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Composition in Some Minor Elements of Tertiary Pelitic Sediments, Shimane Prefecture, Japan

By

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Abstract

Compositions in some minor elements of Tertiary pelitic sediments of Shimane Prefecture, Japan, in 35 surface samples and 2 subsurface samples are described. Three samples of bituminous shales from Thailand were analysed for comparisons.

Some considerations about the composition of above-mentioned rocks when compared with recent bottom sediments of Shinji and Nakaumi lakes are made.

Possibly, the fresh and brackish water sediments are much poor in trace elements than marine deposits, as indicated by results of analysis, however more detailed data are necessary to confirm this hypothesis in these sediments.

Introduction and Previous Works in Shimane Prefecture

Shimane Prefecture is one of the least studied areas within Japanese territory, when compared with other regions of this country.

A geologic map of the province was elaborated in 1962, gathering all the available data (NISHIYAMA and MIURA, 1963). The map was published by the Section of Industrial Development of the Department of Industry and Commerce of Marine Products (Shimane Prefecture) in 1963. Presently there were about ten relatively detailed papers dealing with the geology of this province, however these papers contain only partial informations.

The occurrence of the lignite in the Matsue Formation (Pliocene) and natural gas in Tertiary and Quaternary geological formations have propitiated the development of researches concerning these subjects. Furthermore, the occurrence of metallic deposits ("black-ore," "uranium bearing molybdenite," etc.) started a flux of works related to these deposits.

A group of researchers from the Geological Survey of Japan, headed by Dr. A. MIZUNO, are working on hydrogeochemistry, biogeochemistry and geology of Nakaumi and Shinji lakes to establish the environmental factors that rule the precipitation of uranium in natural water systems.

Presently, public organizations of the Shimane Prefecture, as the Metallic Ore Deposits Prospecting and Development Agency, are accomplishing works of detailed mapping. The group of geochemistry of the Geological Survey of Japan, headed by Dr. K. MOTOJIMA, are working with the hydrogeochemistry and biogeochemistry of pelitic sedimentary rocks, Tertiary in age, near to Izumo, Matsue and Ooda cities. The author of this paper, staying as visiting research associate at the Geological Survey of Japan during the second semester of 1970, had the opportunity to participate in the field works and to use the collected samples to make analysis regarding the trace elements composition of the examined samples.

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General Geology of the Province

Shimane Prefecture is constituted by a relatively narrow and long band, situated between the Japan Sea and the mountainland of "Chugoku" (Inland part of the country). Furthermore, this province forms the main portion of the "Honshu" island (main island of Japan), designated "San-in" and embraces also the Oki Islands, situated in the Japan Sea (See figure 1).

The basement rocks are constituted by the Oki gneisses, probably Pre-cambrian in age. Above them there are Cretaceous intrusive rocks (granites, granodiorites and diorites), volcanic rocks (rhylites and andesites) associated with hydroclastic and pyroclastic rocks (shales, sandstones and andesitic tuffs). The geologic formations of the Tertiary (Miocene and Pliocene) are formed by a sequence of hydroclastic and pyroclastic deposits being interposed by basalts and rhyolites. The stratigraphy of the rocks of the Shimane Prefecture is complicated by differences in nomenclature of the deposits of the mainland in relation to correlated sediments of the Shimane Peninsula. The Quaternary geologic unities are constituted mainly by volcanic rocks and gravels, sands and clays of the Pleistocene and by alluvial and eolian (dunes) sands of the Holocene.

