

Pyrite Concentration and Paleoenvironmental Change of the Hiroshima Delta (Japan)

Jinadasa Katupotha*

Department of Geography, Hiroshima University
1-1-89, Higashi Senda Machi, Naka-ku, Hiroshima 730, Japan

일본 히로시마 삼각주 퇴적층의 황철석 함량과 고 환경변화

지나다사 카투포타
히로시마대학교 지리학과

ABSTRACT

Pyrite (FeS_2) content in brackish and salt marsh sediments is relatively higher than the amount in freshwater marsh sediments. Different values of pyrite sulfur ($\text{FeS}_2\text{-S}$) content in sediments from the Hiroshima Delta indicate that poorly drained salt marsh had developed between 27.0m and 28.0m below mean sea-level and palaeo-sea-level was constant for several hundreds of years in the same depth during the early Holocene Epoch.

요 약

현세 반담수와 염수습지 퇴적층에 함유된 황철석(FeS_2)의 함량이 담수습지 퇴적층에서보다 상대적으로 많은 것으로 나타났다. 일본 히로시마 삼각주 퇴적층에서의 황철석 유황($\text{FeS}_2\text{-S}$)의 함량차이의 이유는 초기 현세동안에 고 해수면(palaeo-sea level)의 위치가 수백년 동안 같았으며 또한 배수가 잘 되지않은 염수습지가 현재의 평균해수면 보다 27m~28m 낮은 위치에 발달하였음을 지시한다.

* Present Address: Department of Geography, University of Sri Jayawardanepura, Nugegoda, Sri Lanka

INTRODUCTION

The process of sedimentary pyrite (FeS_2) formation in marine sediments is controlled by reactive iron minerals and the availability of organic water. Pyrite is found more in brackish water and salt marsh sediments than in freshwater sediments (Berner et al., 1979; Postma, 1982). Berner et al. (1979) have shown that there exists a general correlation between salinity and FeS_2/FeS ratio. In addition, there are many complicating factors which effect the sulfide content in sediments, but not intends to discuss here in detail, e.g. the sedimentation rate, the type of the sediments, the initial organic matter content at the time of deposition and the presence or absence of other detrital sulfide mineral phases etc.

The formation of pyrite in nature is a very slow process, but it forms more rapidly in salt marsh peat (Howarth, 1979). Poorly drained swamp deposits are made up of black mud with a high content of organic matter, and pyrite content is relatively high (0.5 to 3.5%) in such deposits. But, the content of organic matter in a well-drained swamp deposit is very low, and pyrite content also is very low (Reineck and Singh, 1973). Berner et al. (1979) have used the authigenic iron sulfides to examine palaeosalinity in Chesapeake Bay (USA). Thus the content of $\text{FeS}_2\text{-S}$ in sediments can use as an indicator to examine palaeoenvironmental change in coastal areas. The aim of this study is to reveal the palaeoenvironmental changes of the Hiroshima Delta (Japan), based on content of $\text{FeS}_2\text{-S}$ of a sediment core.

STUDY AREA

The study area is situated between $132^\circ 24'$ -

$132^\circ 30'$ E latitude and $34^\circ 20'$ - $34^\circ 26'$ N longitude (approx.), and comprises various types of landforms (Fig. 1). The Ota River flows into Hiroshima Bay (Seto Inland Sea) with six tributaries. Geological profiles indicate that the delta is mainly made up of sand, clay and gravel, marine shells with sandy clay, silt and silt clay layers. These sediments have been deposited on the pebbles and weathered bedrock layers. Piedmont and dissected hills of the adjoining areas, Cretaceous in age, are plutonic (granatic) rocks. Some volcanic (andesitic) rock bands are seen in the hilly islands (National Land Agency, Hiroshima, Prefecture, 1978).

The present mean annual rainfall in the area varies between 1,600mm and 2,000mm. The mean temperature in February ranges from 4°C to 8°C , and in August it ranges from 26°C to 28°C (National Atlas of Japan, 1977). The tidal range of Hiroshima Bay is relatively large, ranging from the MHWS at +370cm and MLWS at -10cm from the MSL (Data based on the Hiroshima datum level, Tide tables for the year 1987). The reclaimed lands and the lower parts of the delta, including sampled area, are not inundated periodically or intermittently by tidal water. But during the MHWS, sea water flows more than 6km interior from the present coast along the tributaries of the Ota river.

