

## BERTHIERINE AND CHAMOSITE IN COAL MEASURES OF JAPAN

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**Abstract**—Berthierine (formerly chamosite) occurs as concretions, lenses, and bands in carbonaceous, kaolinitic shale of freshwater coal-swamp deposits in Paleogene and Upper Triassic coal measures of Japan. Textural relations in thin sections of the Triassic berthierine rocks and a siderite-kaolinite-berthierine-quartz assemblage in Paleogene rocks indicate that the berthierine formed by reaction of siderite with kaolinite. The transformation of siderite and kaolinite to berthierine and quartz occurs progressively under reducing conditions between 65° and 150°C and at burial depths of 2–5 km. Utatsu berthierine is an aluminous, low-Mg variety as compared with berthierine pellets in modern marine and estuarine sediments and in ancient marine ironstones. Fe is the dominant octahedral cation with  $\text{Fe}^{2+} \gg \text{Fe}^{3+}$ . The composition of the berthierine varies between different morphological types. Utatsu berthierine transformed to ferrous chamosite when kaolinite in the host shale changed to pyrophyllite. These transformations are estimated to have occurred at ~160°C and at a burial depth of ~3 km.

**Key Words**—Berthierine, Chamosite, Coal, Genesis, Iron, Siderite.

### INTRODUCTION

Berthierine (formerly chamosite) has been reported from a variety of sedimentary deposits. In modern, tropical, shallow-marine sediments, it occurs as pellets, commonly associated with goethite; e.g., in the Niger delta (Porrenga, 1965, 1967), the Orinoco and Sarawak shelves (Porrenga, 1966, 1967), the Malacca Strait (Porrenga, 1967), the Guinea (von Gaertner and Schellmann, 1965; Schellman, 1966), and Gabon (Giresse and Odin, 1973), coasts. Berthierine pellets occur in brackish, cold-water sediments in Loch Etive of Scotland (Rohrlich *et al.*, 1969). The counterparts of modern berthierine pellets are considered to be berthierine ooids in the post-Cambrian marine ironstones, such as the minette-type ironstones and the Wabana and Clinton hematitic ironstones (Alling, 1947; James, 1966). Some Precambrian iron formations, such as the Transvaal and Swaziland Systems in South Africa (James, 1966) contain oolitic berthierine. Berthierine in ancient ironstones is commonly associated with and replaced by siderite and kaolinite (Taylor, 1949; James, 1966; Greensmith, 1978). It is also a common constituent of the clay fraction of the Lower Ecca shales deposited in a periglacial freshwater lake (Drennan, 1963), and in lateritic claystones of Scotland and Ireland (Brindley, 1951), where it formed by reaction of kaolinite with ferric oxide or hydroxide under reducing conditions. Berthierine also occurs in the Yakovlevo bauxite in the Central Russian Plateau (Aldinger, 1965), as an alteration product in the Evans-Low granitic pegmatite in northern Quebec (Hogarth, 1972), and in altered mafic rock in Ely, Minnesota (Ruotsala *et al.*, 1964).

We have discovered berthierine in some Paleogene and Triassic coal measures of Japan (Iijima and Mat-

sumoto, 1979). The berthierine was apparently derived from kaolinite and siderite and is partly transformed into chamosite. In this article, we describe its occurrence, properties, and transformation, and discuss its origin.

### OCCURRENCE OF THE JAPANESE BERTHIERINE

Berthierine was found in the Late Triassic coal measures in the Utatsu area, northeast Miyagi, and the Ohmine coalfield, west Yamaguchi; and in the Paleogene coal measures in the Ishikari coalfield, central Hokkaido, and in the Kado area, Iwate, Japan (Figure 1). The stratigraphic positions of these units are given in Table 1 and Figure 2. The Kado area was not invaded by seawater after Late Cretaceous time (Iijima, 1972; Tanai *et al.*, 1978). In the Ishikari coalfield, the presence of such molluscs as *Unio*, *Lanceolaria* and *Viviparus* in berthierine-bearing strata indicates a freshwater environment. The close association of coal seams and fossil plant leaves and the absence of marine fossils in the berthierine-containing Triassic strata also suggest a freshwater environment.

Berthierine rocks occur largely as concretions, lenses, or bands in black to dark gray, carbonaceous, claystones and siltstones of the coal measures. They are usually weathered to buff, brown, and brownish red colors due to the oxidation of berthierine and associated siderite. Some concretions have been found in a thick coal seam at the Momonoki colliery in the Ohmine coalfield. In the Ishikari and Ohmine coalfields and in the Kado area, berthierine and kaolinite comprise the matrix of sideritic concretions. It is, however, difficult to distinguish between them under the microscope be-

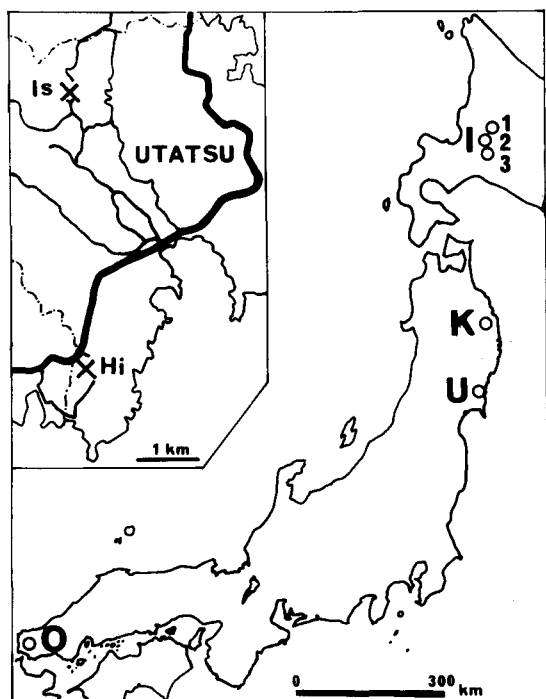


Figure 1. Locality of berthierine in coal measures of Japan. I = Ishikari coalfield, 1. Ashibetsu, 2. Ikushunbetsu, 3. Yubari; K = Kado; U = Utatsu; Hi = Hiramatsu; Is = Ishizumi; O = Ohmine coalfield.

