Aluminous Shale

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1. Distribution and General Properties of Aluminous Shale

Aluminous shale forms ore beds in the Paleozoic coal-bearing formations of Manchuria, North China, and Korea. It occurs in two beds, commonly called the "A" and "G" beds after the writer's suggestion for the Yen-tai coal field, the first locality where the aluminous shale was discovered. The "A" bed lies in the upper part of the productive coal-bearing formation and is Upper Permian in age, while the "G" bed lies below the "A" bed at the base of the Middle Carboniferous formation and covers the plane of unconformity above the Ordovician limestone or dolomite. The vertical distance from "A" bed to "G" bed is 200–500 m. The "A" bed is best developed in Shan-tung, Chi-tung, South Manchuria, and Korea, and the "G" bed is found in Shan-tung, Ho-pei, Ho-nan, Shan-hsi, Inner Mongolia, Manchuria, and Korea. The area of distribution of "A" bed is smaller than that of "G" bed. The latter is almost always found where there is an Upper Paleozoic coal-bearing formation.

The "A" and "G" beds of each coal field are listed in the Table 1.

Both "A" and "G" beds form a thick bed of kaolinite or flint clay, and are intercalated with lenticular aluminous shale. The flint clay bed is 2–17 m thick, and the outcrops are from several to over 100 km in length in each of the coal fields. A single lens in a bed of aluminous shale is 0.5–6 m thick and several hundred meters in length. The lenses in "A" bed are so flat that they can be called beds, while those in the "G" bed are locally variable in thickness and more irregular in shape.

The flint clay is grayish white, grayish-blue or red, compact, massive, fractures conchoidally, and has a smooth, glassy texture. When exposed to the sun, it breaks down into sandy grains in hours. *Hakusan-roseki*[1)] used to be roasted before shipment not only to reduce weight and hence freight costs but also to protect it from rapid disintegration. Its hardness is 3, and its specific gravity 2.7 (apparent s.g. 2.6, sometimes 2.2). Mineral composition: kaolinite and halloysite, with $\pm$40 per cent alumina, $\pm$1–20 per cent ferric oxide.

[1)] A trade name for the light bluish, compact clay mined and exported from the Po-shan coal field, Shan-tung.

Table 1. List of Occurrences of the "A" and "G" Aluminous Shale Beds in Manchuria.

Coal fields	Beds	Thickness (m)	Length of outcrop (km) Actual (possible)	Remarks
Sung-shu-chien	A	—		
	G	—		
Wan-kou	A	—		
	G	—		
Pa-tao-chiang	A	?		Basal conglomerate with round quartz pebbles
	G	—		
Wu-tao-chiang	A	?		With round quartz pebbles
	G	0 – 1	small	
Tieh-chang	A	1.5 – 3		Gray-white and red flint clay
	G	—		
Tien-shih-fu	A	0.8 – 10	5.2	Coal seam on hanging wall
	G	—		
Hsiao-shih	A	2.5 – 7.5	25.1 (3.3)	
	G	—	very small	
Niu-hsin-tai	A	2.5 – 10.5	4.8	Lenticular coal seam (max. thickness 1.5 m) on hanging wall
	G	3 – 10	10	
Pen-hsi-hu	A	4 – 8	6	
	G	5 – 10	7	
Han-po-ling	A	—		Eroded out
	G	0 – 12	2.4	
Yen-tai	A	8	2.9	
	G	10	2 (12)	
Fu-chou	A	—		Eroded out
	G	5 – 17	3.7 (18.3)	
Chin-chou	A	—		Eroded out
	G	5 – 17	2.5	
Hung-lo-hsien	A	—		
	G	2 – 4	4.5	Flint clay only
Nan-piao	A	3.5	small	Flint clay only
	G	0 – 10	〃	Sandy clay
Hsiao-hei-yu-kou	A	none		
	G	1.4 – 4.2	1.7	
Wu-tao-ling	A	none		
	G	0 – 8.95	0.3	Al_2O_3 46%
Sung-shu-tai	A	none		Flint clay, sandy clay
	G	0 – 1.65	0.7	
Hsing-lung	A	none		Non-deposition?
	G	〃		〃

Aluminous shale is grayish-white, bluish-green, yellowish-green, brown, and red. It is compact, massive or pisolitic, uneven and rough in fracture, and has a hardness measured at 3–7 and a specific gravity of 2.8–3.1 (apparent s.g. 2.6–3.0). It has a mixed composition of flint clay and diaspore (with a small amount of boehmite and sporogelite), with 45–70 per cent alumina and ±2–25 per cent ferric oxide. Diaspore and kaolinite form an aggregate of fine crystal grains with diameters of 1–100 microns. The flint clay is soluble in sulphuric acid, while the high-grade aluminous shale, being composed chiefly of diaspore, is soluble with difficulty both in acids and alkalis.