Objectives of the Work

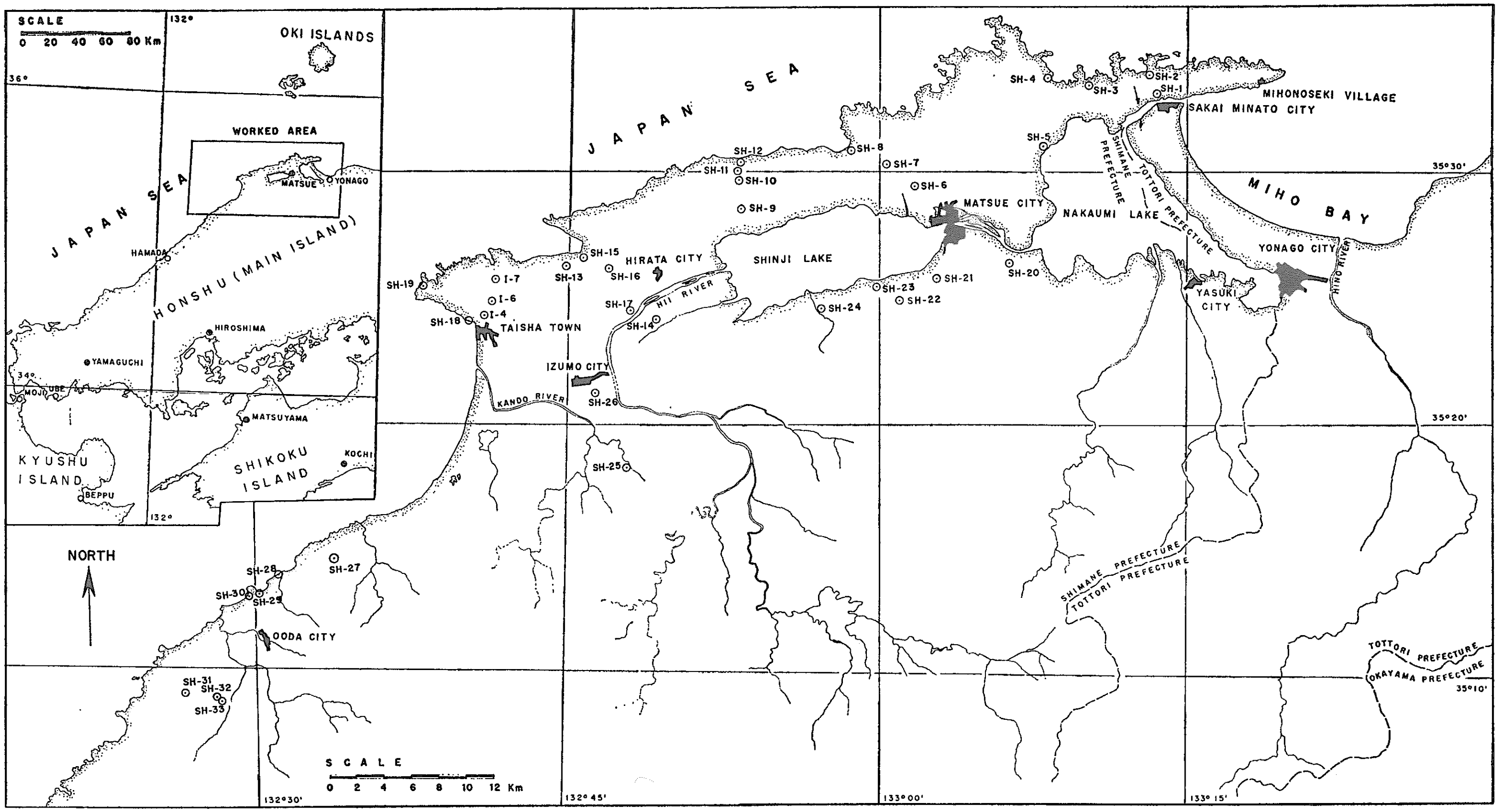
The study of the trace elements composition of the sedimentary rocks from Shimane Prefecture could eventually be useful for stratigraphical correlations, for reconstruction of sedimentary environments and for researches on source rocks of the sedimentary rocks in this Province.

On the other hand, according to recent authors (SANDERS, 1966, pp. 231–236; MANSKAYA and DROZDOVA, 1968), the fossil organic substances in the sedimentary rocks have a significant role, in various stages of their formation, in the concentration of the trace elements. The form of occurrence of the trace elements (chemical precipitation, adsorption, etc.) in the materials of the sedimentary rocks, has a great geological meaning.