cause they occur as a cryptocrystalline mixture. Illite is present in berthierine rocks of the Paleogene coal measures along with quartz and feldspar and is probably of detrital origin. Authigenic siderite is always associated with berthierine except in the Utatsu area where siderite is completely replaced by berthierine and quartz (see below). Siderite is the dominant carbonate in berthierine rocks of coal swamp deposits in the Paleogene and Upper Triassic coal measures and makes up 45–85 wt. % of the rocks (Matsumoto, 1978; Matsumoto and Iijima, 1981). It occurs as cryptocryst-

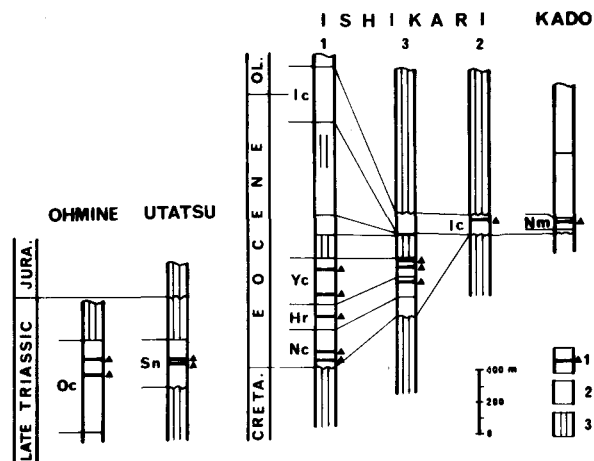


Figure 2. Stratigraphic position of berthierine rock in coal measures of Japan. Stratigraphic formations: Oc = Ohmine coal-bearing; Sn = Shindate; Nc = Noborikawa coal-bearing; Hr = Horokabetsu; Yc = Yubari coal-bearing; Ic = Ikushunbetsu coal-bearing; Nm = Nameiri coal-bearing; 1 = carbonaceous kaolinitic shale containing berthierine concretions; 2 = freshwater strata; 3 = marine strata. Locality: 1. Ashibetsu, 2. Ikushunbetsu, 3. Yubari.

talline particles, mosaics of xenomorphic crystals (0.005–0.12 mm across), spheroidal to rod-shaped grains (0.01–0.03 mm across), idiomorphic rhombohedra (0.01–0.08 mm across), and radial spherulites (0.1–0.5 mm across) in the cryptocrystalline kaolinite-berthierine matrix. It pseudomorphically replaces authigenic, vermicular kaolinite crystals.

At Hiramatsu in the Utatsu area, berthierine occurs in two beds, 570 and 900 cm thick, of dark gray to black, carbonaceous, kaolinitic shales interbedded with some thin coal seams in the middle part of the Shindate Formation of the Norian Saragai Group (Figure 3). It occurs as greenish black concretions and thin bands or as disseminated grains. The concretions and bands are composed predominantly of berthierine and quartz, with minor amounts of pyrite, rutile, and organic mat-

Table 1. Locality, stratigraphy, and geologic age of berthierine rocks from Japan.

Locality	Stratigraphic position	Geologic age
Yamato opencut of the Iwate clay mine, Kado, Iwaizumi, Iwate.	Nanshitsu-Nendo above Coal Seam No. 2 in the Nameiri Formation, Kokawa Group.	Early Oligocene
Ponbetsu, Ikushunbetsu, Ishikari Coalfield, Hokkaido.	Ikushunbetsu Formation, Ishikari Group.	Early Oligocene
Honcho, Yubari, Ishikari Coalfield, Hokkaido.	Horokabetsu and Yubari Formations, Ishikari Group.	Early Eocene
Tanzangawa, Ashibetsu, Ishikari Coalfield, Hokkaido.	Noborikawa, Horokabetsu, and Yubari Formations, Ishikari Group.	Early Eocene
Momonoki abandoned colliery, Ohmine Coalfield, Yamaguchi.	Ohmine Coal-bearing Formation.	Late Triassic
Hiramatsu and Ishizumi, Utatsu, Miyagi.	Fireclay A and B Beds in the Shindate Formation, Saragai Group.	Late Triassic

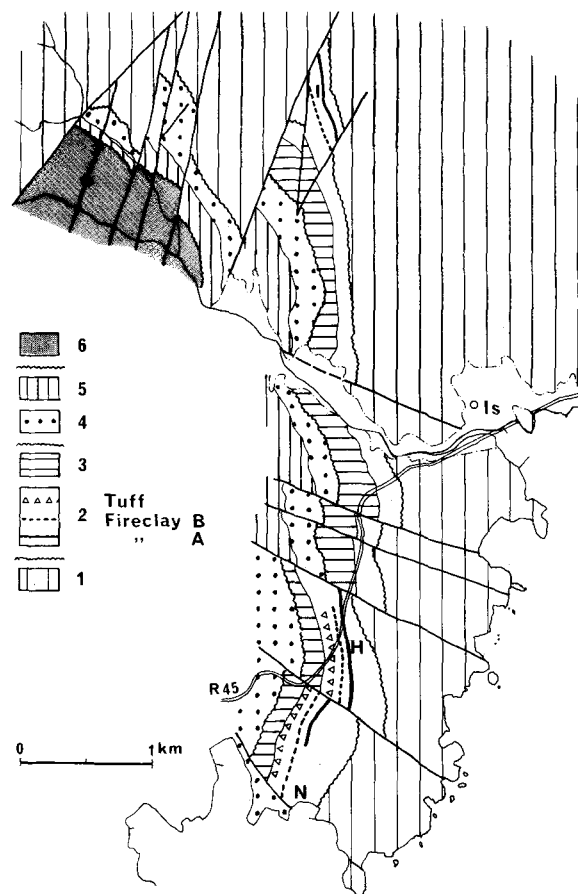


Figure 3. Geological map of Utatsu area. Stratigraphic units are (1) Lower Triassic Inai Group, (2) Shindate and (3) Chonomori Formations of Upper Triassic Saragai Group, (4) Niranohama and (5) Hosoura Formations of Lower Jurassic Shizukawa Group, and (6) Upper Jurassic Hashiura Group. Is = Isatomae; I = Ishizumi; H = Hiramatsu; N = Niranohama.