It is this relative insolubility of diaspore, both in acids and alkalis, under normal pressure that makes the extraction for metallurgical purposes of pure alumina from aluminous shale difficult. However, solution may be possible in a solid phase reaction with concentrated sulphuric acid (sulphuric acid method by Kōemon Hunaki and Yogorō Katō). When roasted with either calcium carbonate (or barium carbonate) or soda ash, it becomes soluble. It is on the basis of this reaction that such combined dry and wet methods as the alkaline earth method (Manchuria Light Metals Manufacturing Co., Inc. and Tsuyoshi Arimori) and similar alkali methods (Shōichirō Nagai, *et al.*) have been established.

Part of the aluminous shale which was called "sporogelite or gelalumino-ferrique" by the writer is amorphous under the microscope. S. Oda of the Continental Research Institute (Tairiku Kagakuin) made X-ray analyses and found it to be boehmite. Ores with sporogelite as their chief constituent are greenish-yellow to gray, compact, and are mixed with chloropal (iron silicate) and halloysite, usually having an alumina content of about 60 per cent. Sporogelite of unusual purity is found in a part of the "A" bed at Po-shan, and the writer thinks that the Bayer process could be applied to these kinds of ore.

The fact that the aluminum hydroxide contained in the aluminous shale occurs not only in the form of diaspore but also in a soluble form is important in connection with its treatment. It is important that this amorphous part was determined mineralogically as boehmite. (The reserves of this type of ore do not amount to much at present, however.)

2. Shape and Profile of the Aluminous Shale Ore Bodies

The aluminous shale forms flat lenses with a maximum thickness of 3 m and a maximum length of several hundred meters along the outcrop, which are intercalated in a thick bed of flint clay. The lenticular aluminous shale, fully developed in "A" bed, shows distinct symmetrical banding along a vertical profile, i.e., with green and grayish-blue aluminous shale at the center and yellowish-blue and reddish-purple flint clay bands both above and below, with the yellowish-blue bands nearest the center. The "A" bed is 3.5–10 m thick, and may be over 100 km long along the outcrop. White quartzose sandstone, cemented by blue to white kaolinite and having an appearance similar to *gairome*,[2] is found on the footwall. The kaolinite often forms small lenticles within the sandstone. A celadon (green) flint clay bed is found near the footwall and consists of pure, bluish flint clay which is quite similar in color and texture to the kaolinite cement of the sandstone, showing both of these beds to be sediments of continuous deposition. An alternation of thin sandstone and variegated shale occurs on the hanging wall of the "A" bed; a thin coal seam is found covering "A" bed in only a few places.

The lower part of "G" bed is reddish or purplish and ferruginous, and the middle and upper parts are grayish-green and grayish-white. Banding is seldom as regular as in "A" bed. Nodular hematite or turgite is found in the lowest part of the "G" bed, popularly known as *lao-kuang*[3] in Shan-hsi. Similar ores were once prospected in Niu-hsin-tai, Manchuria. High grade ores of aluminous shale form irregular lenses in the middle and upper parts. The "G" bed is 2.5–17 m thick, several hundred km in aggregate length along the outcrop, and is as persistent laterally as the "A" bed.

Ordovician limestone or dolomite occurs on the footwall, and sandstone and shale on the hanging wall. The formation on the hanging wall together with "G" bed is in disconformable relationship to the Ordovician limestone or dolomite below. Although projections and depressions due to solution are occasionally met with on the surface of the limestone bed on the footwall, the surface is usually smooth, with thin layers of yellow and brown marl interbedded with thin sandstone and sandy shale, and lacks large engulfing pockets or vein-formed downward protuberances. This is rather a unique feature when compared with the footwall limestone of the *Bohnerz* in Europe, showing serrate depressions, or with the footwall of the terra rossa bauxite, showing similar and sometimes sinkhole shaped pockets.

The "G" bed in the hanging wall is conformably covered by sandstone and sandy shale. The sandy shale is reddish-purple and brown and is intercalated with limestone beds which contain fossil marine fauna. A lenticular coal seam is occasionally found covering the "G" bed. Grayish flint clay with a similar appearance is found about 5–20 m above "G" bed. It is more easily decomposed into "soft" clay than the "G" flint clay, and is utilized as china clay. (Examples are in Yen-t'ai and Kai-lan. The so-called *honso nendo*[4] from Fu-chou is situated above in a different horizon).