However, the available data on the composition of the sedimentary rocks in Shimane Prefecture are still insufficient, restricted only to data of bulk samples, without any information data concerning the fossil organic composition of the sediments. So, we shall report here only our partial results establishing some comparisons with composition of these elements in recent bottom sediments from Shinji and Nakaumi lakes (according to unpublished data of NAKAO et al., 1969) and with three samples of sediments from Thailand furnished by courtesy of Dr. MOTOJIMA.

Samples and the Conditions of the Analysis

The samples here considered are all pelitic (claystones, shales and siltstones) including 32 surface samples, 2 subsurface samples (collected in the Wanibuchi "black-ore" mine) and 3 samples



(K.SUGUIO-1971)

SAMPLES SH - COLLECTED FROM OUTCROPS ON OCTOBER, 1970.
SAMPLES W - COLLECTED IN WANIBUCHI "BLACK ORE" MINE ON OCTOBER, 1970.
SAMPLES I '- COURTESY OF MR. IIZUKA FROM PREFECTURAL TECHN. RESEARCH CENTER.

Fig. 1 Index map of the samples analysed in this work

Table 1 Description of the Samples Collected in Shimane Prefecture in October 1970 and of the Bituminous Shales from Thailand Used for Trace Elements Analysis.

Sample	Date	Locality	Geologic horizon	Lithologic description	Remark
SH–1	Oct. 14	Mihonoseki Village, Ui Quarry	Upper part of lower Furue F.	Grey shale	Marine
SH–2	〃	Mihonoseki Village, Sōdzu Loc.	Lower part of Josoji F.	Black massive argillite	〃
SH–3	〃	Mihonoseki Village, Inazumi Loc.	Uppermost part, Lower Josoji F.	Black massive argillite	〃
SH–4	〃	Mihonoseki Village, Chikumi Loc.	Upper part of Josoji F.	Brownish to black shale	〃
SH–5	〃	Matsue City, Honjo Loc.	Upper part of Josoji F.	Light brownish to black shale	〃
SH–6	〃	Matsue City, Ikima Loc.	Furue F.	Dark grey massive argillite	〃
SH–7	〃	Kashima Vill., Miyauchi Loc.	Upper part of Josoji F.	Grey shale	〃
SH–8	〃	Kashima Vill., Etomo Loc.	Lowermost part of Furue F.	Black, hard shale	〃
SH–9	Oct. 15	Hirata City, Kosakai Vill., Nakanote Loc.	Lowermost part of Furue F.	Light brown to grey siltstone	Marine
SH–10	〃	Hirata City, Kamagadani Loc.	Upper part of Josoji F.	Dark grey, very fine siltstone	〃
SH–11	〃	Hirata City, Chigō Loc.	Lower part of Josoji F.	Dark grey claystone	〃
SH–12	〃	Hirata City, Chigō, East of port	Lowermost part of Koura F.	Dark grey, hard siltstone	Brackish-Fresh wt.
SH–13	〃	Hirata City, Shita Vill., Kawashimo	Uppermost Ushigiri F.	Grey shale	Marine
SH–14	〃	Hikawa Vill., Haraga Loc.	Gas Sample		
SH–15	Oct. 16	Hirata City, Fuse Loc.	Med. to upper part, Furue F.	Dark grey siltstone	Marine
SH–16	〃	Hirata City, Oku-Uga Loc.	Med. to upper part, Furue F.	Light brown to dark grey siltstone.	〃
SH–17	〃	Hirata City, Midani Loc.	Lowermost part of Furue F.	Light bluish grey siltstone	〃
SH–18	〃	Taisha Vill., Coop. of Fishery	Lower part of Josoji F.	Grey shale	〃
SH–19	〃	Taisha Vill., Hinomisaki shrine	Ushigiri F.	Light brownish grey shale	〃
W–1	〃	Wanibuchi Mine- (–150 m level)	Lower part of Josoji F.	Grey shale (not analysed)	〃
W–2	〃	Wanibuchi Mine- (–200 m level)	Lower part of Josoji F.	Grey shale	〃
W–3	〃	Wanibuchi Mine- (–225 m level)	Lower part of Josoji F.	Grey shale	〃