METHODOLOGY

Organic rich samples were collected from a core, 37m depth, from the Hiroshima Delta drilled by Fukken Chosa Sekkei Co. Ltd., Hiroshima, on May in 1987 (Fig. 1). Colour of the soils were identified using Munsell's soil colour charts.

The laboratory procedure for $\text{FeS}_2\text{-S}$ analysis was modified by author, following mostly the procedures described by Berner (1970, 1979).

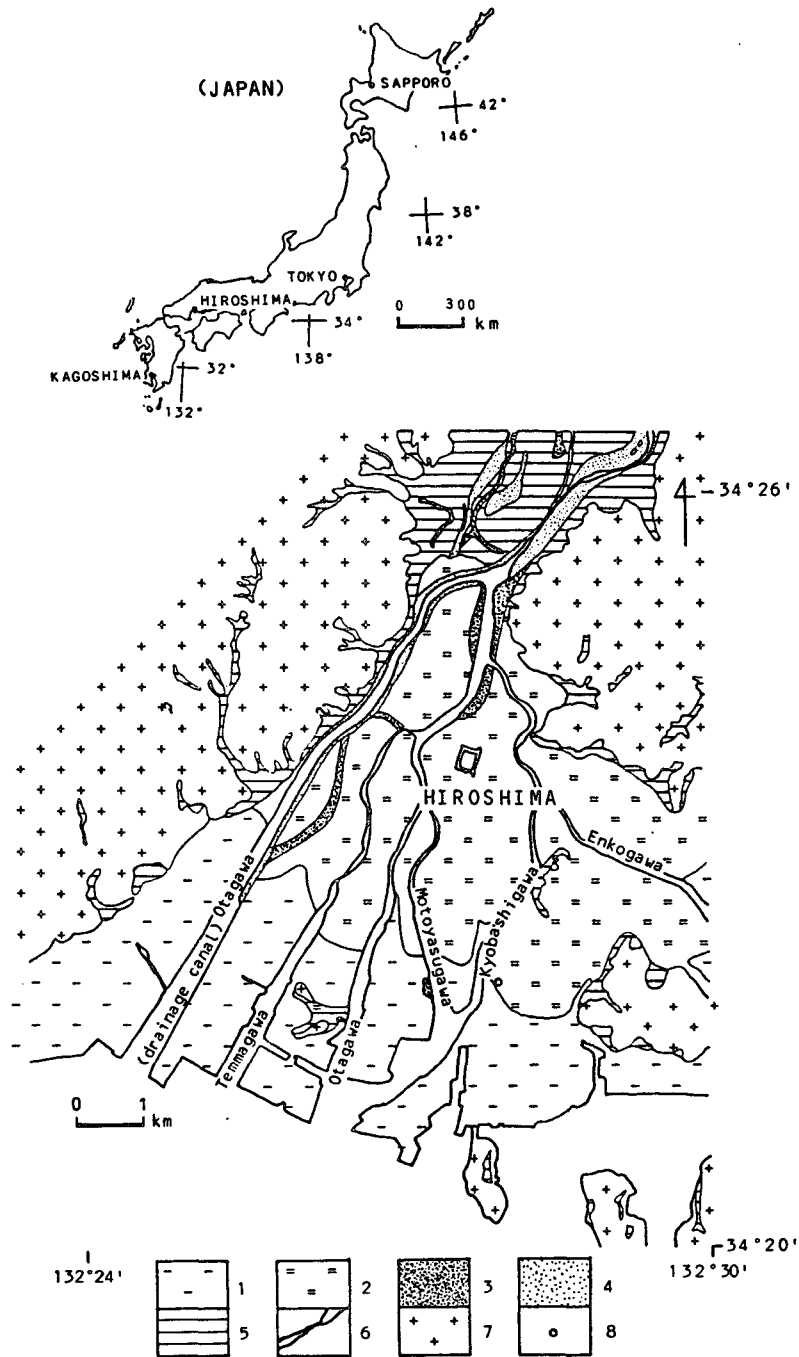


Fig. 1. Location and landforms of the study area. (1) Reclaimed land; (2) Delta; (3) Former river course and wetlands; (4) Natural levee or dry river bed; (5) Valley and flood plains; (6) River or canal; (7) Dissected hill; (8) Sample location.