The color and macroscopic texture of the aluminous shale and flint clay are shown in the following table:

[2] Completely kaolinized arkosic sandstone in Japan, which can be separated into kaolinite and quartz sand for glass making.

[3] *Lao-kuang* (meaning "old iron ore") is an iron ore used in the domestic smelters in Shan-hsi Province, North China.

[4] *Honso nendo* is refractory clay exported to Japan in large quantities, averaging at 300,000 metric tons a year.

Table 2. Color and Texture of Aluminous Shale and Flint Clay.

Bed	Ores	Color	Texture
"A"	Aluminous shale	Yellowish-green or grayish-green	Pisolitic, compact amorphous
		Grayish-blue or gray	Compact crystalline
	Flint clay	Celadon or light purple	Compact, disintegrates into angular hexahedron
		Yellow, light brown or cream white	Compact or porous, soft
		Pink or reddish-purple	Compact or porous, disintegrates into prisms
"G"	Aluminous shale	Grayish-white, grayish-green or red	Pisolitic, compact crystalline
	Flint clay	Gray, pink or red	Compact, disintegrates into prisms

3. Chemical Composition of the Aluminous Shale Ores

The alumina content of the aluminous shale varies from 45 to 70 per cent (silica: alumina mol ratio, 1.8–0). The chief component minerals are diaspore, sporogelite (boehmite), kaolinite, and halloysite. The alumina content of the flint clay is 40 per cent = (silica:alumina mol ratio, $2.0\pm$), consisting almost entirely of kaolinite and halloysite. The aluminous shale occurs as lenses in the flint clay, and the transition between them is gradual, but is only 20–30 cm or narrower in width. The change in mineral composition is also gradual; where it consists only of minerals of the kaolinite series it is called flint clay and where it consists of aluminous hydroxide minerals together with kaolinite minerals it is called aluminous shale. The chemical compositions of aluminous shale and flint clay, as shown by the analyses of ores from different localities, are shown in Table 3.

One thing that attracts our attention in the above analyses is that the ignition loss is almost constant at 12–14 per cent, notwithstanding the fact that a considerable amount of amorphous matter is contained in all the ores except crystalline kaolinite and diaspore. The iron is shown as ferric iron, but as has already been stated, a fairly large amount of ferrous iron is included in it, especially in the green and bluish-gray ores.

4. Mineral Components of Aluminous Shale and Flint Clay

Some of the aluminous shale ores show a scintillating reflection of light upon fresh fractures, indicating the presence of visible, though fine-grained, crystals. But in the majority of the ores such crystal grains can hardly be discerned by the naked

Table 3. Chemical Analyses of the Aluminous Shale in Manchuria.

		Locality	Ore	Ig. 1.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkalis	TiO_2	Analyst*
"A" Bed	Aluminous shale	Pan-tao-ling, Yen-tai	Diaspore nodule (gray)	11.04	1.48	69.95	11.94	0.38	0.57	1.47	3.65	Mita
		,, ,,	Diaspore pisolite	14.52	7.05	68.82	6.00	0.44	0.50	1.26	2.61	,,
		,, ,,	High grade ore (green, pisolitic)	15.55	15.90	60.14	7.98	0.08	0.11	-	-	,,
		,, ,,	Medium grade ore (green, pisolitic)	12.97	18.80	53.52	15.76	tr.	0.18	-	-	Cent. Lab.
		Chang-chia-kou, Hsiao-shih	Low grade ore (bluish-gray, pisolitic)	-	25.08	45.50	15.87	-	-	-	2.08	,,
		Pen-hsi-hu	Low grade ore (bluish-gray, pisolitic)	-	29.84	43.65	13.52	-	-	-	0.95	,,
	Flint clay	Tsu-erh-shan, Yen-tai	High grade ore (celadon)	14.02	45.71	39.19	1.62	0.21	0.17	-	-	Mita
		Pen-hsi-hu	Low grade ore (yellow)	-	39.82	33.80	8.41	-	-	-	1.74	Cent. Lab.
		Pan-tao-ling, Yen-tai	Low grade ore (purple red)	13.58	40.24	36.68	9.45	0.22	0.34	-	-	Mita
"G" Bed	Aluminous shale	San-leng-shan, Fu-chou	Diaspore (compact, massive, gray)	-	3.28	71.60	3.14	-	-	-	3.26	Cent. Lab.
		Yen-tai	High grade ore (white, pisolitic)	14.75	21.64	57.72	1.98	0.58	0.70	1.28	3.05	Mita
		Niu-hsin-tai	Low grade ore (red)	-	25.08	43.60	17.44	-	-	-	-	Cent. Lab.
		,,	Low grade ore (dark green)	-	23.98	28.22	35.28	-	-	-	1.50	,,
	Flint clay	Niu-hsin-tai	High grade ore (gray)	-	42.70	40.53	1.90	-	-	-	1.70	,,

* Analyst: Mita—Masaaki Mita, Research Section, formerly Showa Iron & Steel Works, An-shan; Cent. Lab.—Central Laboratory, South Manchuria Railway Co., Dairen.