ter. It is noteworthy that they do not contain siderite or kaolinite, but are commonly associated with a few segregated quartz veinlets which have not been noted in the host kaolinitic shale. Four types of berthierine can be distinguished in the Utatsu rocks based on morphology: (1) berthierine replacing kaolinite megacrystals (K-type), (2) berthierine replacing various forms of siderite (S-type), (3) berthierine constituting crypto- to microcrystalline matrix (M-type), and (4) berthierine in segregated quartz veinlets (V-type). K-type berthierine occurs as vermicular forms, 0.2–1 mm long, and is pseudomorphous after kaolinite booklets commonly found in the host kaolinitic shale (Figure 4A, 4B). The booklets, some of which originally may have been mica, have transformed to an aggregate of berthierine

and mosaic quartz. The S-type occurs as rhombohedra, 0.04–1.5 mm across, rod-shaped grains 0.1–0.25 mm long, and rosettes and spherulitic aggregates with a diameter of 0.2 mm (Figures 4C–4F). Such forms indicate the replacement of siderite by berthierine and quartz because similar size siderite crystals and aggregates commonly occur as concretions and bands in kaolinitic shales of the Paleogene and Upper Triassic coal measures in Japan (Matsumoto, 1978). Some pseudomorphs consist either of aggregates of crypto- to microcrystalline berthierine or of quartz mosaics, whereas many are composed of a mixture of quartz and berthierine. In the latter material, a pale green, translucent aggregate of crypto- to microcrystalline berthierine replaces the peripheral zone of the pseudomorph on which clear yellowish green, fibrous berthierine has grown. The core is filled by a quartz mosaic with a thin berthierine film along the grain boundaries and with berthierine inclusions (Figure 4D). The M-type occurs as crypto- to microcrystalline aggregates that were probably a cryptocrystalline kaolinite matrix or a microcrystalline siderite mosaic. The V-type occurs as fibrous aggregates, 0.5–2 mm long, or hexagonal prisms, 2–16  $\mu\text{m}$  across and 0.01–0.04 mm long, in segregated quartz veinlets (Figure 4G, 4H). The fibrous and prismatic crystals are length-slow with straight extinction; they grow on and perpendicular to the wall and are overgrown by quartz crystals.

At Ishizumi, 4.4 km north of Hiramatsu, in the Utatsu area, an iron-rich, aluminous chlorite occurs in the same beds (Figure 3). The mode of occurrence and morphological types of chlorite cannot be differentiated from those of the berthierine except that the host rock is dark gray to black, carbonaceous, pyrophyllitic shale. The pyrophyllite formed from kaolinite and quartz when a mid-Cretaceous granitic intrusion produced higher temperatures in the country rock at a depth of  $\sim 3$  km (Iijima, 1977).

