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Magnetic Minerals in Black and Red Beds in Japan

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Abstract

Coexistence of magnetic sulfides and oxides in black shales and red sandstones in Japan was first reported. Some interpretations on the origin of the coexistence were described.

Introduction

It was found that black shales and red sandstones in Japan possess strong and stable magnetization which can be considered as the fossil geomagnetism in Palaeozoic and Mesozoic time.

While the palaeomagnetic study with these rocks has been carried out, ferromagnetic minerals responsible for the remanence were examined by using thermo-magnetic, X-ray analyses and microscopic observations.

The results obtained were shown in part I of this paper. While in part II are discussed some interpretations on the formation of those minerals.

Part I Ferromagnetic Minerals

(1) Ferromagnetic mineral in black shale and sandstone.

60 samples of Lower-Cretaceous, Permian and Carboniferous black sandstones and shales were collected from the sites shown in Fig. 1. They possess strong and stable remanent magnetization and are to be considered as the fossil of the past geomagnetic field[1].

The thermo-magnetic analyses of these rocks were undertaken. The results are shown in Figs 2, 3, 4 and 5 and also in Table I. In all of these diagrams, very large and sharp falls are observed at about 300°C and faint falls at about 575°C. Pyrrhotite would be responsible for the fall at 300°C because we can observe this mineral even by the naked eye in these rocks and also because pyrrhotite has the Curie point at about 300°C[2),3),4)]. X-ray diffraction lines of FeS_{1+x} are remarkable, while those of Fe_3O_4 are very weak as shown in Figs 6 (a), (b) and (c). The microscopic photographs taken on the thin and the polished sections of the rocks are shown in Photos I and III

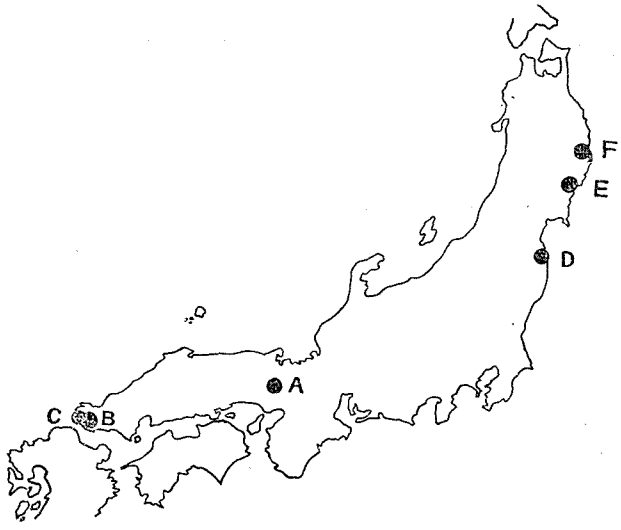


Fig. 1. Distribution of the collecting sites. Red sandstones and shales were collected from the places, A, B and C, and black shales from C, D, E and F.
A: Sasayama (Hyōgo Prefecture), B: Asa (Yamaguchi Prefecture), C: Yoshimi (Yamaguchi Prefecture), D: Kashima (Fukushima Prefecture), E: Ōfunato (Iwate Prefecture), F: Miyako (Iwate Prefecture).

Table I

Sample No.	Locality	Rock	Js at room temperature (c.g.s.e.m.u./g)	Curie points (°C)
2	Yoshimi (Yamaguchi)	Lower-Cretaceous black sandstone	4.85×10^{-2}	310, 560,
3	"	"	5.77	310, 580,
8	"	"	3.49	325,
12	"	"	13.40	315,
16	"	"	2.02	315, 575,
19	"	"	1.14	320, 575, 670,
2	Miyako (Iwate)	Upper-Cretaceous black shale	3.69	300,
5	"	"	6.52	315, 575,
8	"	"	2.29	305, 400, 570,
11	"	"	3.85	320, 585,
1	Kashima (Fukushima)	Permian black shale	1.67	315,
3	"	"	8.78	300, 570,
6	"	"	4.77	310, 580,
10	"	"	9.89	315, 575,
11	"	"	12.80	320, 575,
16	"	"	14.90	315,

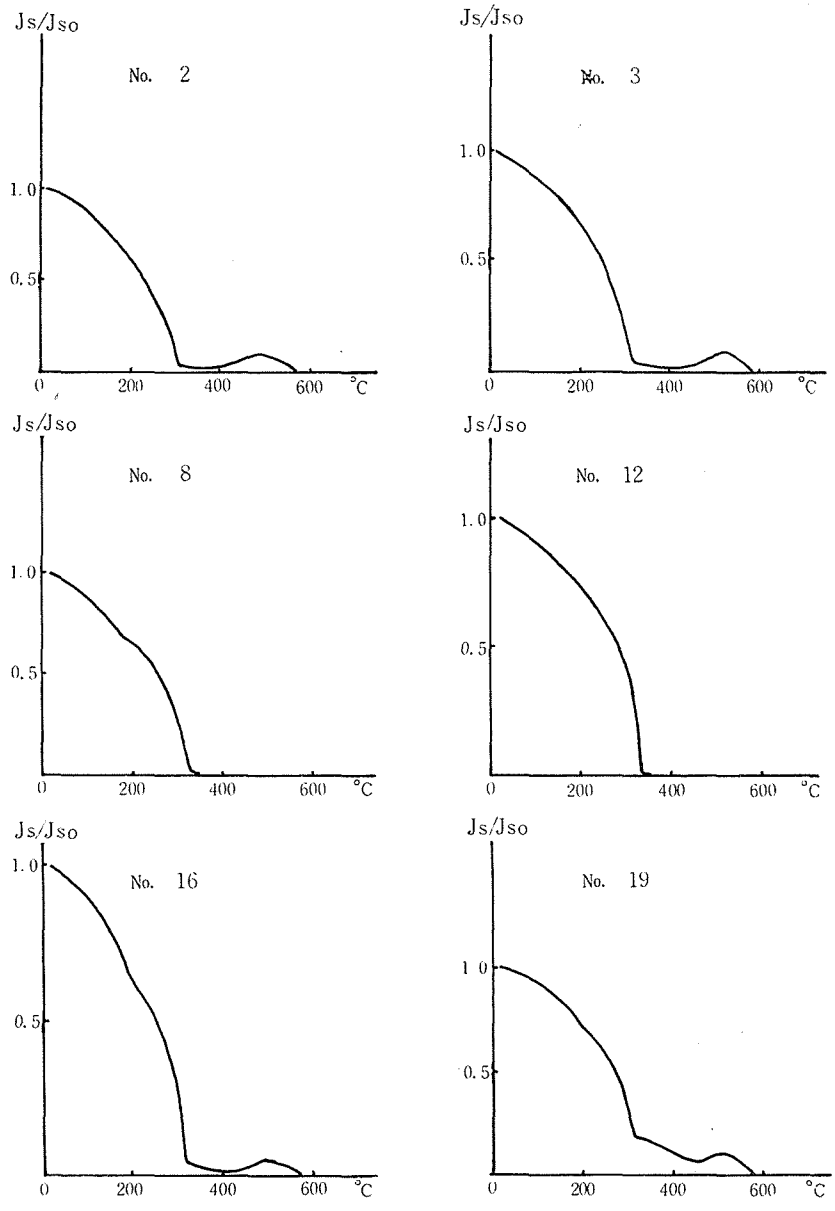


Fig. 2. Thermo-magnetic curves of Lower-Cretaceous black sandstones at Yoshimi, Yamaguchi Prefecture.

(d), (e) and (f), respectively, in which black and very brightly shining minerals are almost FeS_{1+x}. From the above-mentioned results, it may be concluded that the black bed is much more sulfureous than the red bed. And FeS_{1+x} bears major part of natural remanent magnetism of black shale. When the rocks were heated above the Curie point of pyrrhotite, the remanent magnetism decreases to 20~30% of the original.

