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An Occurrence of Melanterite from the Katanoyama Formation in Nishino-omote City, Kagoshima Prefecture

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Abstract

A melanterite occurred as fibrous crystals on the surface of a siltstone of the Katanoyama formation in Nishino-omote City. When the siltstone was dried in air, the fibrous crystals of melanterite have grown-up. The occurrence of melanterite in the Katanoyama formation suggests that the siltstone depositted under the reduction condition.

Key Words: Melanterite, The Katanoyama formation, Pyrite

INTRODUCTION

Siltstones of the Katanoyama formation contain many fossils such as mammals, fishes, shells, molluscs and plants (Saheki, 1929). The first excavation was carried out at Sumiyoshi, Nishino-omote City to study these fossils in 1988, and second excavation was held in 1989. When the second excavation was held, one of the authors found many white fibrous crystals on the surface of the siltstones. The crystals were identified as melanterite. Melanterite ($Fe_2SO_4 \cdot 7H_2O$) usually occurs as a decomposition product of iron sulphides, and it is unusual to be observed on the surface of ordinary siltstones. The authors think that it is useful to estimate the environmental condition of deposition of the siltstone including many fossils to clarify the origin and occurrence of melanterite.

OUTLINE OF GEOLOGY AND MODE OF OCCURRENCE

The Tane-ga-shima island lies about 40 Kilometers southeast of the Kyushu mainland. Geological studies of the Tane-ga-shima were carried out by many researchers so far (Saeki, 1929; Hayasaka, 1973, 1974; Hayasaka *et al.,* 1980, 1983; Hatta, 1988). The exposed bedrocks in the island is the Kumage group. The Kumage group is overlain by the Quaternary Katanoyama formation with

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unconformity. The Katanoyama formation consists of siltstone, lignite layers and gravels and is distributed in the Sumiyoshi area. The geologic map around Sumiyoshi area, Nishino-omote City is shown in Fig. 1, and the geologic columnar section at the sampling point is shown in Fig. 2. Stratigraphic succession of the Katanoyama formation in the Sumiyoshi area can be divided into 6 layers. They are called as A, B, C, D, E, F and G from top to bottom. The G layer consists of organic siltstones, and it is considered that the Kumage group is overlain by the Katanoyama formation with unconformity. The F layer consists mainly of lignite layers (70 cm in thickness) in the upper part and organic siltstones (45 cm in thickness) accompanied with volcanic ash layer with pumices in the lower part. The E layer is observed at a cutting along the road near a bus stop. Stacking of layers of pumice (3 cm), peat deposits (10 cm), pumice (15 cm) and tuffaceous silt (20 cm) is observed from bottom to top. The D layer consists of pebble of sandstones derived from the Kumage group and contains thin organic mudstone layes. The C layer consists of 1) a concentrated layer of oystars (30 cm), 2) sandy silt layer with gravel (1.1 m) and 3) grey silty sand layer (20 cm) from bottom to top. Many shell fossils such as Cerithidea cingulata and Anadara troscheli occur in the layers of 2) and 3). The B layer consists of blackish grey mudstones and a white clay layer is on the top of the layer. The grey mudstones intercalate at least eight thin white volcanic ash layers (T1, T2,......T8). The B layer is divided into four layers. They are the most upper, upper, middle and lower layer. The most upper part consists of white clayey silt layer (50 cm) and bands of limonite often occur in the bottom part. The upper part (20 cm) consists of brown to grey organic silt layers, and intercalates T2 volcanic ash layer (4 cm in thickness) in the bottom. The middle part consists mainly grey silt layers (23 cm) and intercalates four volcanic ashes (T3～T6) in the lower part. Many fossils of fishes, plants and shells occur in this part. The lower part consists of grey silt layer (13 cm) in the upper part and blackish grey silt layer (20 cm) in the lower part. The middle part intercalates two white volcanic ash layers (T7, T8). An old elephant fossil occurs in the blackish grey silt layer. The A layer (55 cm in thickness) consists white coarse-grained sand layer and often shows reddish brown colour due to weathering.