#### PROPERTIES OF THE BERTHIERINE AND CHAMOSITE

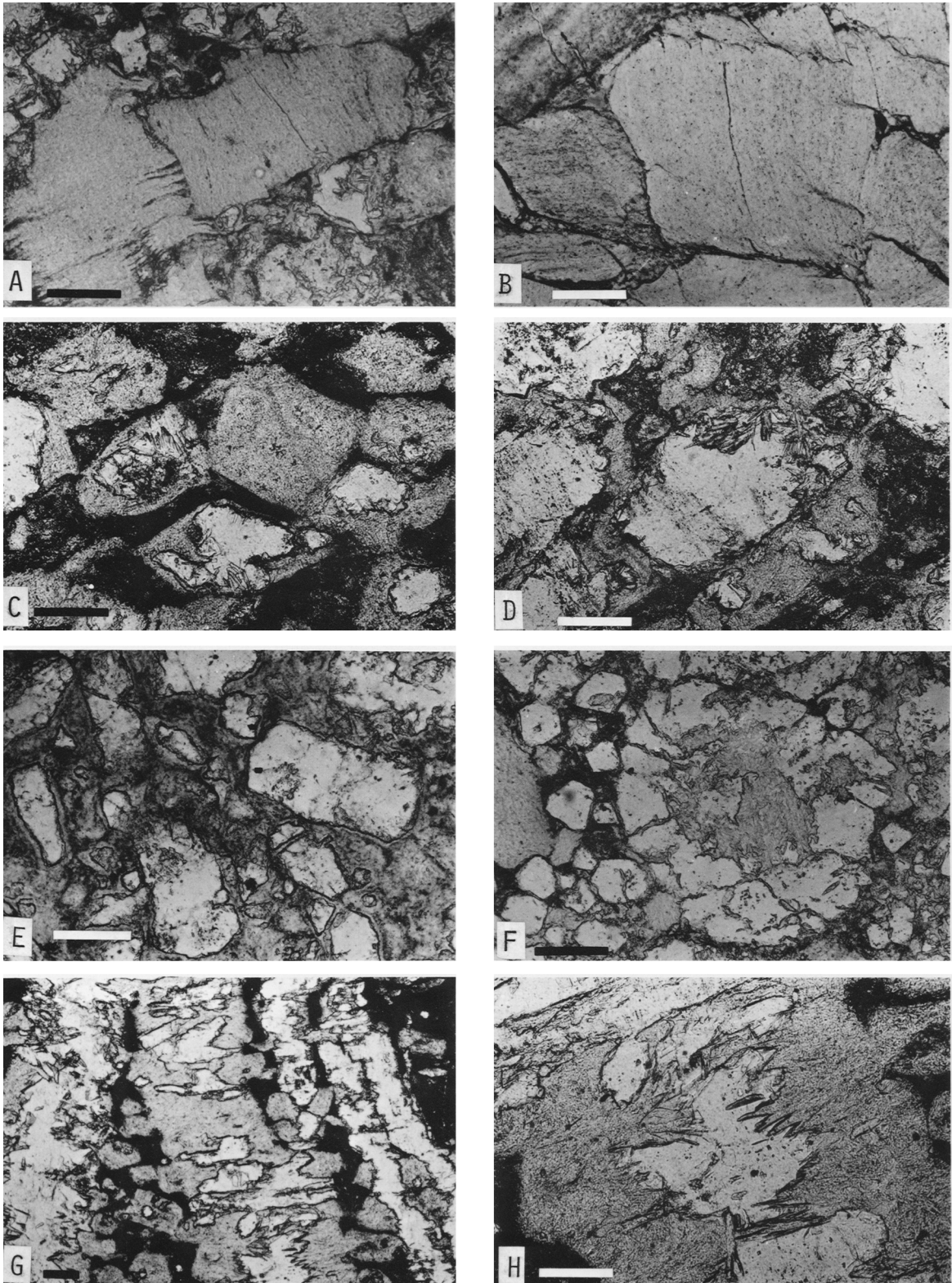
##### *X-ray powder diffraction*

Rock samples were pulverized and a  $<4\text{-}\mu\text{m}$  fraction was separated by decantation. Some selected clay samples were treated with hot 50% HCl for 0.5 to 3 hr, and were also heated at 450°C and 600°C for 1 hr in order to check for admixed kaolinite. Untreated and treated samples were analyzed with a Rigakudenki X-ray diffractometer. The results are given in Table 2 and in Figure 5.

The Utatsu berthierine from Hiramatsu shows a powder diffraction pattern similar to that of the Ayr-

Figure 4. Photomicrographs of berthierine from Utatsu. Scale bars = 0.1 mm. (A) K-type berthierine replacing kaolinite megacrystals. (B) Kaolinite booklets in the host carbonaceous kaolinitic shale. (C) S-type berthierine replacing siderite rhombohedra. (D) Fibrous berthierine and quartz mosaic filling a dissolved cavity of siderite rhombohedra which is fringed by berthierine





lining. (E) S-type berthierine replacing rod-shaped siderite grains. (F) S-type berthierine replacing rosette or spherulitic aggregates of siderite. (G) (H) V-type berthierine occurring as fibrous aggregates in segregated quartz veinlets.

Table 2. X-ray powder diffraction data of berthierine and chamosite in Upper Triassic coal measures in Japan.

Berthierine Hiramatsu, Utatsu			Berthierine Momonoki, Ohmine		Chamosite Ishizumi, Utatsu	
d (Å)	I/I <sub>0</sub>	hkl <sup>1</sup>	d (Å)	I/I <sub>0</sub>	d (Å)	I/I <sub>0</sub>
7.07	100	001			14.1	10
4.72	5	020	7.07	100	7.10	100
4.55	3	110M			4.72	17
3.88	2	021			4.59	10
3.527	51	002, 111M				
2.822	2	022	3.530	50	3.534	47
2.688	4	201M, 130M			2.821	7
2.507	4	201H	2.684	4	2.680	9
2.266	3	201M, 132M			2.501	11
2.140	3	202H			2.264	3
2.001	2	203M, 132M			2.140	8
1.760	2	203H, 240H				
1.558	4	{ 060, 331M 203M, 134M	1.555	9	1.556	9
1.522	3	{ 061 332M, 330M			1.520	5

CuK $\alpha$  radiation with Ni filter; 35 kV, 15 mA; scanning speed = 0.5°/min; chart speed = 20 mm/1°.

<sup>1</sup> hkl after Brindley (1951).

shire berthierine reported by Brindley (1951). According to the indexing of hkl by Brindley (1951), the Utatsu berthierine is a mixture of ortho-hexagonal and monoclinic types. It is not known, however, which morphological and crystallographic types of berthierine correspond. Detailed X-ray powder diffraction patterns of berthierine in the Ohmine coalfield and in the Paleogene coal measures were impossible to obtain because of interferences from siderite and kaolinite reflections. Only the 7.1-Å and 3.53-Å peaks were recognized in the Paleogene rocks. Berthierine was destroyed by treatment with hot HCl.

The Utatsu iron-rich chamosite from Ishizumi is distinct because it shows a weak reflection at 14.1 Å, which is recognized after heating to 600°C. It is likely that the Utatsu chamosite is not a mixture of 14-Å chlorite and berthierine but is a single 14-Å chlorite phase. This possibility is further supported by the fact that the chemical composition of the Utatsu chamosite estimated from the X-ray powder diffraction data—14.1 Å d(001) spacing corresponds to 3.1 Al in tetrahedral sites and 1.556 Å d(060) spacing to 6.7 Fe<sup>2+</sup>, after Shirozu (1958)—is consistent with the chemical analyses given in Table 3.

#### Chemical composition

**Bulk chemical composition.** Table 3 lists the bulk chemical composition of berthierine and chamosite rocks obtained by wet chemical analyses. TiO<sub>2</sub> is essentially due to authigenic rutile, and FeS is derived from authigenic pyrite. P<sub>2</sub>O<sub>5</sub> is principally due to apatite. The H<sub>2</sub>O(+) value reflects the presence of some organic matter. FeO and Fe<sub>2</sub>O<sub>3</sub> are almost exclusively derived

from the berthierine in the Hiramatsu sample and from the chamosite in the Ishizumi sample. FeO always predominates over Fe<sub>2</sub>O<sub>3</sub> in both the berthierine and the chamosite. The Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio is 8.15–10.20 in the former and 6.00 in the latter. Excess SiO<sub>2</sub> is included as authigenic and detrital quartz.

#### Chemical composition of berthierine and chamosite.

The amounts of Si, Al, Fe, Mg, Na, and K in the Utatsu berthierine and chamosite were determined with an JXA-5 electron microprobe using an accelerating voltage of 15 kV and a sample current of 0.002  $\mu$ A on periclase. The matrix corrections to raw data were applied by the method of Bence and Albee (1968). Na and K were either undetected or present in negligible amounts. The results are listed in Table 4.