Sample	Date	Locality	Geologic horizon	Lithologic description	Remark
SH–20	Oct. 17	Matsue City, lignite mine aband.	Matsue F.	Siltstone (organic)	Fresh water
SH–21	〃	Matsue City, Loc. Nogi, Fukutomi	Fushina F.	Sandy, very fine siltstone	Marine
SH–22	〃	Tamayu Vill., Tamayu street	Upper part of Kuri F.	Dark grey, very fine siltstone	〃
SH–23	〃	Tamayu Vill., Ichyoda Valley entran.	Upper part of Fushina F.	Light bluish grey, fine sandstone	〃
SH–24	〃	Shinji Vill., East Kimachi	Lower part of Fushina F.	Bluish grey, medium sandstone	〃
SH–25	〃	Izumo City, Hiebara Loc.	Upper part of Kuri F.	Light bluish grey siltstone	〃
SH–26	〃	Izumo City, Izumo High School	Upper part of Fushina F.	Light brownish grey, fine sandstone	〃
SH–27	Oct. 18	Ooda City, Asayama Vill., Asakura	Kuri F.	Brownish grey, massive argillite	〃
SH–28	〃	Ooda City, Kute Village	Oomori F.	Grey, very fine sandstone	〃
SH–29	〃	Ooda City, Torii Vill., Nitta	Upper part of Oomori F.	Brownish grey, tuffaceous siltstone	〃
SH–30	〃	Ooda City, Torii Vill., Torii	Oomori F.	Light bluish grey, fine siltstone	〃
SH–31	〃	Ooda City, Ooya Vill., Ooya	Upper part of Kuri F.	Brownish grey, massive argillite	〃
SH–32	〃	Ooda City, 500 m W Kuri Village	Upper part of Kuri F.	Light brownish grey, fine siltstone.	〃
SH–33	〃	Ooda City, West of Kuri Village	Lower part of Kuri F.	Light brownish grey siltstone	〃
SH–34	〃	Koryō Vill., S of the Prefect.	Gas sample		〃
I–4	Mr.	Taisha Vill., Inasa Loc.	Josoji F.	Grey shale	Marine
I–6	Iizuka's	Taisha Village	Josoji F.	Grey shale	〃
I–7	offer	Taisha Village, Udo mine proxim.	Josoji F.	Grey shale	〃
T–1		Well no. 11, 84–85 m depth	Mae Sot F. (Thailand)	Oil shale+grey shale (rithmite)	Fresh water
T–2		Well no. 11, 82.5–89.3 m depth	Mae Sot F. (Thailand)	Oil shale	〃
T–3		Well no. 11, 140 m depth	Mae Sot F. (Thailand)	Grey shale	〃

Notes: The samples SH–27 and SH–31 had received weathering action and near to SH–30 collection locality there was a intrusion of a volcanic rock (very weathered).
The probable correlations of the geologic formations between the Tertiary of the Shimane mainland part and Shimane peninsula are:

Shimane Mainland	Shimane Peninsula	Deposition environment
	Matsue Formation	Fresh water
	Kawadzu Formation	Marine
Fushina Formation	Furue Formation	Marine
Oomori Formation	Ushigiri; Wanibuchi Formation	Marine
Kuri Formation	Josoji Formation	Marine
	Koura Formation	Brackish to fresh water

furnished by Mr. IIZUKA of Prefectural Technological Research Center of Shimane, collected from different parts of the Province. Three samples from cores of the well no. 11, in Thailand, were also analysed (See figure 1 and table 1).

Equipment used: JARRELL ASH CO. 3.4 m Ebert type Spectrograph with a 15,000 lines/inch grating.