The melanterite occurred in the B layer of the Katanoyama formation. The sampling point is shown in Fig. 1. When excavation of various fossils was carried out in 1987, the silt layer gave out a sulpheric smell. After a few years later yellowish green fibrous crystals were observed on the surface of the mudstone layer. The crystals have grown-up when they were dried in air at room temperature (Fig. 3).

EXPERIMENTAL METHODS

The melanterite sample collected from the silt stone was pulverized in an agate mortar. The powdered sample was examined by means of X-ray powder diffraction, thermal, and infrared absorption analysis. Scanning electron microscopic observation was done for the sample as it is. X-ray powder diffraction analysis (XRD) was carried out with a Rigaku diffractometer (30 kV, 15 mA) using $1/2^0$ idvergence and scattering slits. Thermal analysis was carried out with a Rigaku differential thermal and thermogravimetric analysis (DTA-TGA) apparatus. Measurement was carried out from room temperature to 1100℃ with a heating rate of 10 ℃ using about 25 mg powdered sample. Infrared absorption (IR) analysis was carried out with a Nihonbunko infrared absorption

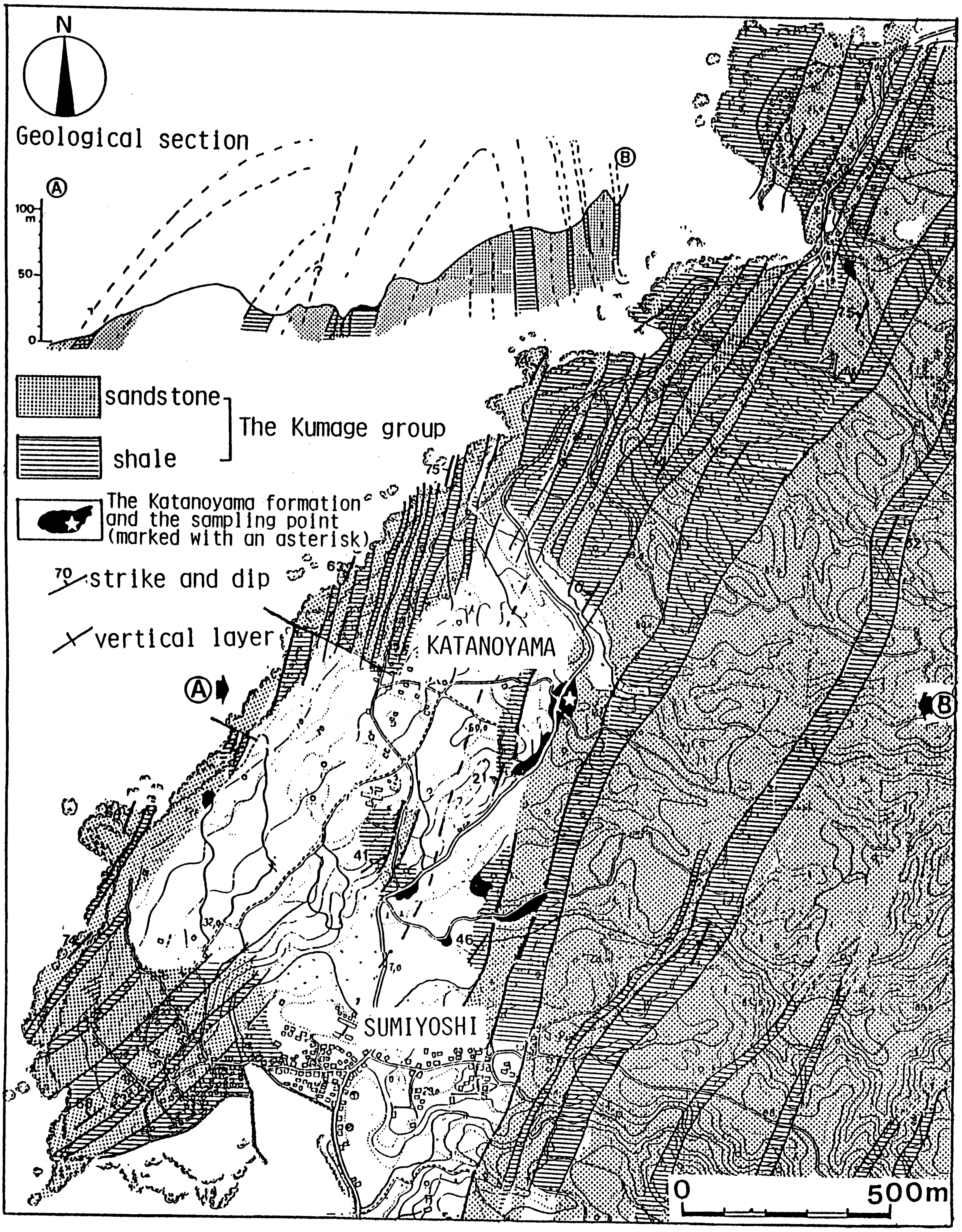

Fig. 1. Geologic map of Sumiyoshi area, Nishino-omote City and the sampling point.

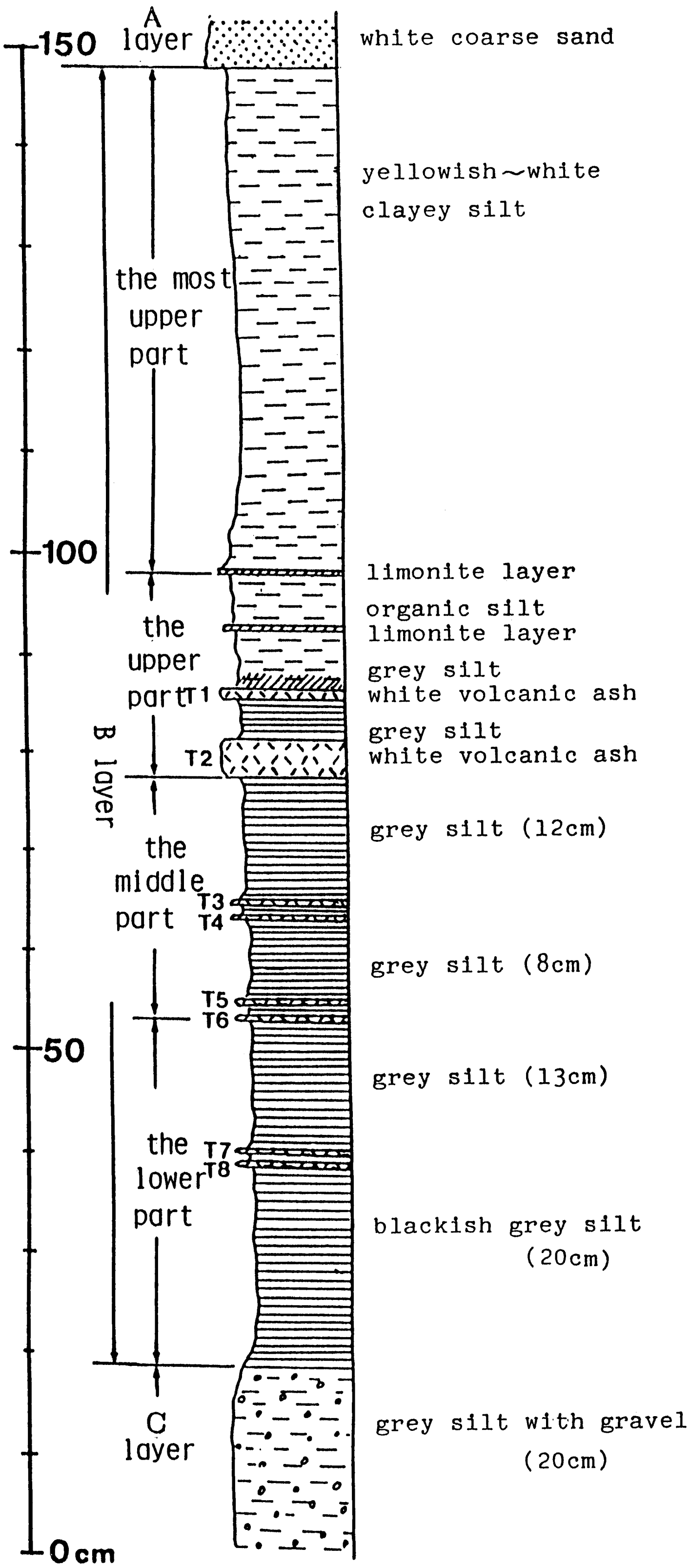

Fig. 2. Geologic columnar section at the sampling point.