Berthierine in kaolinitic shale from Hiramatsu displays a wide range of compositions, even within a single rock specimen (Figure 6). In tetrahedral sites about one third of the Si is substituted by Al. Fe occupies approximately two thirds of the available octahedral positions with Fe<sup>2+</sup> more abundant (~91%) than Fe<sup>3+</sup>. Al and small amounts of Mg (3.7–5.4%) and Ca (0.1–0.2%) fill the remaining octahedral sites. The composition of the berthierine tends to differ in the morphological types described above. Al seems to be slightly more abundant in the K-type berthierine that replaces kaolinite than in the S-type that replaces siderite, whereas Fe seems to show the opposite trend. The V-type berthierine in segregated quartz veins is the most Fe-rich of the three types.

Chamosite in pyrophyllitic shale from Ishizumi shows a much more restricted range of compositions



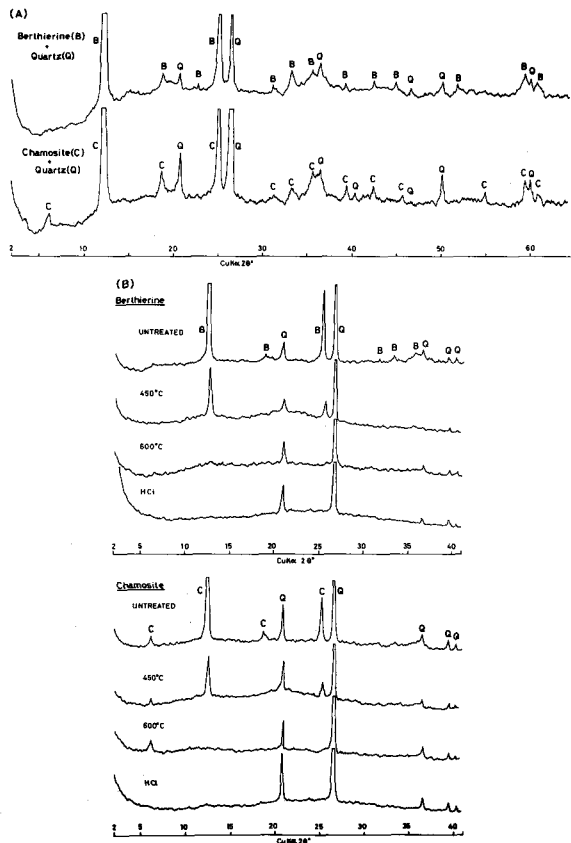


Figure 5. X-ray powder diffraction pattern of the Utatsu berthierine and chamosite. (A) Unoriented slides. (B) Oriented slides. B = berthierine; C = chamosite; Q = quartz.

than berthierine (Figure 6). In tetrahedral sites 36–37% of the Si is substituted by Al. Fe occupies 63–64% of the available octahedral sites with Fe<sup>2+</sup> more abundant (87.5%) than Fe<sup>3+</sup>. Al and normal amounts of Mg (~13%) fill the remaining octahedral sites. It is noteworthy that the Mg content is much higher than that of the Utatsu berthierine, and that compositions, overall, do not vary significantly between the different morphological types. This uniformity of chemical composition indicates that the Ishizumi chamosite is not a mixture of berthierine and chlorite but a single phase. The Utatsu Fe<sup>2+</sup>-rich chlorite is hence referred to a chamosite after Bayliss (1975).

ORIGIN OF BERTHIERINE IN COAL MEASURES

Weaver and Pollard (1973) suggested that organic materials, detrital iron minerals, and a slightly alkaline pH are required for the formation of berthierine in modern environments. Berthierine ooids in sedimentary ironstones are considered to be chemical precipitates (Velde, 1977) and may alter to siderite and kaolinite in the course of diagenesis (Taylor, 1949; James, 1966;

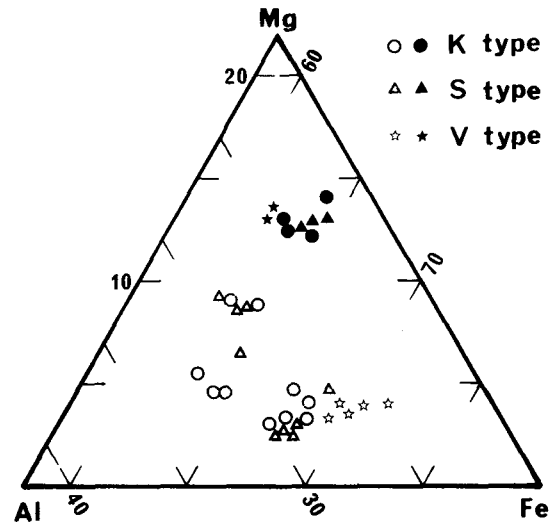


Figure 6. Cation ratios in octahedral sites of the Utatsu berthierine (open symbols) and chamosite (solid symbols).

Deer *et al.*, 1962; Greensmith, 1978). By contrast, berthierine formed by reaction of kaolinite with ferric oxide or hydroxide under reducing conditions and at elevated temperatures in lateritic claystones (Brindley, 1951).

Berthierine in the Upper Triassic coal measures of the Utatsu area is unusual because it occurs as concre-

Table 3. Bulk chemical analyses of berthierine and chamosite rock samples from Utatsu, Miyagi.

	(1)	(2)	(3)
SiO <sub>2</sub>	35.28	42.05	64.30
TiO <sub>2</sub>	0.60	0.37	0.22
Al <sub>2</sub> O <sub>3</sub>	19.02	17.44	9.66
Fe <sub>2</sub> O <sub>3</sub>	4.17	2.85	2.45
FeO	30.56	26.23	15.34
MnO	0.34	0.42	0.12
MgO	0.98	2.75	2.14
CaO	0.04	0.10	0.03
Na <sub>2</sub> O	<0.03	<0.03	<0.03
K <sub>2</sub> O	<0.03	<0.03	<0.03
H <sub>2</sub> O(+)	8.11	7.42	5.29
H <sub>2</sub> O(-)	0.27	0.23	0.13
P <sub>2</sub> O <sub>5</sub>	0.09	0.10	0.06
FeS	0.08	0.08	0.05
F	N.D.	0.010	N.D.
Total	99.60	100.11	99.85

Analyst: Hiroshi Haramura. H<sub>2</sub>O(+) includes organic matter.