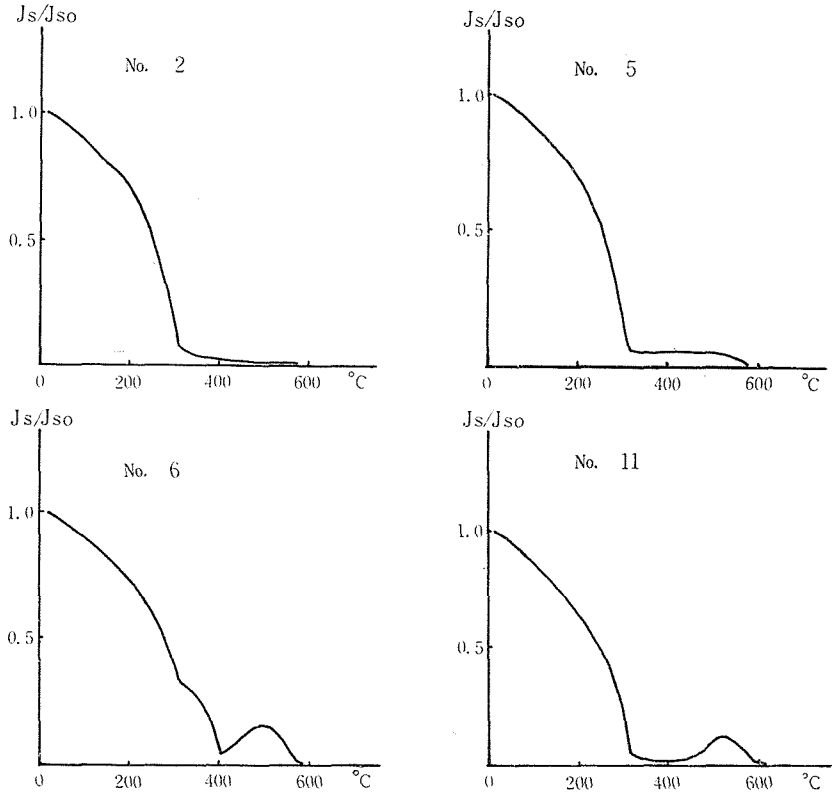


Fig. 3. Thermo-magnetic curves of Lower-Cretaceous black shales at Miyako, Iwate Prefecture.

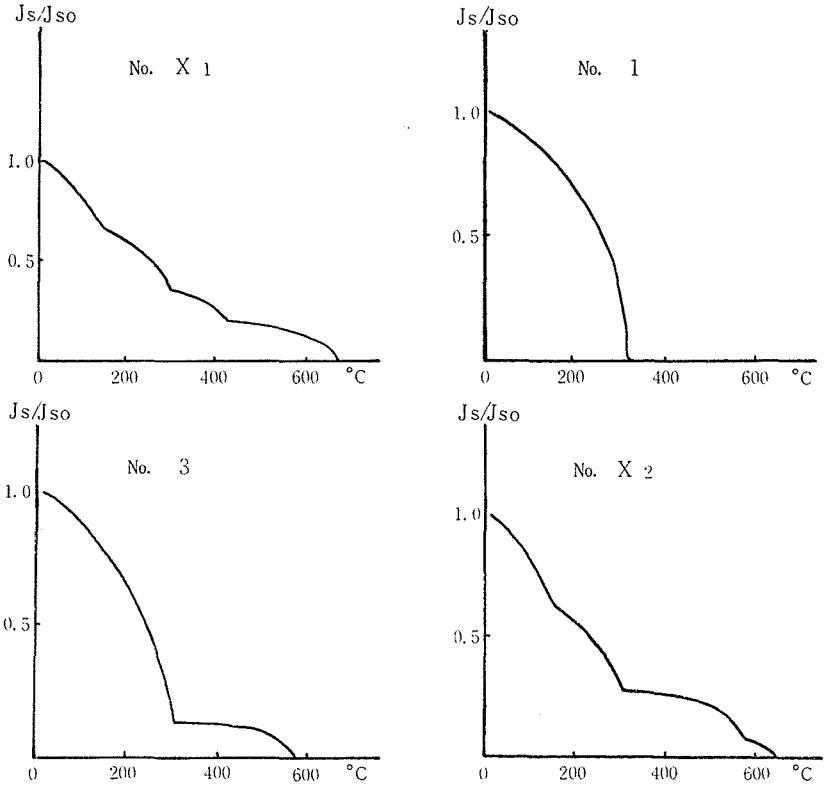


Fig. 4. Thermo-magnetic curves of Permian black shales at Kashima, Fukushima Prefecture.

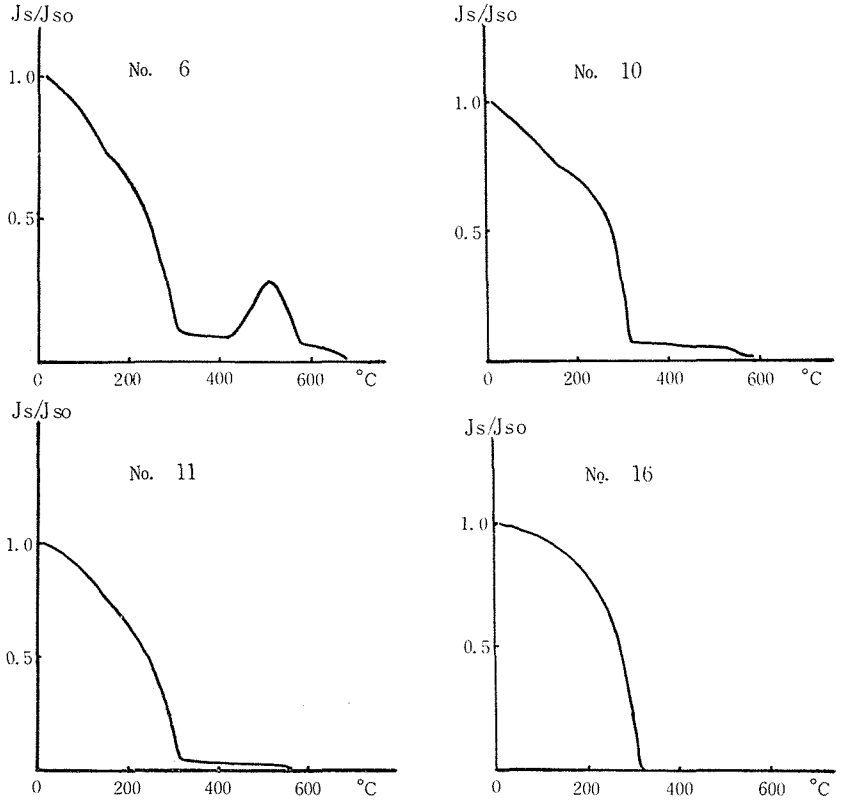


Fig. 5. Thermo-magnetic curves of Carboniferous black shales at Ōfunato, Iwate Prefecture.

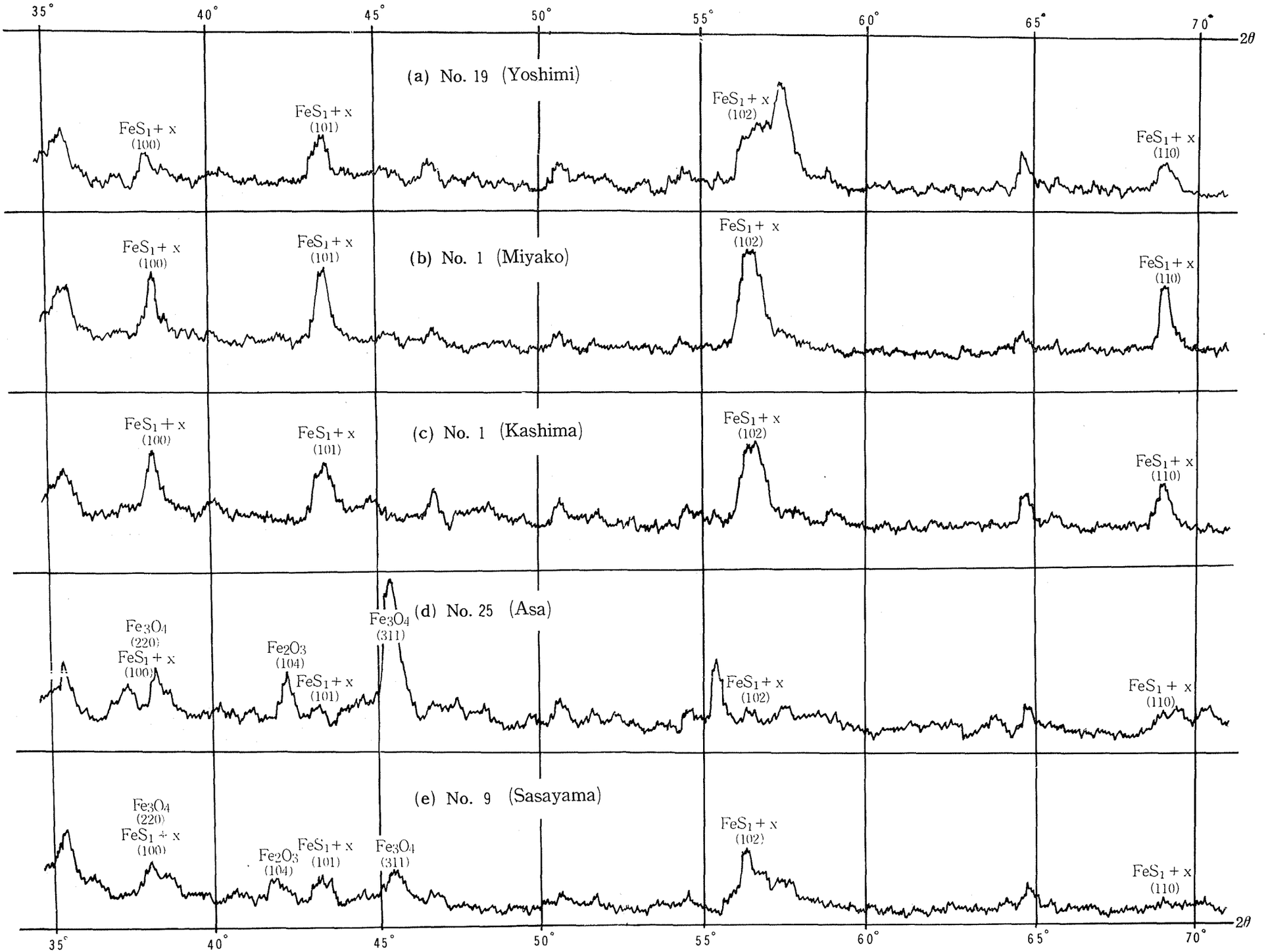


Fig. 6. X-ray powedr patterns of the ferromagnetic minerals extracted from the black and red sediments.