Conditions of the analysis:

a) **Preparations of the samples**—Total weight = 200 mg of the mixture 98.75% of NaCl (buffer)–1.25% of CdO (internal standard) were added to 200 mg of previously powdered sample. This kind of preparation was followed in the unknown samples being analysed and in the SPEX STANDARDS and in the standard rocks.

b) **Standard samples**—Six standard samples of SPEX INDUSTRIES INC. (Metuchen, N.J., USA) each one containing 49 chemical elements in concentrations of 0.0001%, 0.001%, 0.0033%, 0.01%, 0.033% and 0.1%, respectively, were used. Seven standard rock samples, namely: G–1 (granite), W–1 (diabase), GSP–1 (granodiorite), AGV–1 (andesite), BCR–1 (basalt), JG–1 (granite from Japan) and JB–1 (basalt from Japan) were used. The composition of G–1, W–1, GSP–1, AGV–1 and BCR–1 were extracted from THOMPSON, BANKSTON and PASLEY (1969) and FLANAGAN (1967). The compositions of JG–1 and JB–1 were obtained by ANDO, KURASAWA, OOMORI and TAKEDA (1970).

Conditions of utilization of the equipment: Direct current (DC), 220 V–8A, exposure time = 90 seconds, slit = 20/1000 mm, electrodes HITACHI SPECIAL, photographic plates = KODAK spectrum analysis no. 1 plates with developing time of 3 minutes. The photographic spectrum plates so obtained was observed and measured in a microphotometer (NIPPON JARRELL-ASH CO. LTD.).

Results and General Comments

The elements B, Co, Cr, Cu, Ga, Mn, Mo, Ni, Pb and V were semiquantitatively determined, as principal trace elements in the samples here analysed. Moreover, Ag, Ba, Bi, Ge, Li, Sn, Sr, As and Zn were also investigated but their amounts were too little to make quantification, being frequently present in concentrations less than the detection capacity of the equipment used. In this situation any quantification is not significant, due to the extremely low precision in the measurements (See figure no. 2).

Boron

The total amplitude of boron concentration is between 10 ppm (sample W–3) and 120 ppm (SH–6 and SH–16), and the medium value is 50 ppm. The standard deviation of all the samples from Shimane Prefecture here analysed is 22.00.

The concentration of boron in the sedimentary rocks is frequently used as a indicator to establish the distinction between marine and non-marine rocks. In general it's considered that the boron precipitation is accentuated in environments of high salinities (LEBEDOV, 1967). Low concentrations were found in Matsue and Koura Formations, the first one admitted as laid down in fresh water environment and the second one in brackish to fresh water environment. However,