(1) Berthierine-quartz concretion in the basal part of the kaolinitic shale (Fireclay Bed A) of the Shindate Formation in the Saragai Group at Hiramatsu, Utatsu, Miyagi: Sample 76-12-1B.

(2) Berthierine-quartz concretion in the middle part of the same bed from the same locality as (1): Sample 76-12-2-14.

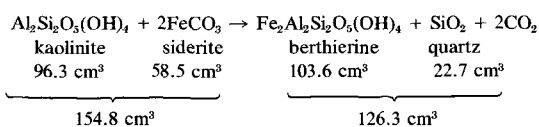
(3) Chamosite-quartz concretion in the uppermost part of the pyrophyllitic shale of the Shindate Formation at Ishizumi, Utatsu, Miyagi: Sample 76-11-10D<sub>1</sub>.

Table 4. Electron microprobe analyses of berthierine and chamosite in the Utatsu district, Miyagi Prefecture, Japan.

	Berthierine at Hiramatsu			Chamosite at Ishizumi		
	K-type (mean of 10)	S-type (mean of 9)	V-type (mean of 6)	K-type (mean of 4)	S-type (mean of 4)	V-type (mean of 2)
SiO <sub>2</sub>	22.87	23.81	22.01	23.13	22.51	23.52
Al <sub>2</sub> O <sub>3</sub>	23.24	22.94	21.21	21.61	21.85	22.17
FeO (total Fe)	40.15	41.01	42.07	41.06	41.53	40.91
MgO	1.77	1.91	1.24	4.75	4.65	4.87
CaO	0.09	0.06	0.68	0.04	0.02	0.03
Na <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00
Total	88.12	89.73	87.21	90.59	90.56	91.50
Number of ions based on equivalent oxygen = 28						
Si	5.20	5.32	5.19	5.14	5.03	5.15
Al	2.80	2.68	2.81	2.86	2.97	2.85
Al	3.43	3.35	3.10	2.81	2.78	2.89
Fe <sup>2+</sup>	7.63	7.66	8.31	7.64	7.76	7.50
Mg	0.59	0.63	0.44	1.58	1.55	1.59
Ca	0.02	0.01	0.02	0.01	0.00	0.01

K-type = replacing kaolinite megacrystals; S-type = replacing siderite; V-type = in quartz veinlets.

tions, lenses, and bands in freshwater, sideritic, kaolinitic shale deposited in coal swamps. The textural relationships under the microscope prove that the mineral formed by the reaction of kaolinite with siderite (Figure 4) as shown below,



Approximately 18% by volume of the original material is lost in the process of the reaction. Segregated quartz veins within the Utatsu berthierine rocks probably fill shrinkage cracks resulting from the reaction.

Berthierine in other Triassic and Paleogene coal measures coexists with siderite. In the Upper Triassic Ohmine Coal-bearing Formation, siderite is at least partly replaced by berthierine in the sideritic band whereas all of the kaolinite is replaced by berthierine. In the Paleogene coal measures, the berthierine-kaolinite-siderite assemblage suggests a similar origin for berthierine, although textural relationships are obscured because of cryptocrystallinity. The abundance of Fe<sup>2+</sup> in berthierine in the coal measures indicates that the reaction progressed under reducing conditions and in the presence of abundant plant remains. Most sideritic rocks in freshwater coal swamp deposits form at a burial depth less than 300 m during early diagenesis (Matsumoto, 1978; Matsumoto and Iijima, 1981). The siderite to berthierine transformation should, therefore, occur at greater depths. Table 5 shows burial temperatures for the berthierine-bearing coal measures estimated from the maximum reflectance of reactive vitrinite in coal—0.51% in Kado, 0.74–0.92% in Ishikari, and 3.29% in Ohmine—according to Castaño and

Sparks (1974) and Shimoyama and Iijima (1978). These temperature estimates are not inconsistent with the diagenetic zeolite zones (Iijima, 1980). The mineral composition of the berthierine rocks is also included in the Table. The siderite, kaolinite, and berthierine contents of the Kado, Ishikari, and Ohmine samples were based on the ordinary X-ray powder diffraction method: The berthierine and chamosite contents in the Utatsu sample were calculated from the bulk chemical composition and the mean of microprobe analyses in Tables 3 and 4. The amount of authigenic quartz was obtained from thin-section analyses. There is a tendency for berthierine and authigenic quartz to increase and for siderite and kaolinite to decrease as the temperature increases from 65°C in Kado to 130°C in Ohmine. This fact indicates that the transformation of siderite and kaolinite to berthierine is progressive; i.e., that it takes place rather slowly between 65° and 130°C. The reaction progresses more rapidly at higher temperatures (~150°C). The formation of berthierine is more closely related to the decomposition of siderite than kaolinite, because the latter mineral remains as the main constituent of the host shale even in Utatsu. Furthermore, quartz and idiomorphic berthierine fillings in voids after dissolved siderite suggest the decomposition of siderite prior to the formation of berthierine. However, the range of compositions shown by the separate morphological types, even in individual rock specimens, demonstrates that the Utatsu berthierine has not reached equilibrium with its surroundings.

Figure 7 illustrates the wide range in chemical composition of berthierine from various occurrences. The Utatsu berthierine is characteristically aluminous with the Si/Al ratio <1. The cations occupying octahedral sites are predominantly Fe (especially Fe<sup>2+</sup>), and Al,

Table 5. Mineral assemblage, geologic age, and maximum burial depth and temperature of berthierine and chamosite rocks in coal measures of Japan.