(2) Ferromagnetic minerals in red sandstone and purple shale.

160 samples of Upper-Cretaceous red sandstones and purple shales were collected from the south-western part of Japan (Fig. 1) and the same experiments as those mentioned in the section (1) were carried out. The results of the thermo-magnetic analyses are shown in Figs 7, 8 and 9 and in Table II. As seen in these diagrams, there exist four distinct falls in every thermo-magnetic curve at about 670°, 575°, 400° and 300°C. Of these, the highest fall evidently corresponds to the Curie point of α-haematite and the second

Table II

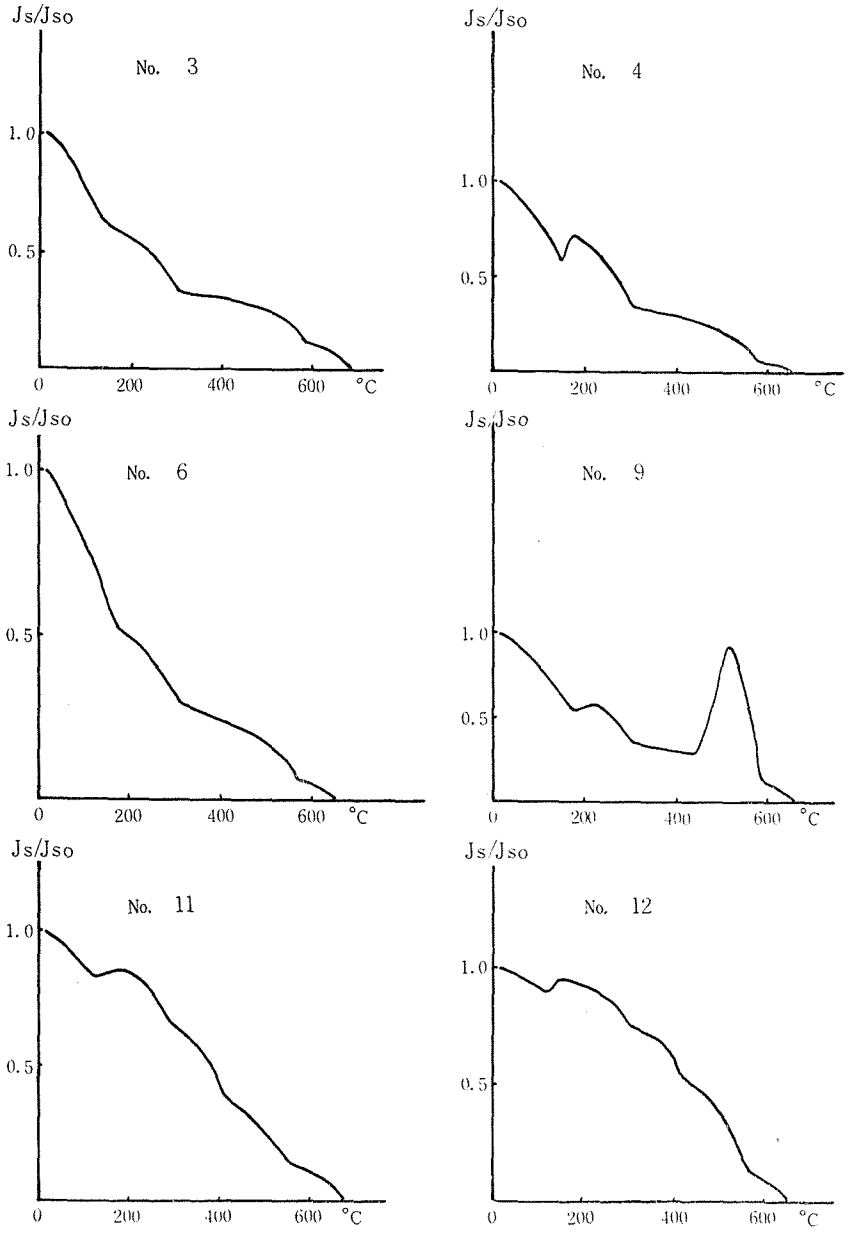
Sample No.	Locality	Rock	Js at room temperature (c.g.s.e.m.u./g)	Curie point (°C)
3	Sasayama (Hyōgo)	Upper-Cretaceous grey sandstone	2.35×10^{-2}	305, 575, 675,
4	〃	〃	2.97	300, 575, 650,
6	〃	〃	1.48	305, 580, 640,
9	〃	〃	1.63	300, 580, 660,
11	〃	〃	6.55	280, 395, 555, 670,
12	〃	〃		285, 410, 560, 645,
13	〃	〃		290, 575, 660,
16	〃	Upper-Cretaceous red sandstone	3.17	275, 415, 550, 650,
18	〃	〃	6.67	305, 405, 575, 680,
19	〃	〃	9.33	285, 415, 560, 660,
21	〃	〃	2.76	290, 570, 680,
22	〃	〃	9.70	290, 395, 565, 660,
24	〃	〃	4.02	290, 580, 670,
25	〃	〃		290, 400, 570, 660,
26	〃	〃	7.47	295, 395, 565, 670,
27	〃	〃	14.84	290, 410, 555, 640,
30	〃	〃	5.67	280, 415, 555, 670,
31	〃	〃	10.08	310, 550, 665,
36	〃	Upper-Cretaceous green sandstone	9.01	300, 410, 575, 665,
37	〃	〃	9.35	285, 430, 580, 670,
41	〃	〃	10.64	280, 400, 570, 665,
42	〃	〃		285, 415, 560, 650,
44	〃	〃	2.71	285, 400, 560, 645,
50	〃	Upper-Cretaceous red shale	2.50	295, 405, 560,
54	〃	〃	17.50	305, 410, 565, 650,
55	〃	〃	47.58	280, 420, 570, 630,

Table II

Sample No.	Locality	Rock	Js at room temperature (CG Semu/gr)	Curie points (°C)
4	Asa (Yamaguchi)	Upper-Cretaceous red shale	2.31×10^{-2}	280, 570, 640,
5	"	"	1.40	570, 665,
10	"	"	3.37	330, 575, 680,
11	"	"	1.64	290, 575, 665,
12	"	"	1.68	565, 680,
15	"	"	2.72	400, 570, 665,
20	"	"	7.81	315, 410, 575, 670,
25	"	"	24.88	300, 400, 580, 660,
28	"	"	11.82	300, 400, 575, 640,
29	"	"	0.83	295, 575, 670,
35	"	Upper-Cretaceous red sandstone	1.50	280, 420, 570, 650,
37	"	"	0.95	310, 580, 650,
44	"	"	0.85	285, 565, 665,
47	"	"	1.19	285, 405, 565,
52	"	"	1.60	285, 660,
55	"	"	1.70	285, 570,
4	Yoshimi (Yamaguchi)	Upper-Cretaceous red sandstone	1.20	400, 575, 660,
7	"	"	16.96	295, 405, 575,
14	"	"	2.42	295, 415, 585,
21	"	Upper-Cretaneous dark red shale	175.67	310, 410, 575,
25	"	"	76.09	290, 410, 580,
28	"	"	28.68	290, 405, 570,
36	"	"	32.32	290, 400, 565,
40	"	"	43.26	290, 390, 570,
45	"	"	62.50	315, 580,

to that of magnetite. If the existence of FeS_{1+x} (pyrrhotite) is assumed in these red beds, the lowest fall at 300°C should be due to the Curie point of this mineral, although the phase responsible for the fall at 400°C is still unknown.