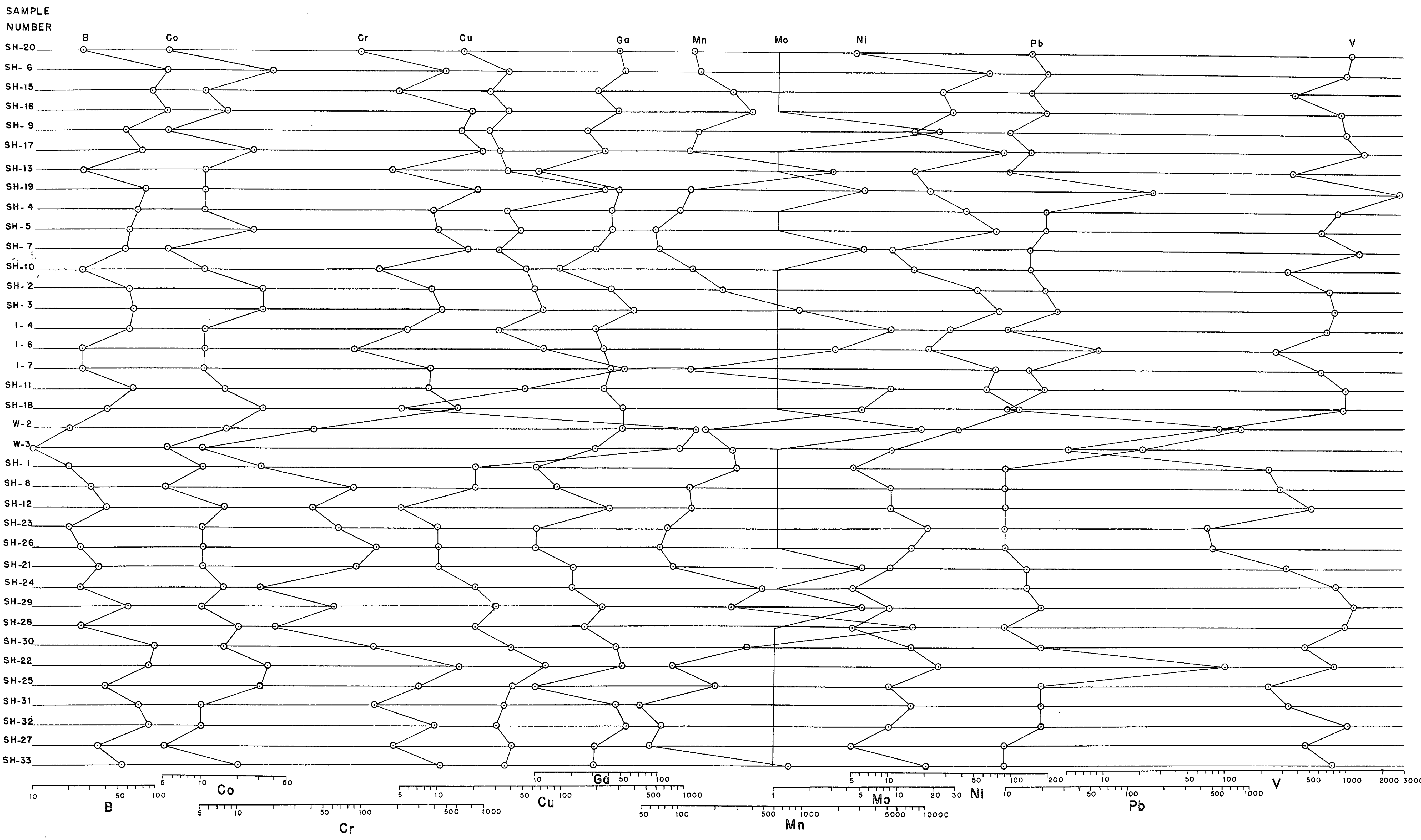


Fig. 2 Distribution of some trace elements in Tertiary sediments-Shimane Prefecture, Japan

equivalent low values were found in typically marine sediments and so this assumption is questionable. The same situation was observed in Nakaumi and Shinji lakes bottom sediments by NAKAO et al. (1969).

Cobalt

The total amplitude of cobalt concentration is between 5 ppm (SH–7 and SH–8) and 35 ppm (SH–6 and SH–22), and the medium value is 15 ppm. The standard deviation calculated for the cobalt was 0.82, showing little variation around the medium value.

Chromium

The total amplitude of chromium concentration ranged between 5 ppm (W–3) to 920 ppm (SH–17), and the medium value was 290 ppm. The standard deviation was 9.86.

Copper

The total amplitude of copper concentration is situated between 5 ppm (sample SH–12) and 1,200 ppm (W–2), and the medium value was 100 ppm. The standard deviation was 3.28.

Concentrations of copper superior to 500 ppm appear to be abnormal in the sedimentary rocks from Shimane Prefecture and was found only in the samples W–2 (1,200 ppm) and W–3 (900 ppm) due to mineralization by "black-ore."

Gallium

The total amplitude of gallium concentration ranged from 10 ppm (SH–1, SH–23, etc.) to 60 ppm, and the medium value was 35 ppm. The standard deviation calculated for all samples was 10.69.

Manganese

The total amplitude of manganese concentration ranged from 50 ppm (SH–31) to 8,000 ppm (SH–28), and the medium value was 835 ppm. The standard deviation was 106.85, showing very dispersed values with concentrations certainly affected by weathering processes.

Molybdenum

This element was not detected in the majority of the examined samples. Concentrations higher than in other samples were verified in SH–9 (20 ppm) and W–2 (15 ppm).