In brief, the analytical procedure is as follows: First, the colour and constituents of weighed samples (20-30 grams) were identified. HCL (10 ml) and H₂O₂ (5 ml) were added to each sample, and diluted by water (60ml) to remove CaCO₃ and other organic matter and also the acid-volatile monosulfides, and pyrite represent the sediments. The prepared samples were remained over night, and water was decanted carefully. The residue of each sample was washed several times to remove chemicals and dried for one night (100°C). Later, the sample was ground into powder and HNO₃ (7.5 ml), HCL (2.5 ml), Br (1.0 ml) and pure water (20.0 ml) were added to each weighted sample. The all samples were boiled nearly one hour to dissolve Fe, Mg, Na, Ca etc. The dissolved material was filtered and washed several times. The solutions (about 300 ml) were filtered again and heated for nearly two hours. During these two hours, 10 ml of 5% BaCl₂ was added first, subsequently 5ml of 5% BaCl₂ was added several times to precipitate BaSO₄. Next day, the water was decanted carefully from the samples using filter paper, and the residue (BaSO₄) was washed three or four times using pure water. The residue (BaSO₄) was put into a weighed bowl, and heated to 900°C for nearly 30 minutes. The bowl was placed in to cool, and weighed again to obtain the weight of BaSO₄ for each sample. Finally, the content of FeS₂-S (Dry weight = Dwt) was counted using the following formula.

$$\frac{\text{Dwt of sample BaSO}_4}{\text{Dwt of sample(ground residue)}} \times \frac{\text{FeS}_2\text{-S}}{\text{BaSO}_4} = \frac{\text{Content of FeS}_2\text{-S (Dwt)}}{\%}$$

All laboratory work was carried out at the Radiocarbon Dating Laboratory in the Department of Geography, Hiroshima University.

RESULTS

Results of the FeS₂-S concentration in each sample of the core are shown in Table 1 and Fig. 2. FeS₂-S was not found in the sample from surface level upto 4.5m depth. Approx. 5.0m to 26.75m depth, FeS₂-S content showed somewhat high values, and varied between 0.551% and 0.754%. Fairly high values were found in between 26.75m and 27.5m. Beyond 30.0m depth, the FeS₂-S content gradually decreased. These sequences showed a good relationship between the FeS₂-S content and different soil layers in the core (Fig. 2). An organic layer was found between 26.0m to 27.7m depth in the core, it indicates that a brackish or salt marsh had developed in the area.

DISCUSSION

Marine sediments often contain more than 1% pyrite sediment but rarely contain more than 10% in organic matter (Berner, 1970). Therefore, Berner et al. (1979) reported that for salinities between 35‰ and 26‰ the FeS₂/FeS ratio is normally high and it is greater than 10.0. Between 26‰ and 18‰ values of FeS₂/FeS are available and strongly dependent upon the rate of deposition. At salinities distinctly less than 18‰ the ratio is generally less than one. According to Howarth (1979), pyrite formation in salt-marsh ecosystem occurred more rapidly without intermediate monosulfid formation than is generally in any natural system. Postma (1982) explained that pyrite is rare in freshwater sediments. Those indicates that there are different values of FeS₂-S content of sediments in salt marsh, brackish water marsh or fresh water marsh during their deposition.