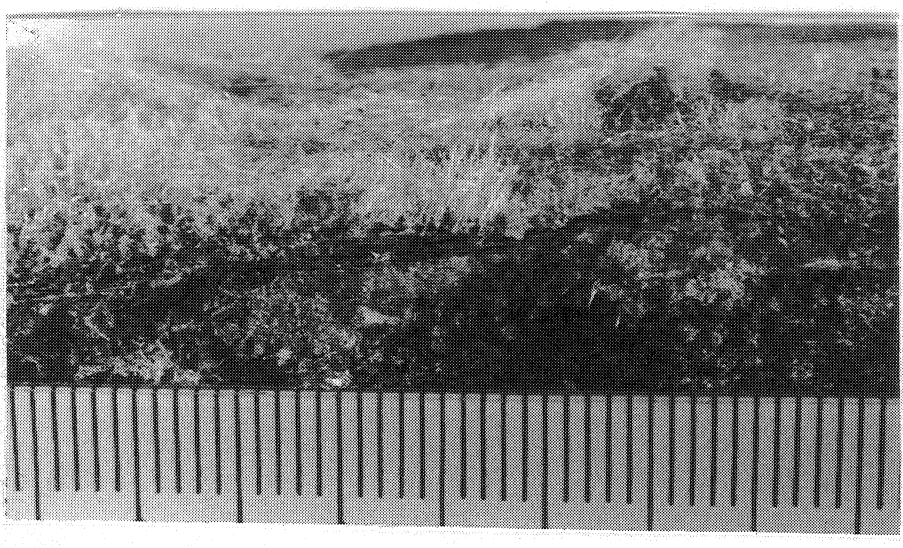

Fig. 3. Photograph of melanterite from Sumiyoshi, Nishino-omote City.

spectrophotometer. The IR spectrum was recorded by KBr method. Scanning electron micrograph was obtained with a JEOL JSM-25SII scanning microscope.

RESULTS

X-ray powder diffraction pattern of the melanterite is shown in Fig. 4, and diffraction data are listed in Table 1 together with data of National Bureau of Standards (1970). Unit cell parameters for the melanterite calculated with a program LCLSQ (Burnham, 1991) are listed in Table 2.