Locality	Age	Siderite (%)	Kaolinite (%)	Berthierine (%)	Chamosite (%)	Authigenic quartz	Maxim. depth (km)	Maxim. T (°C)
Kado	Early Oligocene	53-65	10-25	5	—	?	2	65
Ishikari	Eocene	44-85	0-10	5-10	—	minor	3-4	90-100
Ohmine	Late Triassic	45-65	0-10	15-20	—	minor	5	130
Utatsu	Late Triassic	—	—	77-84	—	common	3	—
Utatsu	Late Triassic	—	—	—	46	abundant	3	160

— = not detected.

with smaller amounts of Mg and Ca. The composition of berthierine that originated from kaolinite and iron oxide or hydroxide in lateritic claystone of Ayrshire, Scotland (Brindley, 1951) falls into the same range as the Utatsu material. Berthierine in post-Cambrian, shallow marine ironstones, which are thought to be syndimentary or early diagenetic and are replaced by siderite and kaolinite (Taylor, 1949; Deer *et al.*, 1962; James, 1966), tend to be slightly more siliceous than the Utatsu material. The composition of berthierine in the matrix of a Jurassic sideritic rock from Northamptonshire, England (Brindley and Youell, 1953), however, falls into the same range as the Utatsu material. In octahedral sites of the ironstone berthierine, Fe is the dominant cation, but Mg is also abundant in the Minnet (Deudon, 1955) and Clinton ironstones (Schoen, 1964), whereas Al is abundant in the berthierine-kaolinite bed of Northampton (Youell, 1958). Berthierine pellets in modern marine and estuarine sediments are usually siliceous, but have octahedral sites that may contain abundant Al and Mg as in the tropical Guinea coastal sands (Schellmann, 1966), or Fe as in the sediments in Loch Etive, Scotland (Rohrlich *et al.*, 1969).

The composition of berthierine seems to depend on the nature of the original material. Berthierines derived from kaolinite are aluminous with Si/Al ratios <1 (e.g.,

the Utatsu and Ayrshire berthierines). By contrast, berthierine pellets originating from fecal pellets in modern sediments are siliceous, with Si/Al ratios of 2-3. It is debatable whether berthierine with an intermediate Si/Al ratio in ancient marine ironstones was derived from a different source material or modified by diagenesis.

The cationic abundances of Fe, Al, Ca, and particularly Mg in the octahedral sites of berthierine seem to depend on the nature of the sedimentary environment and the original material. Low-Mg berthierine occurs in freshwater and continental deposits. The Utatsu berthierine, for example, is derived from sideritic rock in carbonaceous, kaolinitic shale of freshwater coal-swamp deposits. This seems to reflect the fact that the siderite in these deposits is a low-Ca, low-Mg variety with nearly an end-member composition (Matsumoto, 1978; Matsumoto and Iijima, 1981). On the other hand, intermediate- to high-Mg berthierine is found in both modern and ancient, brackish water and shallow-marine sediments. Most Mg is probably derived from sea water trapped in interstitial pores. Siderite having a high Mg content commonly occurs in brackish water and marine deposits in the Japanese coal measures (cf. Matsumoto and Iijima, 1981). The above considerations are summarized in Table 6.

Table 6. Formation and transformation of berthierine in various depositional environments.

Depositional environments	Freshwater coal swamp kaolinitic shale	Continental lateritic claystone	Brackish water and shallow-marine
Original materials	Kaolin clay Iron oxide & hydroxide Phytoclasts	Kaolin clay Iron oxide & hydroxide	Fecal pellets Iron oxide & hydroxide Mg ions in seawater
Early diagenesis	Low-CaMg siderite concretions in kaolinitic shale 65°C	?	Siliceous and high-Mg berthierine pellets and ooids
Late diagenesis	Low-Mg berthierine concretions in kaolinitic shale 160°C	Low-Mg berthierine	Moderate- to low-Mg berthierine, siderite, and kaolinite
Anchimetamorphism	Chamosite concretions in pyrophyllitic shale		



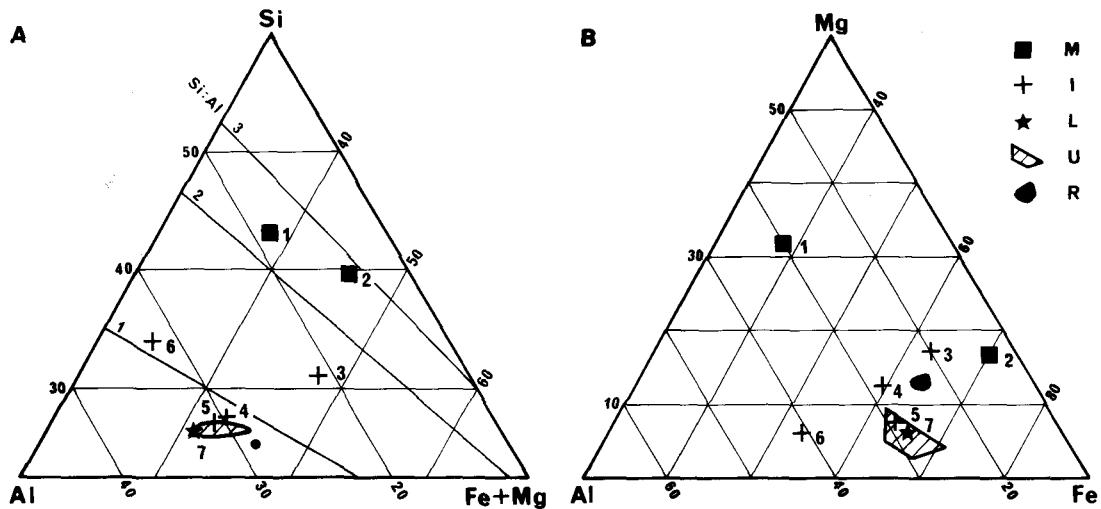


Figure 7. Variation diagrams of composition of berthierine from various occurrences: in modern sediments (M), ironstones (I), lateritic claystone (L), and carbonaceous kaolinitic shale in this study (U). Composition of the Utatsu chamosite (R) is also shown. 1 = Guinea Coast; 2 = Loch Etive, Scotland; 3 = Meurth et Moselle, France; 4 = Clinton, New York; 5 = Northamptonshire, England; 6 = Wellingborough, England; 7 = Ayrshire, Scotland. Data are from Weaver and Pollard (1973).