The result of this study shows that the

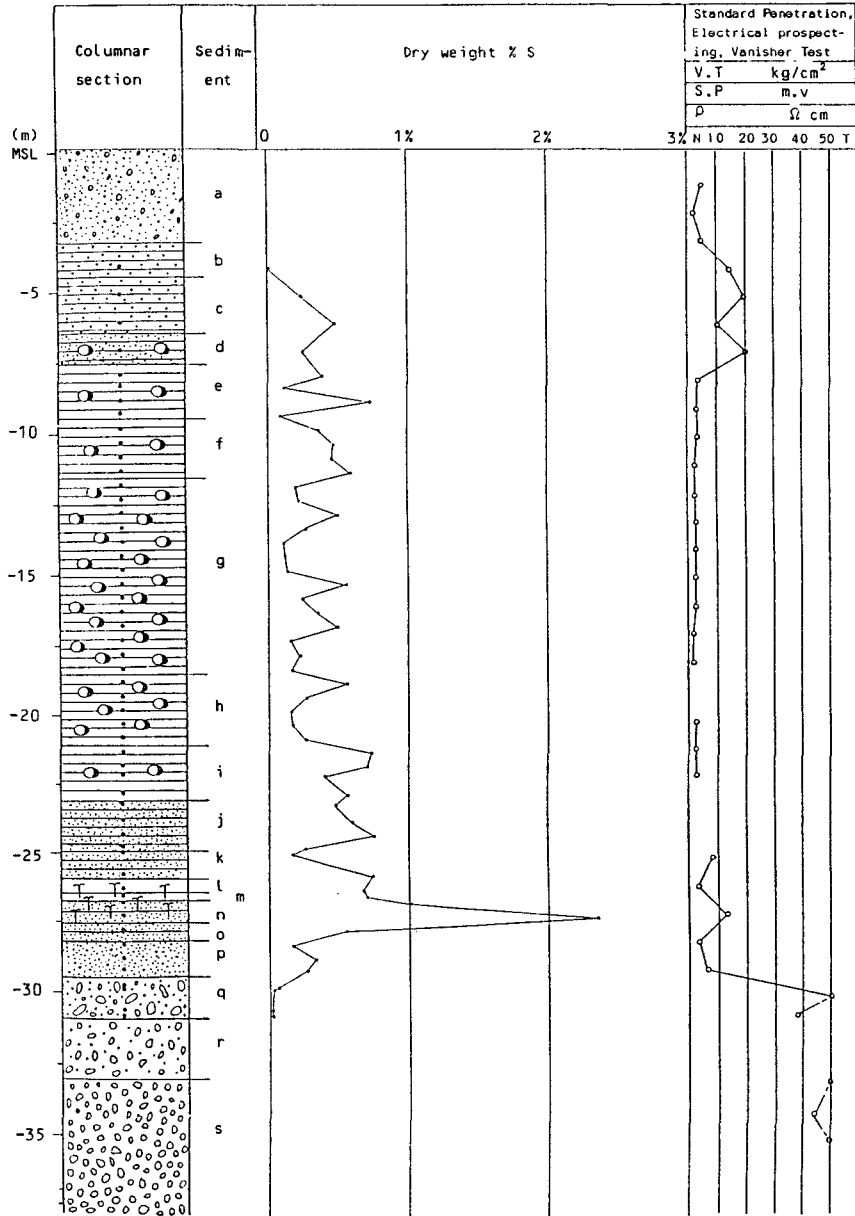


Fig. 2. Columnar section of the core sediments from the Hiroshima Delta showing the correlation between various sediments and content of $FeS_2 \cdot S$ (a) Sand, clay and gravel (reclaimed land); (b) Dark bluish gray clay and coarse sand; (c) Bluish gray clay, coarse sand and shell fragments; (d) Gray clay, fine to medium sand and shell fragments (7.5 Y, 4/1); (e) Olive black clay and shell fragments (7.5 Y, 3/2); (f) Dark olive gray clay and shell fragments (2.5 GY, 3/1); (g) Dark olive gray clay and many shell fragments (5 GY, 3/1); (h) Dark olive gray clay and many shell fragments (2.5 GY, 4/1); (i) Dark olive gray clay and shell fragments (2.5 GY, 3/1); (j) dark olive gray clay and fine sand (2.5 GY, 3/1); (k) Dark greenish gray clay and fine to medium sand (7.5 GY, 4/1); (l) Greenish gray clay and organic matter (10 GY, 5/1); (o) Dark greenish gray clay and fine sand (little compact, 10 GY, 4/1); (p) Fine to medium sand and little coarse sand (little compact, 10 GY, 4/1); (q) Coarse sand and pebbles (5 cm-7 cm); (r) Coarse sand and many small pebbles (1 cm-3 cm); (s) Many large size pebbles.

FeS₂-S was not concentrated in the area from the surface to about 5.0m depth. The soil layer is mainly made up of terrestrial materials which were brought from adjoining hilly areas. A thick clayey sand and clay layer with shells in the core (this study) was between 5.5m to 26.75m depth. Such sediments have been found in the areas of Temma Cho (town), Hachchobori, Matoba Cho, Ujina Kanda Cho in the Hiroshima Delta (the thickness of layers was varied locally), and extended between about 10m and about 25m beneath from the surface level (National Land

Agency, Hiroshima Prefecture, 1978). The FeS₂-S concentration fluctuates between 0.082% and 0.754% percentages in the sediments of different colour (Fig. 2). It can therefore be inferred that low salinity conditions (brackish water conditions) have occurred intermittently on the Hiroshima Delta. Shiragami (1985 and 1986) obtained similar results in the samples of recent sediments from the Hiroshima Delta to examine the evolution of coastal lowlands during the Holocene.