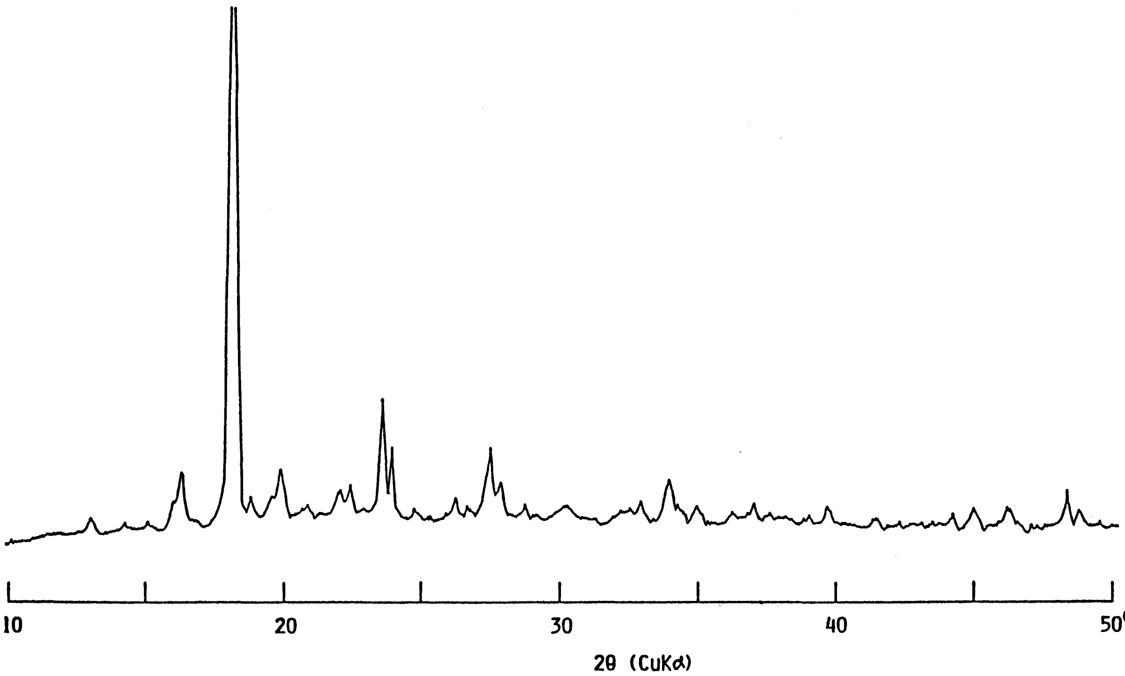

Fig. 4. X-ray powder diffraction pattern of melanterite from Sumiyoshi.

Table 1. X-ray powder diffraction data for melanterites.

	1		2	
hkl	d (A)	I/I_0	d (A)	I/I_0
200	6.79	8	6.81	3
110	5.88	<2	5.87	2
011	5.56	8	5.56	6
$\bar{1}02$	5.49	12	5.47	8
$\bar{1}11$	5.41	4	5.41	7
002	5.33	8	5.30	2
111	4.90	100	4.90	>100
$\bar{2}02$	4.87	50		
102	4.56	10	4.55	4
$\bar{1}12$	4.20	<2	4.18	2
211	4.028	14	4.04	5
$\bar{3}11$	3.776	60	3.77	20
112,202	3.732	20	3.73	12
400	3.392	8	3.39	4
$\bar{4}02$,311	3.291	16	3.29	3
020	3.256	5	3.243	12
$\bar{1}13$	3.209	12	3.200	6
$\bar{2}13$	3.125	8	3.130	2
013,021	3.117	6	3.110	3
$\bar{1}21$	3.084	4	3.070	2
302	3.062	6		
410	3.009	6	3.000	3
121	2.980	<2	2.979	3
$\bar{4}12$,220	2.937	4	2.940	3
$\bar{3}13$	2.905	<2		
$\bar{1}22$	2.799	10	2.788	4
312	2.772	8	2.772	3
$\bar{1}04$	2.757	8	2.755	3
$\bar{5}02$,411	2.731	10	2.722	5
$\bar{2}22$	2.704	<2	2.691	2
$\bar{3}21$,004	2.665	4	2.660	4
122	2.649	8	2.650	7
320	2.643	10	2.644	8
$\bar{4}13$,304	2.625	8	2.623	4
402	2.564	<2	2.570	3
$\bar{3}22$	2.531	4	2.535	2
$\bar{2}14$	2.527	4		
104	2.488	4	2.488	2
321	2.475	4	2.475	2
222	2.453	2		
$\bar{4}04$,$\bar{3}14$	2.434	6	2.430	4
023	2.399	4	2.400	2

420	2.346	2	2.344	2
$\bar{5}13$	2.336	2		
$\bar{4}22,511$	2.314	12	2.310	2
204	2.277	2	2.270	3
502	2.190	<2	2.191	3
$\bar{6}12$	2.181	6	2.181	3
$\bar{4}23,214$	2.149	<2		
$\bar{1}31$	2.117	<2		
$\bar{2}24$	2.096	<2		
$\bar{1}15$	2.081	8	2.080	2
413,304	2.063	2		
$\bar{3}15$	2.054	2	2.053	4
015	2.023	6	2.020	4
422	2.014	8	2.014	3
231,611	1.999	<2	1.994	2
124,323	1.977	<2	1.977	2
$\bar{3}31$	1.964	10	1.964	5
$\bar{4}24$	1.951	8	1.949	3
115	1.931	6	1.930	2
$\bar{7}11,\bar{7}12$	1.913	6	1.910	2
331	1.885	10	1.883	7

1. Synthetic melanterite. Data from National Bureau of Standards, Mono. 25, sec. 8, 38 (1970).
2. Melanterite from Sumiyoshi, Nishino-omote City, Kagoshima Prefecture.