Next, the authors observed the polished and the thin sections of these rocks under microscope. As the Photos II and III (a), (b) and (c) indicate, beside euhedral or subhedral magnetites, very finely dispersed and very brightly shinning particles (evidently brighter than haematite and magnetite) can be observed. These fine particles are probably FeS_{1+x}.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°C
Js/Jso
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400
600
°C
Js/Jso
No. 6
1.0
0.5
0
200
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°C
Js/Jso
No. 9
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400
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°C
Js/Jso
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°C
Js/Jso
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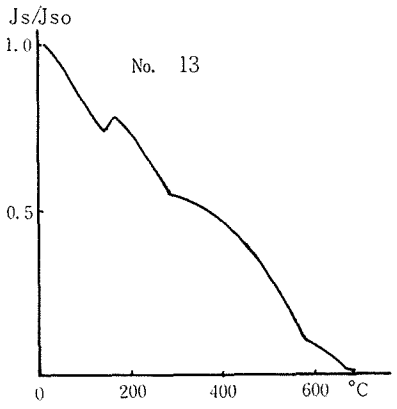
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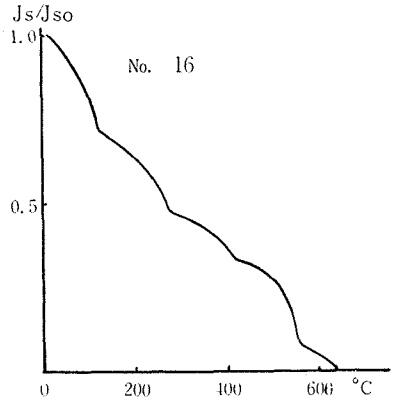
°C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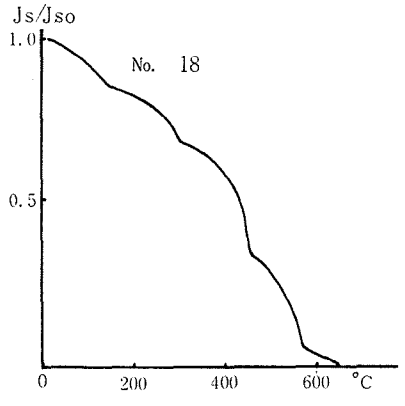
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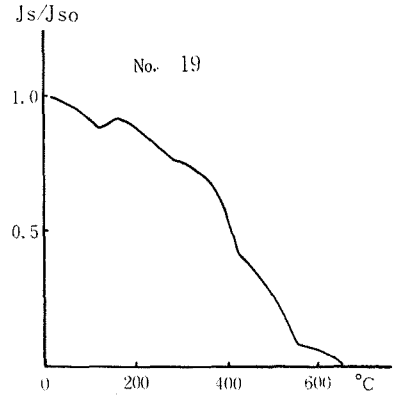
600
°C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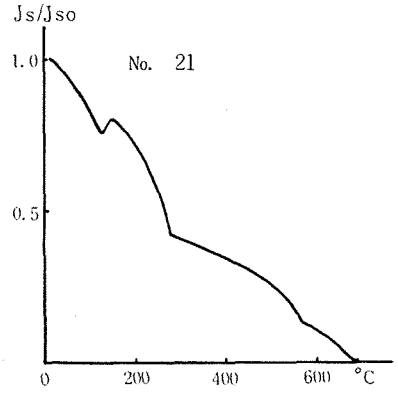
600
°C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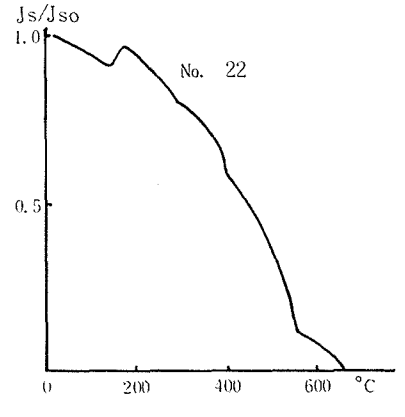
600
°C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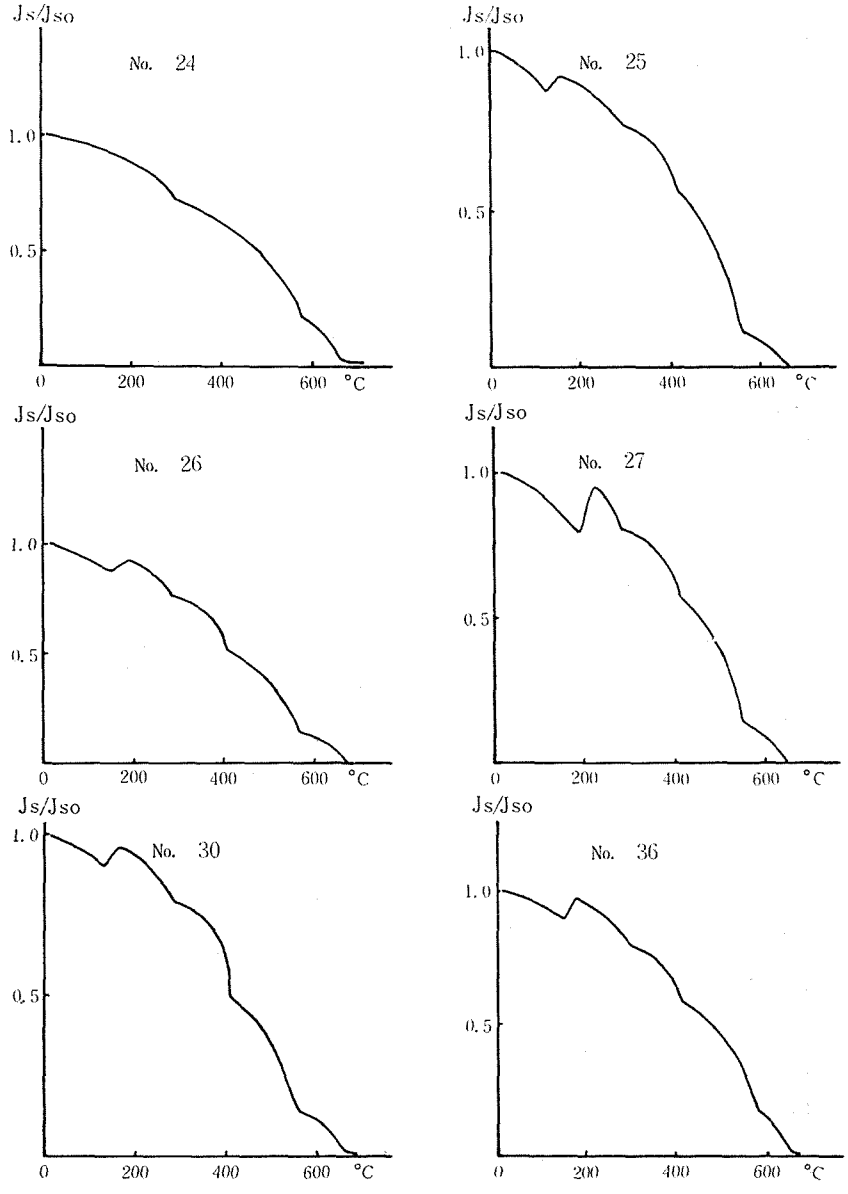
400
600
°C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°C
Js/Jso
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0.5
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Js/Jso
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0.5
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Js/Jso
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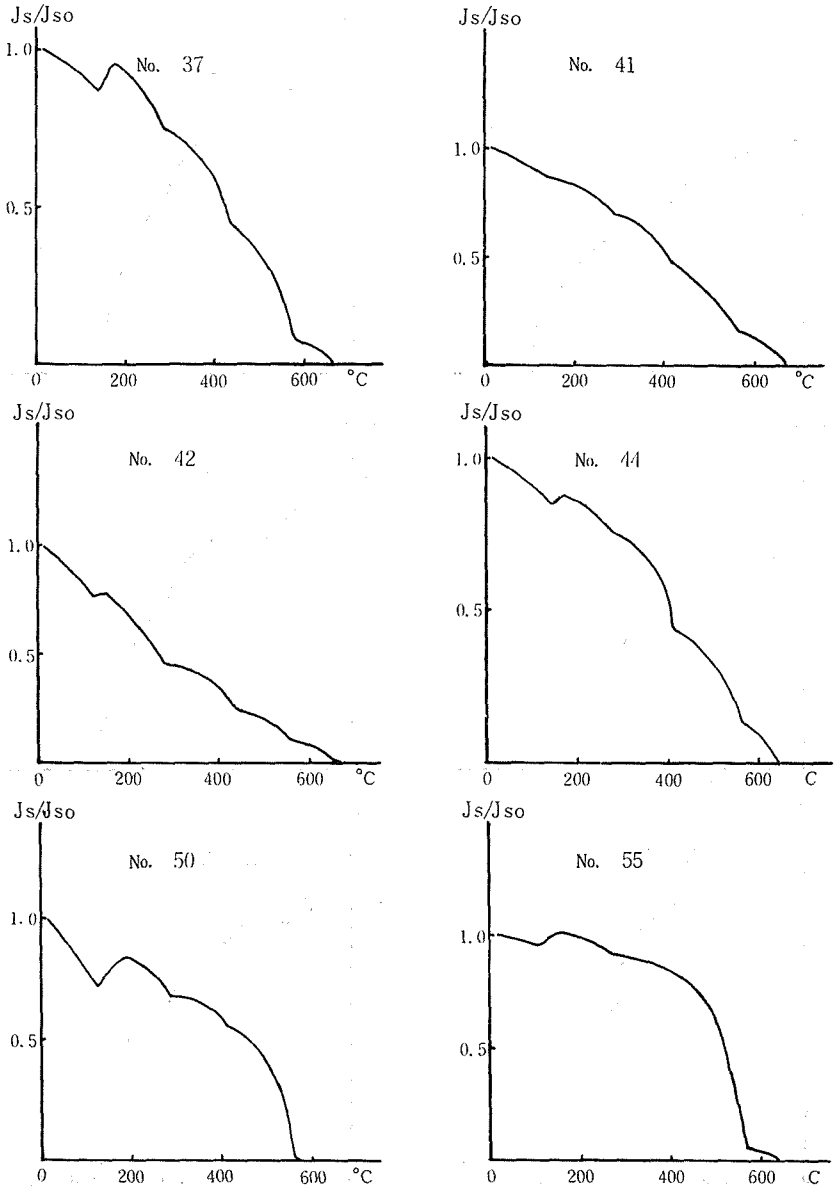
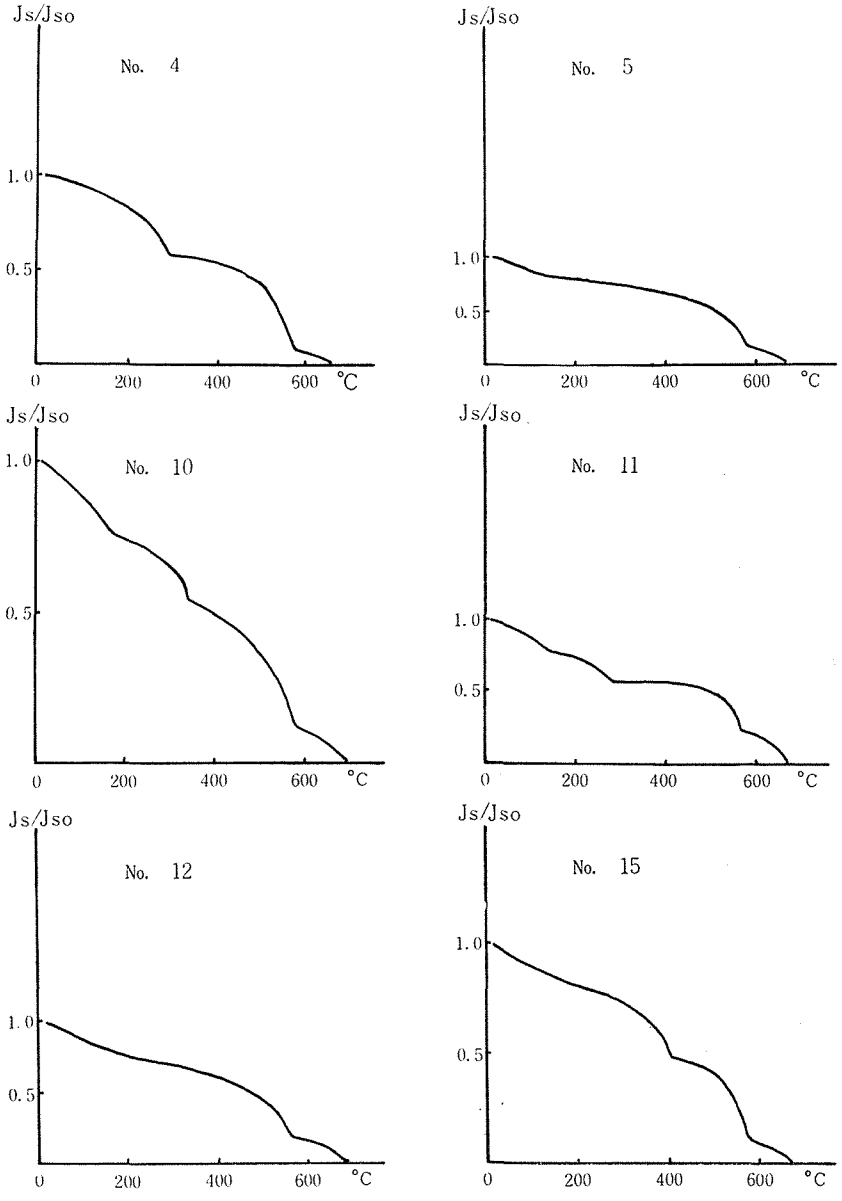