Table 4. Mineral Components and Crystal Grain Size of the Aluminous Shale and Flint Clay.

	Minerals	Pisolitic ores		Compact massive ore	Remarks
		Pisolite	Matrix		
Chiefly microcrystalline	Diaspore: α–Al 0 (0H)	Macro-Micro	Micro-crypto	Crypto	Macrocrystalline: 50–200 microns
	Kaolinite: $Al_2Si_20_5$ $(0H)_4$	Micro	Micro	Crypto-Micro	Microcrystalline: 5–50 microns
	Chamosite: $(Al, Fe^{3+}, Fe^{2+})_6$, $(Al, Si)_4$ 0_{10} $(0H)_8$	Macro (rare)-Micro	Macro (rare)-Micro	Crypto	Cryptocrystalline: 1–5 microns
	Nontronite: $(Fe^{3+}{}_2)$ $(Al_{.33}Si_{3.67})0_{10}(0H)_2$. n H_20	Macro-Micro	Micro-Crypto	Crypto	Cryptocrystalline: <1 microns
	Rutile: $Ti0_2$	Micro	Micro	Crypto	
	Turgite: $2Fe_20_3$ $2H_20$	Powdery or filmy			
Gel-like or cryptocrystalline	Boehmite: α–Al0 (0H)		Crypto		
	Halloysite: $Al_2Si_20_5$ $(0H)_4$		Crypto	Crypto	
	Chamosite: $(Al, Fe^{3+}, Fe^{2+})_6$ Al, $Si)_40_{10}$ $(0H)_8$		Crypto	Crypto	
	Doelterite: $Ti0_2$ $2H_20$		Crypto?	Crypto?	
	Limonite: Fe0 (0H) nH_20		Stain	Stain	

Table 5. Mineral Components of the Aluminous Shale in Manchuria.

Beds	Localities	Fu-chou	Chemical analysis				Mineral components						
			SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Diaspore (grain size: dia. microns)	Sporogelite, Boehmite	Halloysite, Kaolinite	Chamosite	Chloropal, Nontronite	Hematite, Turgite	Doelterite Rutile
"A"	Pan-tao-ling, Yen-tai	Grayish-brown, compact, hard	9.93	63.85	9.40	2.80	◯ 2–30	◯	+	+	△		+
〃	〃	Yellowish-brown, compact	18.15	54.86	11.30	1.95	○ 2–10	◯	△	+	○		+
〃	Niu-hsin-tai	Gray, pisolitic	17.38	65.92	1.74	1.03	◎ 3–50		◯				+
"G"	〃	Dark grayish-brown, hard	9.86	58.90	17.65	-	◎ 10–25		○		+	△	-
〃	Fu-chou	Gray, compact	22.36	58.10	2.63	-	◎ 2–5		◯				R +
〃		Grayish-white, compact, hard	16.18	65.87	1.81	2.79	◎ 2–10		◯				R +

Weight %: ◎ 50–75 ◯ 25–50 ○ 15–25 △ 5–15 + <5

eye. All of the minerals are extremely fine-grained or under 100 μ in diameter. Under the microscope the compact and apparently opaque portion is seen to be an aggregate of fine, dusty crystal grains; the individual grains can be first observed with a magnification of over 200. These grains are 1–3 μ in diameter. At first glance under the microscope the compact translucent part which appears to be amorphous is also present in a fairly large amount. With a magnification of 200 or more and by inserting a condenser under the crossed nicols, minute grains show slight double refraction which suggests that they are crystalline. The mineral components of this part can be inferred on the basis of the degree of recrystallization as well as chemical analyses. Besides, by means of X-ray and differential thermal analyses, the components have been nearly determined.

Grain size and distribution of each mineral are shown in Table 4.

In the table the flint clay corresponds to the compact massive ores which consist of kaolinite and halloysite. Microscopical examinations of thin sections of ores from different localities are summarized in Table 5.

By means of differential thermal analyses, heating aluminous shale and flint clay and measuring the dehydration and inversion temperatures, it was established that flint clay consists of kaolinite and halloysite, and aluminous shale of a mixture of kaolinite, halloysite, and diaspore.