Table 2. Unit cell parameters for melanterites

	1	2
a (Å)	14.077	14.072
b (Å)	6.509	6.500
c (Å)	11.054	11.043
β	105°36'	105°32'

1. Synthetic melanterite. Data from National Bureau of Standards, Mono. 25, sec. 8, 38 (1970).
2. Melanterite from Sumiyoshi, Nishino-omote City, Kagoshima Prefecture.

Figure 5 shows DTA and TGA curves for the melanterite. The DTA curve shows a double low-temperature endothermic peak, corresponding to loss of water in two stages. The exothermic peak is due to crystallization of α-Fe_2O_3.

The IR spectrum of the melanterite is shown in Fig. 6. The several absorption bands in the 900-700 cm^{-1} region are attributable to —OH bending modes. The spectra of the melanterite are listed in Table 3.

Figure 7 shows scanning electron micrographs of the melanterite. The sample exhibits fibrous habits (Fig. 3, Fig. 7A) and each fiber is an aggregate of small crystals (Fig. 7B, 7C).

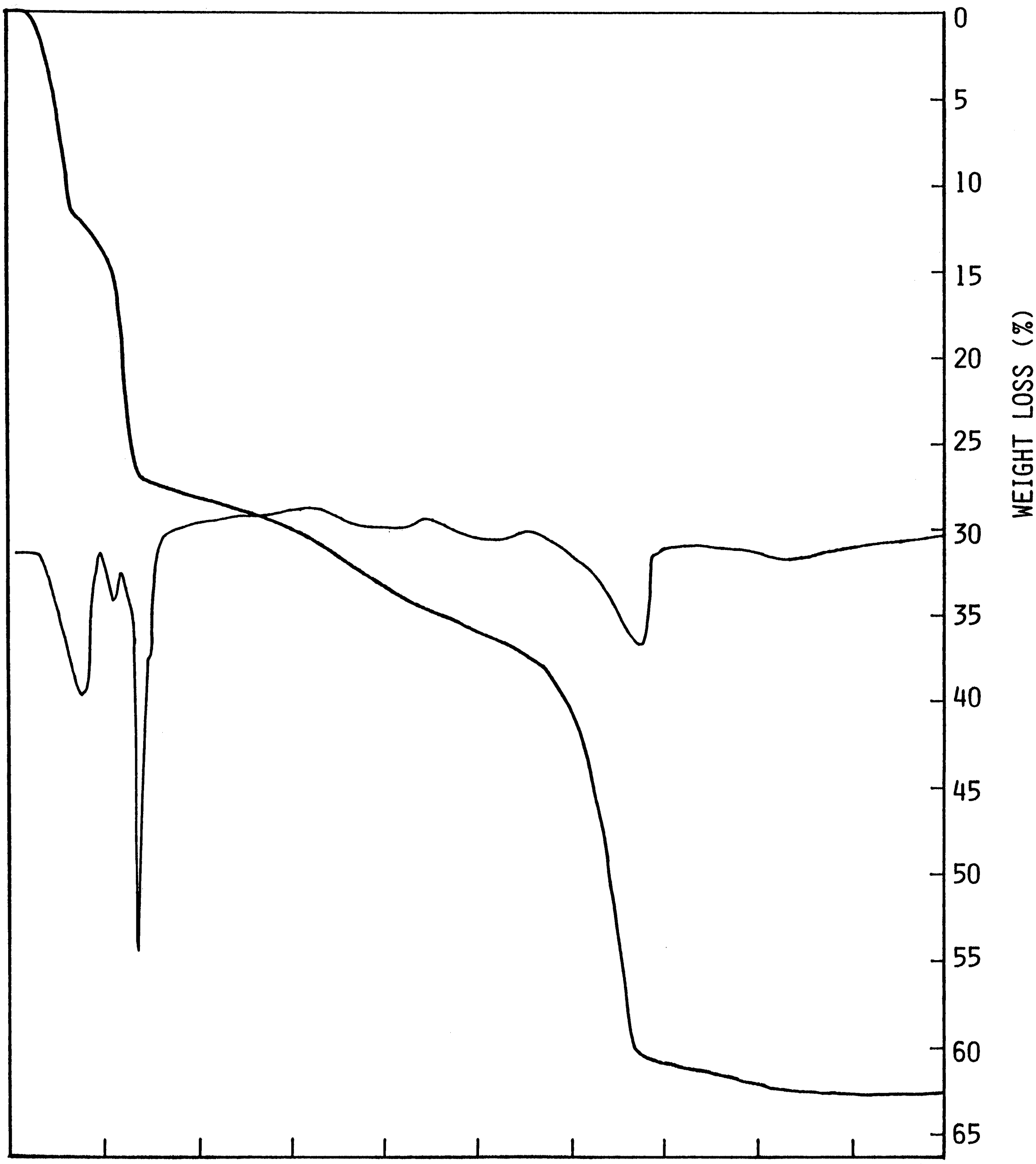

Fig. 5. DTA-TG curves of melanterite from Sumiyoshi.

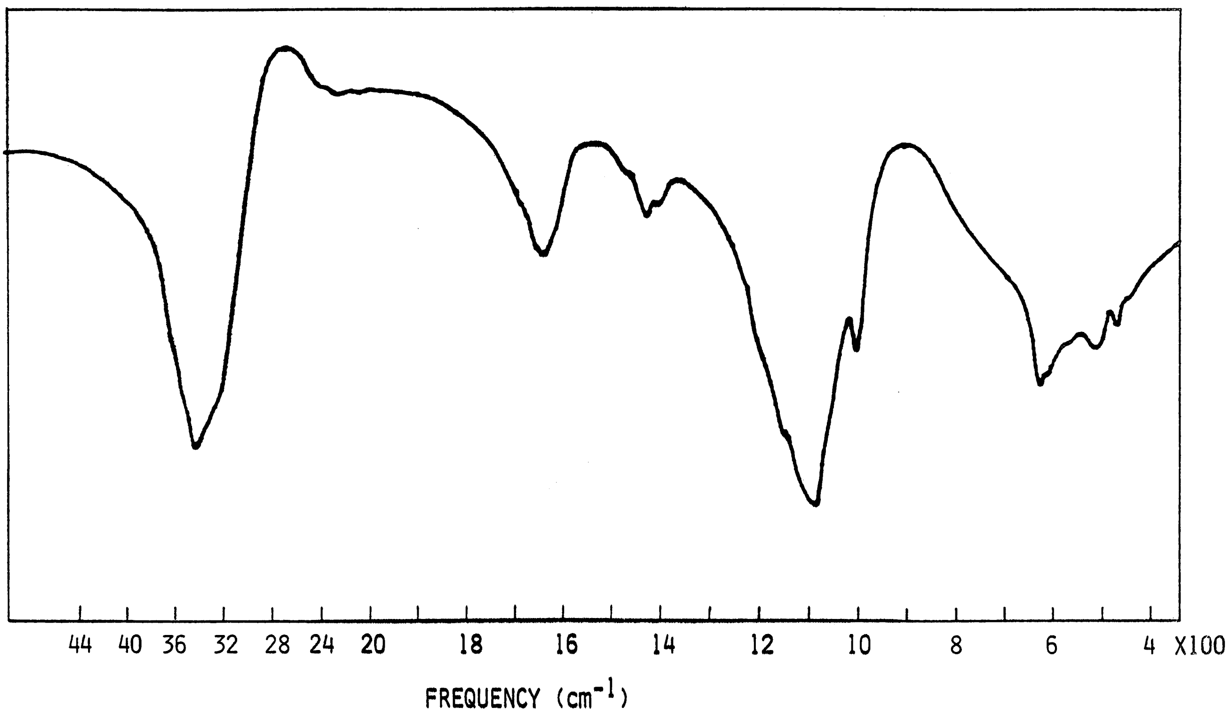

Fig. 6. IR spectrum of melanterite from Sumiyoshi.