Fig. 7. Thermo-magnetic curves of Upper-Cretaceous red sandstones and shales at Sasayama, Hyōgo Prefecture.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Js/Jso
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600
°C
Js/Jso
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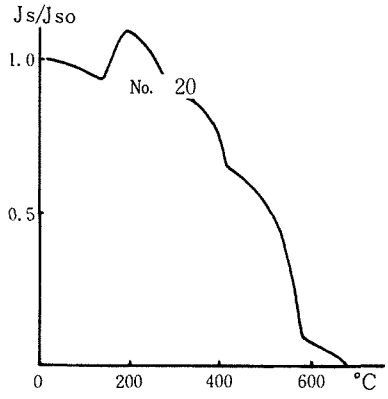
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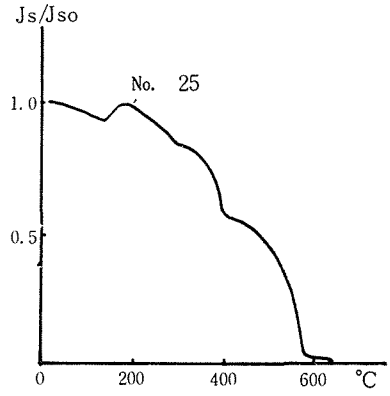
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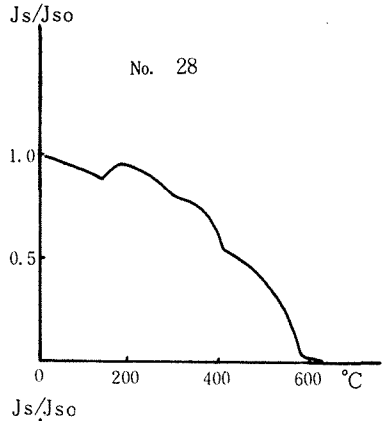
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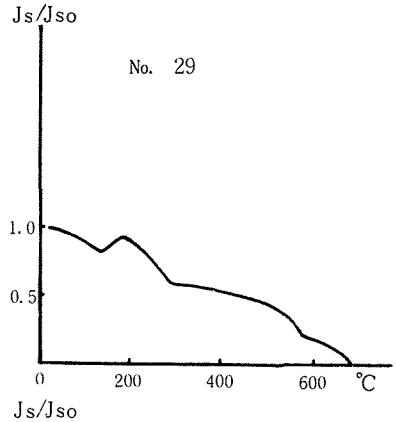
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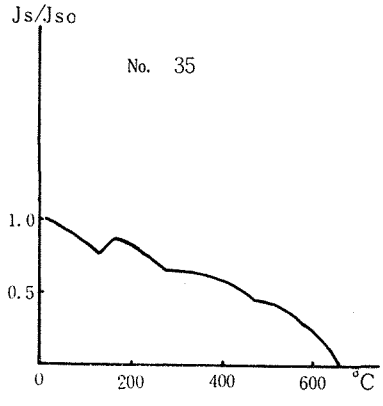
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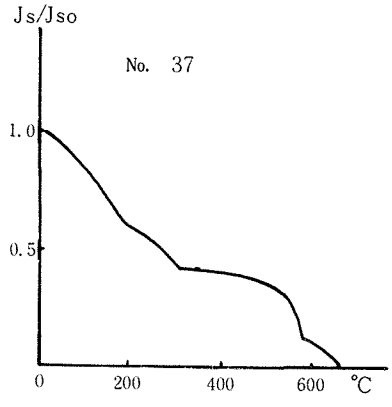
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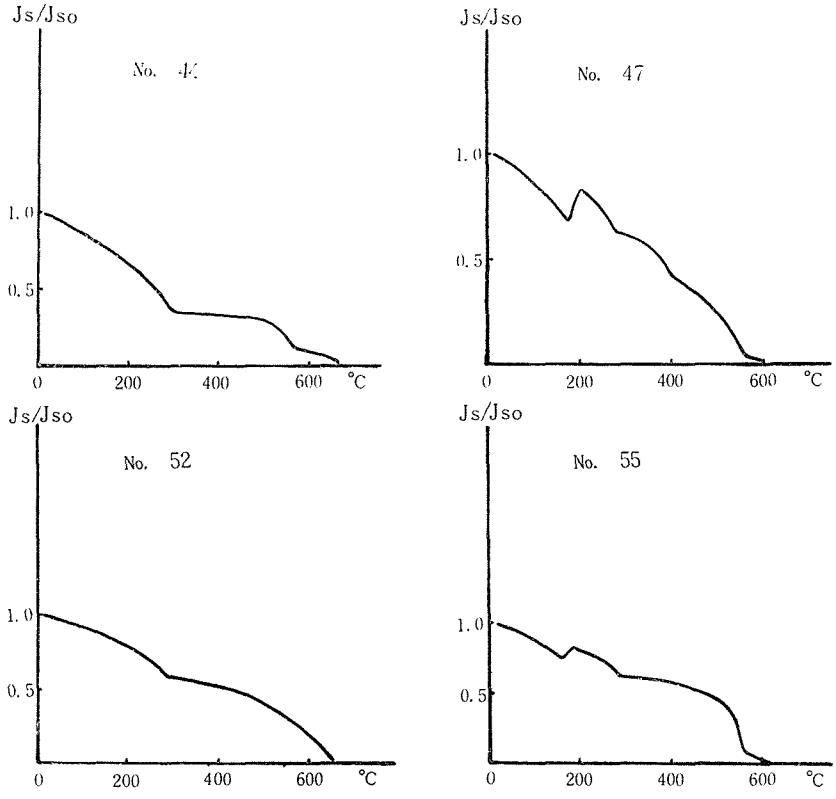
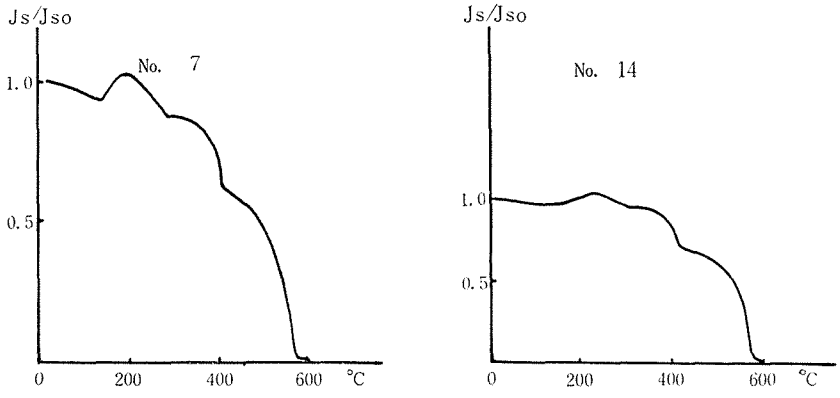