It has been stated that the outcrop of the rich ore body of the "A" bed at Pan-tao-ling, Yen-tai, shows a symmetrical banding in a profile perpendicular to the bedding, that is, with green aluminous shale in the middle, and yellowish-brown to purple flint clay both above and below. The chemical analyses of each band by M. Mita are shown in the following table:

Table 6. Chemical Analyses of Aluminous Shale and Flint Clay, taken along the Profile of an Outcrop of the Rich Ore Body in the "A" Bed at Yen-tai (M. Mita).

Samples	Ig. l.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Color
E-No. 11	13.25	43.82	40.30	1.46	0.46	0.23	Celadon
10	15.42	43.90	39.58	2.24	0.24	0.11	Gray
9	13.58	40.24	36.68	9.45	0.22	0.34	Reddish-purple
8	14.39	42.30	38.33	4.83	0.27	0.15	Purplish-gray
7	16.24	39.92	39.27	4.43	0.05	0.13	Grayish-yellow
6	16.54	33.55	37.66	12.38	0.04	0.26	Grayish-brown
5	16.00	25.15	45.88	14.41	0.14	0.14	Green
4	15.55	15.90	60.14	7.98	0.08	0.11	〃
3	13.60	25.72	47.92	9.88	0.07	0.25	Grayish brown
2	15.18	37.70	41.40	5.72	0.09	0.13	Brown
1	14.55	42.77	36.88	4.98	0.16	0.23	Grayish-purple

Sample numbers: 11 at footwall; 1 at hanging wall; others intermediate.

M. Mita analyzed these samples by the differential thermal method. Green aluminous shale in Table 6 exhibits a diaspore curve which grades successively upward and downward into a kaolinite curve. This sequence is perfectly in accordance with optical observations and chemical analyses, showing a typical profile of the "A" bed.

Yasuo TANAKA discovered through thermal analyses and measurement of vapor tension that the aluminous shale from Chin-chou consists of a mixture of diaspore and kaolinite (*Jour. Chem. Soc. Japan*, v. 58, p. 176–181).

Shōichirō NAGAI *et al.* made a comparative study by thermal analyses of bauxite, aluminous shale, and diaspore from different localities.

The X-ray analyses performed at the Continental Research Institute revealed the presence of boehmite in some of the ores as well as diaspore and kaolinite. From optical observation the writer suspected the presence of boehmite in some ores from Shan-tung Province. Boehmite is the chief constituent of the terra rossa type bauxite in France and elsewhere and is soluble in soda. The ores with a large amount of boehmite may be economically utilized by the Bayer process.

The results of ODA's X-ray analyses are shown in the following table (Saburo ODA, X-ray studies on clays from Manchuria, Report No. 1; On the boehmite in the aluminous shale in Manchuria: *Report of the Continental Research Institute*, v. 5, no. 10, p. 293–308, 1940).

Table 7. Chemical Components of the Aluminous Shale and its Mineral Composition as Determined by X-ray Analyses (S. Oda).

Localities	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	MgO	CaO	Ig. l.	Minerals det. by X-ray*
Ku-yeh	77.67	2.46	1.96	2.49	–	–	14.89	D. K
Sho-ko-zan	69.50	7.12	4.51	2.76	–	0.21	14.98	D. K
N. China	72.59	8.86	1.41	2.60	–	–	14.55	D. K
Fu-chou	69.60	10.70	1.76	3.43	–	–	14.30	D. K
Yen-tai	57.06	15.28	12.15	1.99	–	–	13.24	D. K. B
〃	54.51	17.98	12.24	1.92	–	–	13.40	D. K. B
〃	52.70	18.66	13.40	1.70	–	–	13.43	D. K. B
Niu-hsin-tai	52.98	18.92	12.66	1.96	–	–	13.34	B. K. D
Yen-tai	53.31	20.00	9.63	2.36	–	–	14.21	B. K

* D—Diaspore, K—Kaolinite, B—Boehmite

Observations, both by the naked eye and under the microscope, are not discussed in detail by ODA, but the last-mentioned sample from Yen-tai is said to be "greenish-yellow" to the naked eye. Therefore, it is almost certain to be a compact, massive, rich aluminous shale ore containing pisolites. The ores of this class appear to be amorphous under the microscope, and from both observations under the microscope and chemical analyses, have been supposed to consist of a mixture of halloysite with either sporogelite or gel-alumino-ferrique. Judging from results obtained by S. ODA, however, the sporogelite may be cryptocrystalline boehmite.