Table 3. IR spectra of melanterite

ν_1	ν_2	ν_3	ν_4	H_2O and OH	
				Stretching	Bending
1005	470	1090 1150 1195	627 610	3590 3410	1640

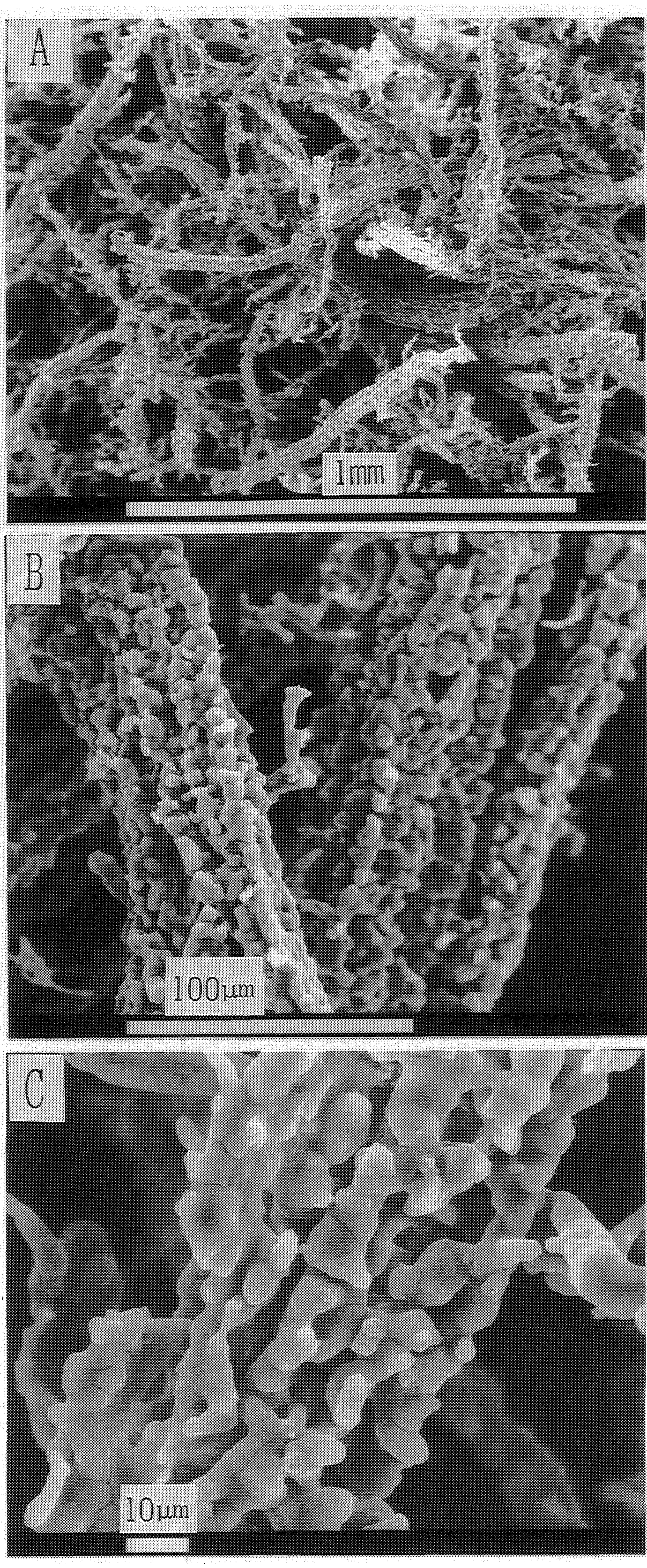

Fig. 7. Scanning electron micrographs of melanterite from Sumiyoshi.

CONCLUSION AND DISCUSSION

Fibrous crystals formed on the surface of siltstone in the Katanoyama formation was identified as melanterite ($Fe_2SO_4 \cdot 7H_2O$). Melanterite is usually formed as a decomposition product of iron sulphides such as pyrite, marcasite, chalcopyrite, etc.. The siltstone at Sumiyoshi was smashed to pieces and fine particles were washed out by decantation. Many pyrite grains were observed in the residual materials under a microscope. It is considered that the melanterite was formed from this pyrite by decomposition. It is known fact that pyrite is formed in the water under reduction conditions (Fleischer *et al.,* 1976). The Katanoyama formation is considered as bay sediments in the blackish water. Judging from the mode of occurrence of the fossils in the Katanoyama formation, it is considered that mass death due to oxygen deficiency happened in the past.

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