Nickel

The total amplitude of nickel concentration ranged from 5 ppm (SH–1, SH–27, etc.) to 110 ppm (SH–18), and the medium value was 30 ppm. The standard deviation calculated for the nickel was 13.80.

Lead

The total amplitude of lead concentration ranged between 10 ppm (SH–12, SH–13, etc.) to 870 ppm (W–2), and the medium value was 65 ppm. The highest value (870 ppm) is abnormal and was verified only in the sample collected in the Wanibuchi "black-ore" mine, but the sample SH–22, collected in the surface (Kuri Formation) showed also high value of lead concentration (640 ppm). The standard deviation was 12.32.

Vanadium

The total amplitude of vanadium concentration ranged between 5 ppm (W–3) to 2,650 ppm (SH–19), and the medium value was 680 ppm. The standard deviation calculated was 4.10.

The three samples from Thailand showed lower concentrations of all the trace elements here examined when compared with the samples from Shimane Prefecture. The molybdenum was absent in all the samples and the vanadium was detected only in one sample. The available data is not sufficient to explain the reasons for the differences above-mentioned, however, it's possible that non-marine sediments, as these from Thailand, are much poor in trace elements than marine ones. The geology and the economic aspects (oil-shales) of the Mae Sot Formation, Thailand, from which these samples came, were investigated by HARAGUCHI (1957). This fact can be verified in the samples from Shimane Prefecture, where Matsue and Koura Formations showed concentrations in trace elements lower than other formations of typically marine origin.

Some Considerations about the Trace Elements Composition of the Tertiary Deposits and Bottom Sediments of Shinji and Nakaumi Lakes

It's impossible to make a direct comparison between compositions in trace elements of Tertiary and recent bottom sediments because the involved factors in their distribution, as the geochemical conditions of the sedimentary environment, are very complicated and only few data are still available. Moreover, there are certainly complex mechanisms due to the diagenetic processes in all phases of lithogenesis and the chemical elements involved in these processes don't have the same behavior.

However, a rapid glance at the data presented by NAKAO et al. (1969) permit to reach the conclusion that the great majority of common trace elements examined are similar to concentrations found in the Tertiary sediments of Shimane Prefecture. Moreover, perhaps higher concentrations of some trace elements are related to partial elimination of the intersticial waters in older sediments during their compaction. It's possible to note that more erratic distribution of some elements is verified in the Tertiary sediments than in the bottom sediments of the lakes, indicating a possible action of the weathering in the older sediments.

Conclusions

a) These data of trace elements in Tertiary sediments from Shimane Prefecture are not sufficient to make more detailed considerations. I think that is necessary to make a more detailed analysis to know about their composition in different sizes (clay, silt and sand) in order to get some informations on the form of occurrence of these elements in the rocks.

b) When more numerous and detailed data will be available on the trace elements composition of the Tertiary sediments and the bottom sediments of Nakaumi and Shinji lakes, and with informations about the derivation of the lake sediments, physico-chemical conditions in the lake environment, etc. possibly we shall have good indications of the deposition environments of the Tertiary sediments and its possible implications in the trace elements distribution.

c) Certainly, the organic compounds are very effective agent in the concentration of the trace elements, as established by various authors; the analysis that Dr. K. MOTOJIMA's group of geochemistry will perform will be of great value for a more correct interpretation of the data here presented and for future data that will be obtained by other investigators.

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要　約

主として島根県の新第三紀の中新世と鮮新世の地層より採取された泥岩中の微量成分，組成を発光分光法により半定量分析で求めた。ここでは，B, Co, Cr, Cu, Ga, Mn, Mo, Ni Pb とVの含有量を知ることができた。Ag, Ba, Bi, Ge, Li, Sn, Sr, As および Zn はその分析感度以下の量しか存在しなかった。同地域にて行なわれた中尾ら（1969）—未発表—の中海，宍道汽水湖の底質の分析結果とも比較をこころみた。

多分，海水域堆積物では一般に微量成分の含有量が多いように思われるが，どちらも全岩試料のデータなので，このような分布の関係を議論するのは無理であろう。