Fig. 8. Thermo-magnetic curves of Upper-Cretaceous red sandstones and shales at Asa, Yamaguchi Prefecture.



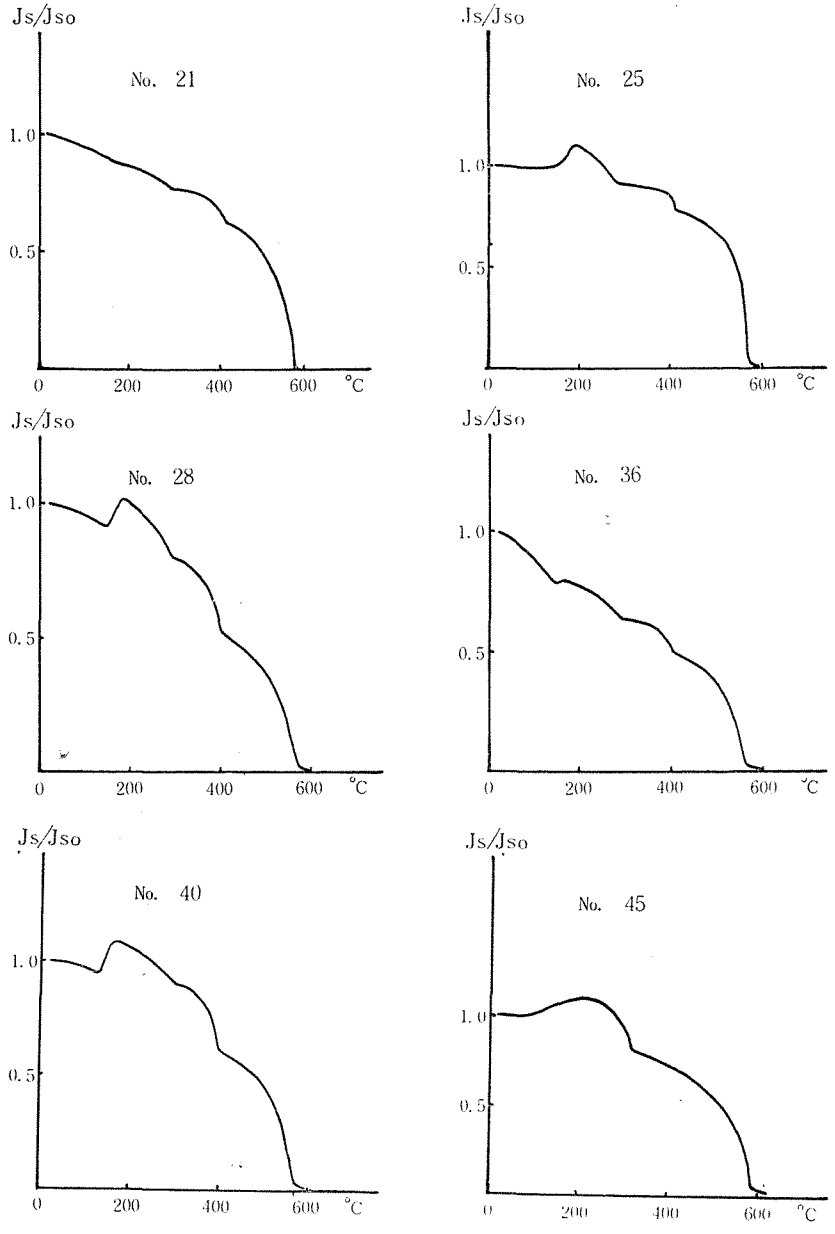


Fig. 9. Thermo-magnetic curves of Upper-Cretaceous red sandstones and shales at Yoshimi, Yamaguchi Prefecture.

Next to be employed for the further identification is the X-ray analysis. Very weak but sufficiently detectable diffraction lines characteristic to pyrrhotite appeared with the diffraction lines of α-haematite and magnetite. Thus, the results of X-ray analyses also support to conclude that α-Fe_2O_3, Fe_3O_4 and FeS_{1+x} coexist in the red bed as shown in Figs 6 (d) and (e).

The α-haematite possesses parasitic ferromagnetism of which the intensity is about 10^4 times less than those of Fe_3O_4 and FeS_{1+x}. Consequently, coexistence of even very small amount of these ferromagnetic minerals in red beds is significant in their remanent magnetism. This is clearly indicated in the measurement of these rocks at temperature 300°C at which the fine FeS_{1+x} powders lose their magnetism and the remaining components due to the higher Curie point phases are found to be less than 70% of the original remanences.

Part II Interpretation on the Coexistence of Iron Sulfides and Oxides

It is generally accepted in geology and petrology that very fine iron sulfide powders such as FeS, FeS_2, and $FeS \cdot nH_2O$ are all black in colour[5]. It has also been found that black shale contains organic substances whose colour are dark grey[6]. The contained magnetite powders are also black in colour.

In contrast, colour of α-Fe_2O_3 is red. It changes from purple or dark red to bright red as the grain size decreases[7),8)].

Thus, in the red and black bed we can say that the rock colour is very sensitive to the existence of ferric and ferrous oxides and sulfides, of which only the former oxides are red or purple and the other all black. It is well known that red bed is formed at places where oxygen circulates to oxidize the ferrous ions or salts in sediments, whereas black bed is formed at places where the reduction is taking place, or otherwise where organic matter exists whose decomposition may prevent the ferrous ion from the oxidation[9].

In general black bed is a rather deep marine product or a oxygen lacking lake and non-circulating water deposit, whereas the red bed a land or shallow-sea deposit. Cretaceous red bed in south-western part of Japan contains land fossils[10] and the Cretaceous, Permian and Carboniferous black shale yields marine ones[11),12),13)].

Thus we can say that the rock colour may change from black to red as the oxidation of the sediment proceeds and change from red to black as the reduction of the sediment proceeds.

However, no direct proof is given yet on the coexistence of iron sulfides with other iron oxides, especially on that of the FeS_{1+x}, which is a ferromagnetic mineral of special importance in rock magnetism. Regarding the coexistence, we have at present following two tentative conceptions. The one is a direct formation of iron sulfides such as markasite, pyrrhotite, melnikovite and hydrotroilite in sea water associated with marine volcanic activity. And the other an indirect formation by some biochemical procedures.