Organic matter with silt as well as with clay

Table 1. Concentration (in % Dry weight) of FeS₂-S in the core sediment from the Hiroshima Delta

Core depth (m)	Sample weight (g)	Residue Dwt (g)	BaSO ₄ Dwt (g)	FeS ₂ -S % Dwt
3.0-3.5	30.48	1.876	—	—
4.0-4.5	30.08	1.985	—	—
5.0-5.5	30.39	2.638	0.046	0.240
6.0-6.5	25.00	3.405	0.120	0.484
7.0-7.5	25.00	2.425	0.043	0.247
8.10	24.00	9.583	0.270	0.387
8.50	16.80	7.666	0.069	0.124
9.00	19.80	8.841	0.471	0.732
9.46	17.30	8.086	0.048	0.082
10.00	20.34	9.392	0.243	0.355
10.47	24.94	9.753	0.333	0.459
11.00	25.53	9.593	0.319	0.457
11.50	24.93	9.901	0.402	0.558
12.00	25.30	9.200	0.129	0.193
12.50	22.00	9.748	0.155	0.218
13.00	20.31	8.970	0.325	0.498
13.50	20.10	9.015	0.179	0.273
14.00	20.27	9.277	0.073	0.108
14.45	20.12	8.899	0.096	0.148
15.00	20.08	9.680	0.098	0.139
15.50	23.10	9.807	0.365	0.139
16.00	22.49	9.560	0.170	0.244
16.50	22.45	9.840	0.251	0.350
17.00	16.79	9.594	0.340	0.487
17.45	23.39	9.245	0.109	0.162

Table 1 (Continued)

18.00	22.64	9.325	0.150	0.221
18.50	21.55	8.677	0.109	0.173
19.00	23.46	8.623	0.355	0.566
19.50	21.24	9.322	0.182	0.268
20.00	24.08	9.201	0.110	0.164
20.50	19.06	9.482	0.114	0.166
21.00	20.66	9.612	0.183	0.261
21.50	24.47	9.809	0.524	0.734
22.00	28.02	9.779	0.492	0.691
22.35	24.39	9.292	0.268	0.396
23.00	22.75	9.785	0.407	0.572
23.40	26.72	9.233	0.315	0.469
24.00	24.59	9.077	0.387	0.586
24.50	25.53	9.745	0.535	0.754
25.00	25.75	6.481	0.124	0.263
25.20	25.17	3.756	0.047	0.172
26.00	29.00	4.830	0.261	0.742
26.50	22.69	8.563	0.419	0.672
26.75	22.20	8.270	0.426	0.708
27.00	32.31	4.097	0.302	1.013
27.50	29.56	2.383	0.408	2.352
28.00	25.10	7.424	0.298	0.552
28.50	24.44	6.555	0.808	0.168
29.00	28.89	6.086	0.162	0.438
29.40	30.62	5.019	0.098	0.268
30.00	32.00	5.032	0.093	0.068
30.20	28.50	1.252	0.003	0.033
30.70	27.72	2.005	0.004	0.027
31.00	29.51	1.792	0.003	0.023

layers were seen in the areas of Funairi Cho, Hiroshima University and Kasumi Cho (National Land Agency, Hiroshima Prefecture, 1978). High FeS₂-S percentages showed the layers between 27.0m and 27.5m depth (Table 1 and Fig. 2). It can be inferred that a brackish or salt marsh had developed, and the palaeosea-level was constant for several hundred years. The underlain materials of this silt and clay layer (with shells or organic matter) consist of coarse sand, pebbles and weathered rocks. The

FeS₂-S content had considerably decreased from 30.0m of the coarse sand with partly rounded or rounded pebble layers, and it is assumed that those sediments were fluvial in origin.

CONCLUSIONS

Concentration of FeS₂-S in sediments of the core showed a good relationship with the constituents of each soil layer. FeS-S was not found from the surface level to about 5.0m depth,

which was made up of terrestrial materials. Relatively high FeS₂-S content (0.083%-0.754%) was seen between about 5.5m and about 26.75m depth which was made up mainly of clayey sand and clay. Fairly high FeS₂-S content (1.013%-2.352%) in organic matter with greenish clay and fine sand layer (27.0m and 28.0m depth), showed that poorly drained salt marsh had developed in the area, and it can be inferred that the palaeo-sea-level was constant for several years and sea level had risen continuously later.

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