#### BERTHIERINE TO CHAMOSITE TRANSFORMATION

The chamosite at Ishizumi in Utatsu resulted from the transformation of berthierine at elevated temperatures. During the same thermal conditions, kaolinite in the host carbonaceous shale was completely transformed to pyrophyllite. This is because both berthierine and chamosite occur in the same manner in the same stratigraphic horizon in Utatsu as described previously. Nelson and Roy (1958) showed experimentally that berthierine can be transformed to chamosite at temperatures higher than 400°–500°C. Hydrothermal experiments by Henmi and Matsuda (1975) showed that pyrophyllite is formed by the reaction of kaolinite with quartz at 263°C and 1 kbar. However, the berthierine to chamosite and the kaolinite to pyrophyllite transformations in Utatsu occurred at a lower temperature, ~160°C as estimated from the maximum reflectance of reactive vitrinite ( $R_0 = 2.6$ ) and the content of volatile matter (9.9%) in the pyrophyllitic shale and the burial time of 75 MY, according to Castaño and Sparks (1974).<sup>1</sup> The maximum burial depth of the shale is estimated at about 3 km, and hence there was a steeper geothermal gradient (47°C/km) which might have been influenced by mid-Cretaceous granite intrusion (Iijima, 1977). Pyrophyllites resembling the occurrence of Utatsu pyrophyllite were found in Triassic unmetamorphosed claystone and anchimetamorphosed shale and slate from the Swiss Alps (Frey, 1970, 1978), in Pennsylvanian underclays from northeastern Pennsylvania

<sup>1</sup> The temperature is estimated at about 190°C according to Bostick *et al.* (1978).

(Hosterman *et al.*, 1970) and in Precambrian and Upper Paleozoic shales from South Africa (Hayashi, 1980).

The Utatsu chamosite has a higher octahedral Mg content than the original berthierine (Figure 7). It also seems to have reached equilibrium with the host rock, because no significant differences in composition are observed between the morphological K-, S-, and V-types.

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**Резюме**—Бертиерин (раньше хамосит) выступает в виде конкреций, лент, и полос в карбонатных, каолинистых сланцах в свежесложившихся, углеболотных осадках в палеогенных и выше-триасовых каменноугольных пластах Японии. Текстуальные отношения в тонких сечениях триасовых бертиериновых пород и скоплений сидерит-каолинит-бертиерин-кварц в палеогенных породах указывают на то, что бертиерин образовался путем реакции сидерита и каолинита. Трансформирование сидерита и кординита в бертиерин и кварц выступает прогрессивно в восстановленных условиях между 65° и 150°C на глубине погребения 2 до 5 км. Бертиерин из Ютатсу является алюминиевого, низко-Mg сорта по сравнению с бертиериновыми таблетками в современных морских и эстуарных осадках и в древних морских железных рудах. Fe является основным октаэдрическим катионом с  $Fe^{2+} \gg Fe^{3+}$ . Состав бертиерина различен для разных морфологических типов. Бертиерин из Ютатсу преобразовался в железистый хомосит, когда каолинит в материнском сланце изменился в пиррофиллит. Оценивается, что эти преобразования осуществились при температуре 160°C и на глубине погребения порядка 3 км. [Е.С.]

**Resümee**—Berthierit (früher Chamosit) tritt als Konkretionen, Linsen, und Bänder in kohligem, Kaolinit-haltigem Schiefer-ton von Süßwasser-Kohlelagerstätten in paläogenen und obertriassischen Kohle-schichten von Japan auf. Die Gefügemerkmale in Dünnschliffen der triassischen Berthierit-Gesteine und eine Siderit-Kaolinit-Berthierit-Quarz-Vergesellschaftung in paläogenen Gesteinen deuten darauf hin, daß sich der Berthierit durch die Reaktion von Siderit mit Kaolinit bildete. Die Umwandlung von Siderit und Kaolinit in Berthierit und Quarz findet in zunehmendem Maße unter reduzierenden Bedingungen zwischen 65° und 150°C und bei einer Überlagerung von 2–5 km statt. Der Berthierit von Utatsu ist verglichen mit Berthierit-Pellets in jungen marinen und ästuarinen Sedimenten und alten marinen Eisensteinen eine Al-haltige Varietät mit wenig Mg. In oktaedrischer Koordination tritt vor allem Fe auf, wobei  $Fe^{2+} \gg Fe^{3+}$ . Die Berthieritzusammensetzung schwankt zwischen den einzelnen morphologischen Typen. Der Utatsu Berthierit wandelte sich in Fe-haltigen Chamosit um, wenn sich der Kaolinit im Muttergestein in Pyrophyllit umwandelte. Es wird angenommen, daß diese Umwandlungen bei ~160°C und bei einer Überlagerung von ~3 km stattfanden. [U.W.]

**Résumé**—La benthierine (autrefois la chamosite) est trouvée en concrétions, en formes lenticulaires, et en bandes dans du shale kaolinitique de dépôts de charbon-marécage d'eau douce dans des mesures de charbon d'âge paléogène et haut triassique du Japon. Des relations texturales dans des sections minces des roches benthierine triassiques et un assemblage benthierine-kaolinite-quartz dans les roches paléogènes indiquent que la benthierine a été formée par la réaction de sidérite avec la kaolinite. La transformation de sidérite et de kaolinite en benthierine et quartz se passe progressivement sous des conditions de réduction entre 65° et 150°C et à des profondeurs d'ensevelissement de 2–5 km. La benthierine Utatsu est une variété alumineuse, à bas Mg comparée aux boulettes de benthierine dans des sédiments marins et estuariens modernes et dans d'anciennes roches ferreuses marines. Fe est le cation octaédral dominant avec  $Fe^{2+} \gg Fe^{3+}$ . La composition de la benthierine varie entre différents types morphologiques. La benthierine Utatsu s'est transformée en chamosite ferreuse lorsque la kaolinite dans le shale hôte s'est changée en pyrophyllite. On estime que ces transformations se sont passées à 160°C et à une profondeur d'ensevelissement de ~3 km. [D.J.]