(1) Direct formation by volcanic activity.

Since Palaeozoic and Mesozoic time volcanic activities have occurred so frequently around peripheral zone of the continent (especially around Circum-Pacific zone). H_2S gas from the submarine volcano rendered the ferrous ions in both the sea water and in the ejected substances to form monosulfide, disulfide or hydrosulfide, in which is contained syngenetic or epigenetic FeS_{1+x} and other oxides. This idea of direct formation of sulfides is rather strongly supported among many mining geologists in Japan[14),15)].

It is indeed interesting to presume that FeS and FeS_{1+x} thus made by such a volcanic activity have been stratified and buried, and the Palaeozoic and Mesozoic iron-copper sulfide mines in Japan were formed when those sulfides have suffered no oxidation, whereas the red beds in the same age were formed when they had been oxidized from FeS_2 or FeS_{1+x} to Fe_2O_3. Such intermediate states of the oxidation from one to the other could be observed in the photographs (Photos I, II and III).

What has been mentioned so far can be summarized in the following schematic chemical equations.

Fe^{++} + Submarine volcanic activity → Disulfide + Monosulfide + Oxyhydrate +

$$Fe_3O_4 + \gamma\text{-}Fe_2O_3 + \alpha\text{-}Fe_2O_3 .$$

(2) Indirect formation of iron sulfides and oxides by biochemical procedure.

It is well-known in geology that iron bacteria produces large oolitic haematite and also that some sulfide, likewise, has been formed by reducing bacteria of sulfates[16),17),18)]. These bacteria maintain themselves by destroying organic materials around them and taking energy directly from the exsothermal organic and inorganic chemical reaction and changing it to their vital powers.

When the organic material, which consists of carbon, sulfur, oxygen and hydrogen etc., is decomposed by these bacteria, CO_2 and H_2S gas may be generated and make more or less reducing environment in which probably magnetite and monosulfide are more stable than haematite as suggested by Pettijohn[18)] in the following equations.

$$RSO_4 + 2C \rightarrow 2CO_2 + RS .$$

In the equations carbon from organic materials plays an important role in the production of sulfide or oxide with the cooperative reaction by bacteria. One of the most remarkable examples indicating the cooperation is the magnetism in coal. Japanese Tertiary coals possess sometimes fairly strong remanent magnetism. Ferromagnetic minerals responsible for the remanence are FeS_{1+x} or Fe_3O_4.

It is interesting to infer the palaeomagnetism from the measurements of coal beds.

Sulfur-content in organic as well as in inorganic substances may be larger in Japan due to the volcanic activity than these in the inter-continent area. The decomposition of the organic materials, therefore, produce more sulfides in Japanese beds. The authors' observations of the black and red beds seem to suggest the above-mentioned sulfureous ferromagnetic nature.

Acknowledgment

The authors' thanks are to Emeritus Professor N. KUMAGAI and Professor S. MATSUSHITA with whom the discussion on the geology of black and red shale made the study advanced.

Their acknowledgments are to Professor H. YOSHIZAWA and Dr. T. TAKADA who helped in carrying out the microscopic observations and X-ray analysis. They also thank to Mr H. ITO who offered many black shales from his collections.

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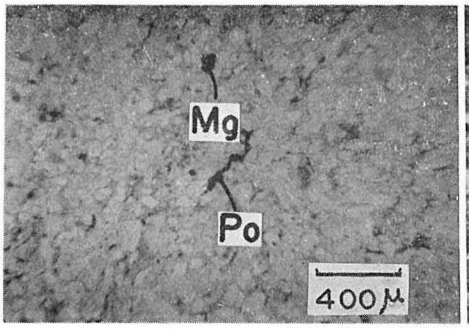
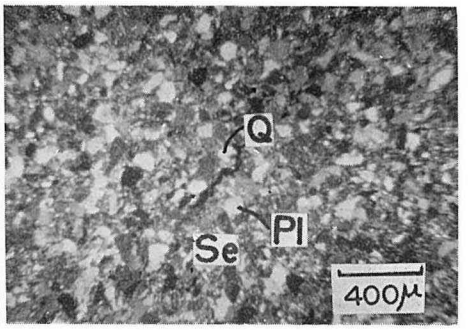
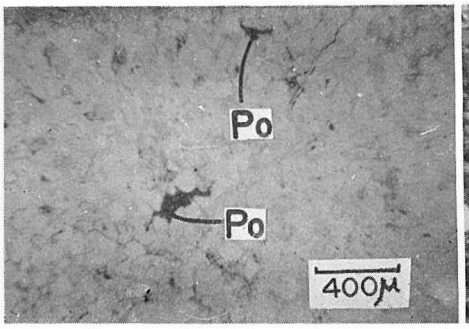
Photo. I. The microscopic observations on the thin sections of the black shales and sandstones under // nicol are shown on the left side and those under ⊥ nicol on the right side. The notations in the photographs are as follows:
Mg: magnetite, He: haematite, Po: pyrrhotite, Py: pyrite, Q: quartz, Pl: plagioclase, Se: Sericite, Bi: biotite, Ca: calcite, Ho: hornblende etc.



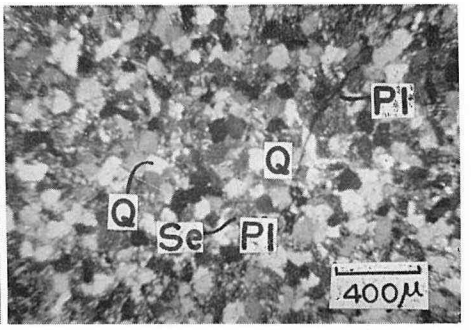
(a) Sample No. 3 (Yoshimi)



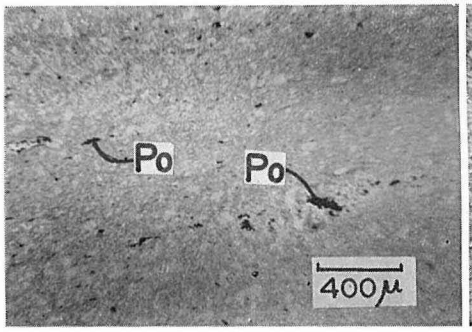
(a′) Sample No. 3 (Yoshimi)



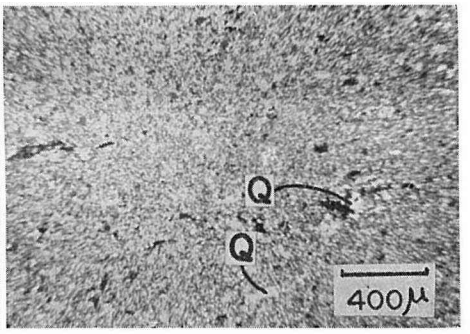
(b) Sample No. 9 (Yoshimi)



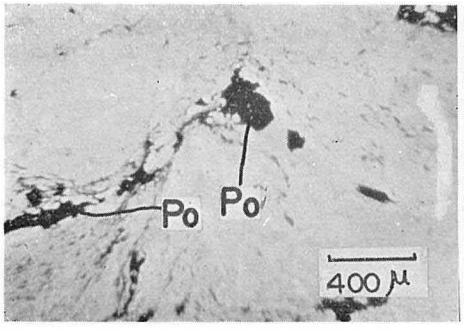
(b′) Sample No. 9 (Yoshimi)



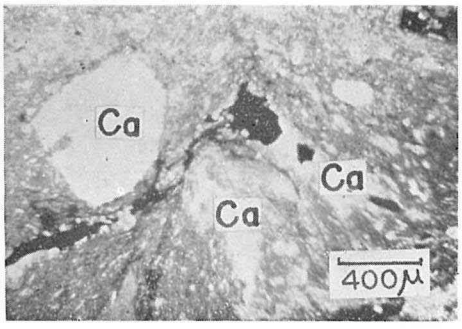
(c) Sample No. 2 (Miyako)



(c′) Sample No. 2 (Miyako)

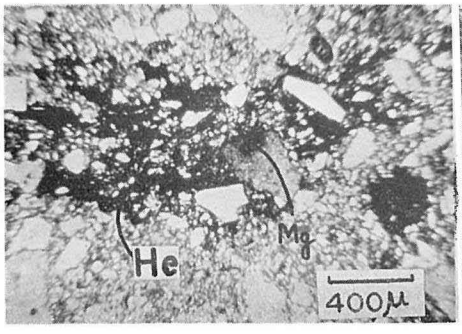


(d) Sample No. 1 (Ōfunato)

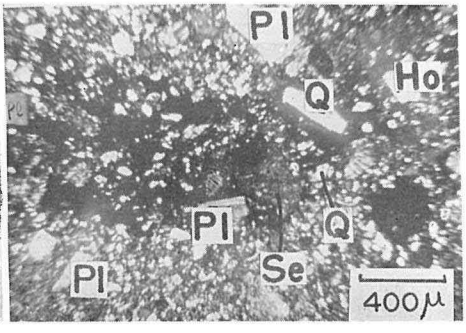


(d′) Sample No. 1 (Ōfunato)

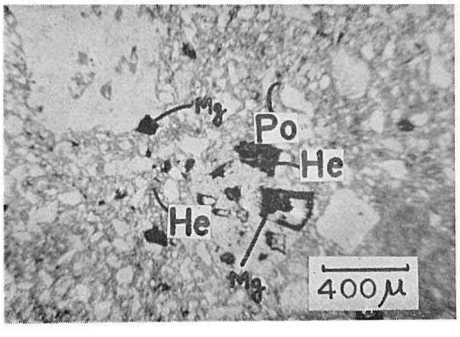
Photo. II. The microscopic observations on the thin sections of the red sandstones and shales under // nicol are shown on the left side and those under ⊥ nicol on the right side. The notations in the photographs are the same as in Photo. I.



