predicted that interlayer population and degree of hydration possibly are not unique even in A, B, or C layers of such a complex mixed-layer structure. The kinds of layers are only grouped into three types based on idealized heights. Occurrence of a weak 19.6 Å reflection in the Yonago material suggests that the manner of stacking of layers is partly similar to the Gotō material, but that its structure actually is more complex. Generally speaking, the behavior of the layer assemblage of the Yonago material is intermediate to that of the Gotō and Honami–Misawa materials.

In summary then, properties of component layers of these complex mixed-layer clays, which are related to the mica clay minerals, are appropriately expressed as having intermediate characters of an illite–vermiculite–montmorillonite assemblage. They are a group of minerals derived from mica clay minerals as a result of various degrees of hydration and leaching. It is strongly suggested that hydration and leaching are more advanced in the order (1) Gotō, (2) Yonago, and (3) Honami and Misawa materials.

In the materials other than those from Gotō, a slightly advanced hydration effect has formed a 12.5 Å layer (B layer), in which K^+ is replaced completely by a single layer of water, in their structure. The structure is built up then of a complex stacking of three kinds of layers: (A) 10 Å layer of mica clay mineral, (B) 12.5 Å layer, and (C) a 15.2 Å layer containing a double layer of water.

MIXED-LAYER MINERALS ASSOCIATED WITH METALLIC ORE DEPOSITS

As reported in earlier papers, mixed-layer minerals commonly have been found associated with alteration zones developed around epithermal ore deposits (Sudo and Hayashi, 1956, 1957; Sudo and Kodama, 1957; Sudo, Hayashi and Yokokura, 1958). Recently Hayashi made further detailed mineralogical analyses of about 500 specimens collected from alteration areas of the following epithermal ore deposits: the Hanaoka mine, Akita Prefecture; the Kamikita mine and the Aomori mine, Aomori Prefecture. He subdivided the alteration halos on the basis of clay mineralogy at each mine as follows:

(a) At the Tsutsumizawa ore bodies of the Hanaoka mine, which contain pyrite, galena, sphalerite and gypsum, the zoning is country rock (liparitic tuff) — montmorillonite zone (about 10 m wide) — chlorite–illite zone (about 1 m) — ore body.

(b) At the Honkō ore body of the Kamikita mine, which is composed of pyrite, the zoning is country rock (liparite and liparitic tuff) — pyrophyllite zone — pyrophyllite–diaspore zone — pyrite ore body.

(c) At the Ōtaki ore body of the Aomori mine, where pyrite is mined, the zoning is country rock (liparite and liparitic tuff) — kaolin zone (kaolinite, dickite, nacrite and a small amount of alunite) — pyrophyllite zone — pyrite ore body.

Silica-enriched areas are found in Tsutsumizawa and Yonago. Inasmuch as these areas are found from place to place in the various alteration zones, they are not recognized as a zone surrounding the ore. In Tsutsumizawa, they are distributed near the main ore bodies, are rich in pyrite, and are worked as pyrite ores.

Regular mixed-layer chlorite–montmorillonite, and hydrous complexes of randomly and regularly interstratified mica clay minerals, are found in the alteration zones. Regular mixed-layer montmorillonite–chlorite occurs (a) at the margin of ore bodies (in contact with the ore bodies) of sphalerite and galena (Tsutsumizawa), (b) in a transitional·zone between the montmorillonite zone and the chlorite–illite zone (Tsutsumizawa), and (c) in pyrite veinlets at the margin of the main ore body (Honkō). In (a) and (c), the chlorite layers are of the aluminan type.

Hydrous complexes of mica clay minerals of the regular type occur (a) in the transition zone between the montmorillonite zone and the chlorite–illite zone developed around gypsum deposits (Tsutsumizawa) and (b) in interspaces of pyrite crystals at the margin of the main ore body (Honkō). Hydrous complexes of mica clay minerals of the random type occur: (a) filling interspaces of the siliceous area (Tsutsumizawa), and (b) in the transitional zone between the montmorillonite zone and the chlorite–illite zone developed around gypsum deposits or sphalerite–galena ore bodies (Tsutsumizawa). The ratio of the 10 Å and 15 Å layers is about 70 : 30 to 80 : 20.

Origin of Mixed-layer Minerals

The modes of occurrence of hydrous complexes of mica clay minerals and the mixed-layer minerals associated with epithermal ore deposits may be grouped as follows: (a) in a transitional zone between two adjacent alteration halos; (b) in lenticular vein-shaped masses in alteration areas; (c) filling interspaces of ore minerals, mostly at the margin of main ore bodies; and (d) in areas of silica enrichment. All these are considered to be places subjected successively to different conditions of chemical environment. However, physical conditions should not be ignored. Cavities in an alteration zone may indicate places where residual solutions successively attacked minerals previously formed in the cavities. Interspaces between ore minerals at the margin of ore bodies may indicate places where ore

solutions successively attacked minerals previously formed near the ore bodies. Areas of siliceous enrichment indicate places where a residual solution successively attacked original materials and influenced leaching processes.

The origin of the mixed-layer minerals is not unique. But in reference to the mineralogical data of hydrous complexes of mica clay minerals and the mode of occurrence of mixed-layer minerals in epithermal ore deposits, the following statement may be permitted: the mixed-layer mineral is a mineral state modified to various degrees from an original mineral by an alteration process, wherein the original material is altered in response to successive changes in environmental conditions.

Why are some layers selectively altered? The writers consider that one of the mechanisms of the formation of the mixed-layer mineral originates from a defect structure that is latent in an original mineral. What kinds of defect structures should be considered? One of the possible models is as follows: layers are slightly different from one another with regard to distribution or ratios of isomorphous ions. When the degree of defect is noticeably greater in some groups of layers than in other groups, chemical attack may cause selective alteration in the more defective layers whereby a random mixed-layer mineral may be formed.

For formation of the regular type of mixed-layer structure, the following model can be considered. It is possible that a defect configuration may give a clearly polar character to each layer; that is, two tetrahedral layers of a silicate layer are quite different from each other in the distribution of Si and Al ions or the ratio of Si to Al. Following the general concepts of crystallography, polar structure units tend to join with each other to form nonpolar units by twinning. A model, therefore, can be considered as being constructed of polar layers stacked on one another with the polarity always in reverse in any two adjacent layers. When chemical attack occurs in such a structure, it will produce alteration at intervals of one layer and a regular mixed-layer structure may be formed. The mechanism presented above does not necessarily exclude the possibility of other mechanisms.

The formation of the deviation type of intermediate mineral is not necessarily due to a defect structure. Even a perfect crystal will be changed to the deviation type by slight alteration. But in this case, because of the perfect structure of the original mineral, a long-continued weathering or intense hydrothermal action will be necessary to cause slight alteration. If the original mineral has a defect structure, it will be more easily altered to the deviation type and possibly will be altered to the mixed-layer mineral by chemical attack which causes selective alteration toward even more defective layers.

Thus again we can see that the deviation type and mixed-layer type of clay are in intimate mutual relation. Indeed, it may be that some com-

ponent layers of a mixed-layer mineral can be designated as of the deviation type.

In conclusion, the following general statement can be made.

(1) In an environment that is favorable for formation of mineral A, the mineral tends to form by stacking of layers without defect. It is possible that the mineral is later altered to the deviation type by chemical attack.

(2) In an environment that is becoming unfavorable for its formation by decrease of temperature or change of chemical environment, the mineral will consist of crystals with various degrees of defect configuration. The defect mineral will be altered easily to the deviation type, and possibly will be further altered to the mixed-layer type.

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