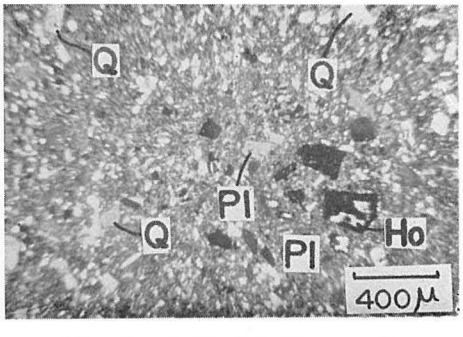
(a) Sample No. 25 (Sasayama)



(a′) Sample No. 25 (Sasayama)



(b) Sample No. 27 (Sasayama)



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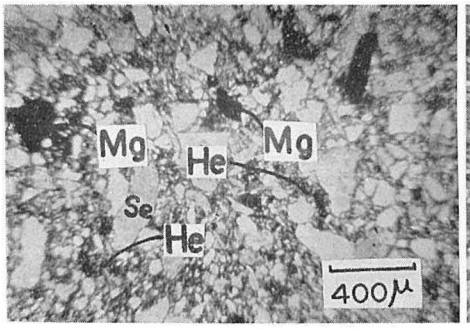
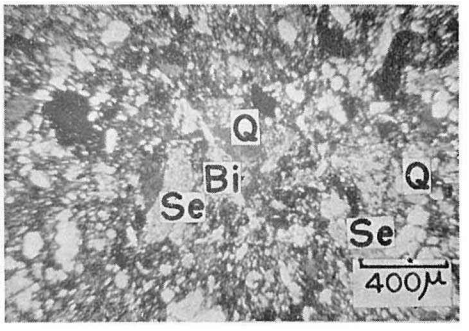
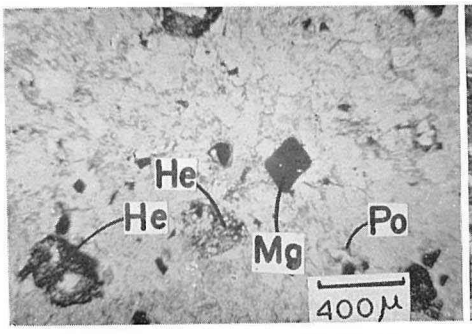


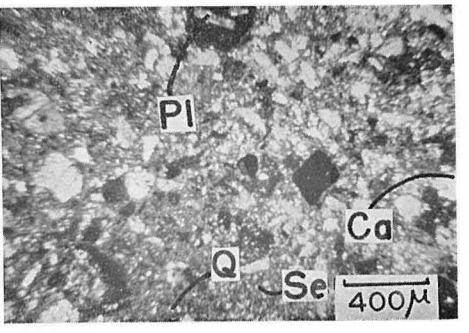
(c) Sample No. 25 (Asa)



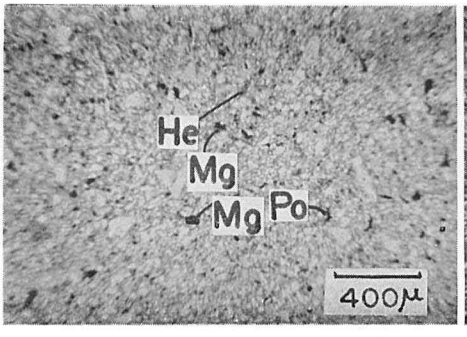
(c′) Sample No. 25 (Asa)



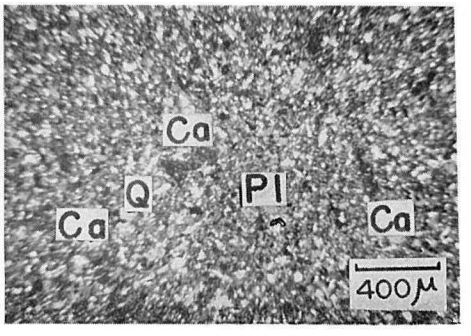
(d) Sample No. 20 (Yoshimi)



(d′) Sample No. 20 (Yoshimi)

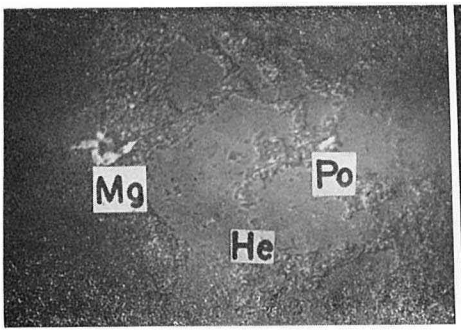


(e) Sample No. 43 (Yoshimi)

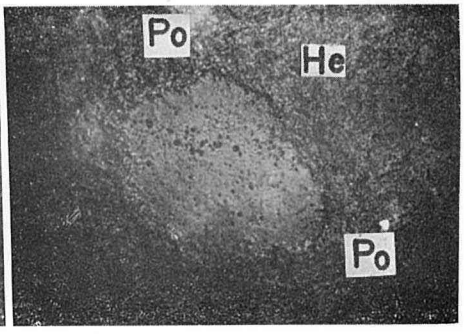


(e′) Sample No. 43 (Yoshimi)

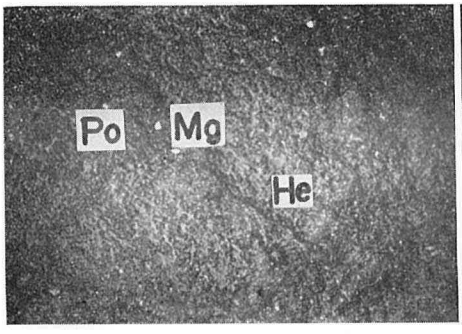
Photo. III. The microscopic observations (×400) on the polished sections. The notations in the photographs are as follows:
Mg: magnetite, He: haematite, Po :pyrrhotite etc.



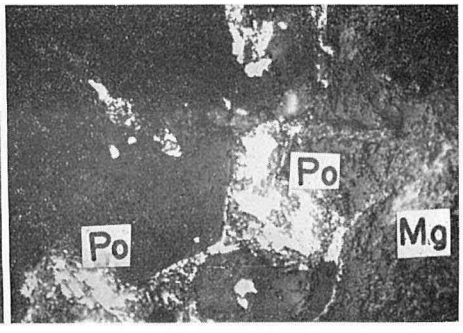
(a) Sample Mo. 5 (Asa; red shale)



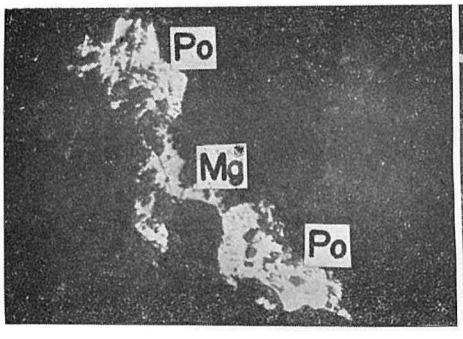
(b) Sample No. 55 (Asa; red sandstone)



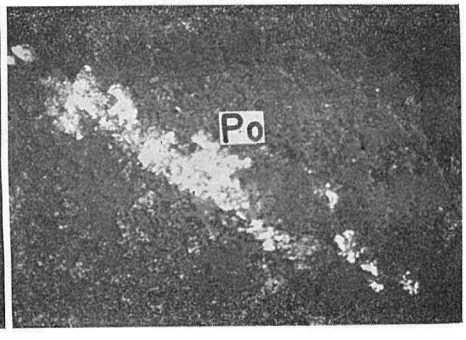
(c) Sample No. 36 (Yoshimi; red sandstone)



(d) Sample No. 2 (Yoshimi; black sandstone)



(e) Sample No. 5 (Miyako; black shale)



(f) Sample No. 1 (Kashima; black shale)