On the Boron Content of the Shallow-Water Deposits*

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Abstract: The Abundance of boron was studied in the shallow-water deposits from Nanao Bay, Ishikawa Prefecture, and further in order to find the relation of boron content to depth and coastal geology, the deposits taken in Kasaoka Bay, Okayama Prefecture, at Oki Island, Shimane Prefecture and at the several small islands around Honshu, Japan were analysed.

The boron contents Nanao Bay deposits ranged from 16 to 103 ppm and the average was 67 ± 20 ppm. The boron content in the deposits of North Bay of Nanao which is affected by the open sea (av. 56 ± 12 ppm), is considerably lower than that in those in South Bay of Nanao which is subjected to slight influence of the open sea (av. 90 ± 9 ppm). The boron contents of the deposits increase with the increase in the contents of organic matter. There are positive correlations between the contents of boron and those of sulfur, organic carbon, nitrogen and vanadium.

The abundance values of boron in the samples collected in Kasaoka Bay and at Oki showed the range of 16—29 and 28—40 ppm respectively, but the result is insufficient to prove a definite relation with the depth.

The deposits collected at the several small islands around Honshu, Japan, which consisted mainly of detrital sands, showed the values of boron from 11 to 48 ppm, with the average of 23 ± 10 ppm which is about one-third of 67 ± 20 ppm in Nanao Bay deposits. The boron contents of these samples have a close relationship to the coastal geology, and the samples collected at the islands where acidic igneous rocks predominate are relatively rich in boron (av. 20 ± 5 ppm) but those derived from basic igneous rocks are meager in it (av. 12 ± 1 ppm). The deposits obtained at the islands composed mainly of sedimentary rocks except upper paleozoic formations have a comparatively rich boron content, ranging from 25 to 48 ppm.

1. Introduction

In the previous paper (YAMAMOTO, 1968), the contents of major and minor elements in 21 samples of the shallow-water deposits from Nanao Bay were reported.

The present investigation was undertaken to find the abundance of boron in the same samples. Boron, like gallium and lithium, is known as one of environmental discriminators. It is, therefore, of interest to make a research on the relationship between the boron content of Nanao Bay deposits and the contents of major and minor elements, environments of deposition, coastal geology, or the water depth. Further, in order to find out relation of boron content to coastal geology, the abundance and distribution of boron in the shallow-water deposits taken at several small islands, which have relatively simple

geological structure and are influenced little by the geology of remote place were studied. The shallow-water deposits of Kasaoka Bay, Okayama Prefecture and Oki Island, Shimane Prefecture were also analysed.

2. Analytical methods

Boron was determined by the methylene blue-dichloroethane extraction methods of UTSUMI *et al.* (1965) and MUTO *et al.* (1966), as follows.

10 to 15 mg of sample, ground finely and dried to a constant weight, is placed in a platinum crucible. The sample is decomposed on a sand bath by heating with 1—2 ml of 1 M phosphoric acid and 5 ml of 5 % hydrofluoric acid. After complete decomposition, 3 ml of 5 % hydrofluoric acid and 2 ml of 1 N sulfuric acid are added to the residue and the solution is diluted to 15 ml with water. The solution, allowed to stand for 30 minutes at the temperature higher than 20°C, is transferred to a 100-ml separatory funnel made

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Table 1. Boron content of the shallow-water deposits in Nanao Bay.

Sample No.	Locality	Type of deposits	Depth (m)	Boron content* (ppm)
1	West Bay	mud	5	70
2	West Bay	mud	9	62
3	West Bay	mud	7	68
4	West Bay	mud	11	73
5	West Bay	mud	10	68
5P	West Bay	sandy mud	9	16
6	South Bay	mud	20	96
7	South Bay	mud	7	103
8	South Bay	mud	13	91
9	South Bay	mud	19	87
10	South Bay	mud	24	78
10 ₁	South Bay	mud	7	86
11	North Bay	mud	23	58
12	North Bay	mud	29	46
13	North Bay	mud	30	64
14	North Bay	mud	45	75
15	North Bay	mud	35	61
16	North Bay	mud	17	64
17	North Bay	mud	19	49
18	North Bay	mud	25	32
19	North Bay	mud	31	54

* In these values, the analytical error is found, at highest, to be 10 %.

Table 2. Average boron contents of the deposits of West, South and North Bays of Nanao (summary of Table 1).

Deposit of Nanao Bay	Number of samples	Average depth (m)	Boron content (ppm)	
			Range	Average
Deposits of West Bay	6	9	16—73	60 ± 22
Deposits of South Bay	6	15	78—103	90 ± 9
Deposits of North Bay	9	28	32—75	56 ± 12
All the deposits of Nanao Bay	21	19	16—103	67 ± 20

of polyethylene. Boron is then extracted as methylene blue-tetrafluoroborate complex by shaking for 1 minute with 3 ml of 0.001 mol/l methylene blue and 10 ml of 1,2-dichloroethane. After separation of each liquid phase, the lower organic layer is poured into another separatory funnel and washed with water by shaking for 1 minute. The 1,2-dichloroethane phase is then transferred to a 10 mm-cell and its absorbance is measured at 660 m μ against a dichloroethane

blank.

3. Results and discussion

1) The boron content of Nanao Bay deposits In the deposits of Nanao Bay born contents range from 16 to 103 ppm and the average is 67±20 ppm, as is shown in Tables 1 and 2. Generally, boron is more abundant in the deposits of South Bay rich in sulfur, nitrogen and organic carbon than in those in West and North Bays.

The average boron content of group *S* (South Bay), 90 ± 9 ppm, is approximately 1.5 times greater than the respective averages of 60 ± 22 and 56 ± 12 ppm in the groups *W* (West Bay) and *N* (North Bay). This is probably due to the differences of the sedimentation environments in North, South and West Bays which are classified topographically into semi-open, semi-closed and closed types respectively.

Among these deposits Sample 5P which consisted mainly of detrital sand shows the lowest value of boron, 16 ppm, while the highest value, 103 ppm, is found in Sample 7, which is derived mostly from nondetrital mud and is comparatively rich in copper and zinc. Generally, no appreciable enrichment of boron occurs in shallow-water deposits consisting of detrital sands, as is shown in Table 4.

The average boron content of the deposits from Nanao Bay, 67 ± 20 ppm, is approximately 2–3 times greater than the averages of 22 ± 7 , 33 ± 6 , and 23 ± 10 ppm in the deposits collected at Kasaoka Bay, Oki and several small islands around Honshu, Japan respectively, but is slightly lower than the average boron content of the muds at Paria (HIRST, 1962) 81 ppm and is approximately in the middle between 50 and 93 g/ton in the deep sea sediments (LANDERGREN, 1948), as is shown in Table 6.

HARDER (1959) stated that the boron content of the clay sediments is dependent on the mineral assemblage of the sediment, the grain size, and other conditions. As to adsorption of boron on clay minerals HOSOKAWA (1962) stated that little plays an important part and boron is fixed into crystal structure (FREDICKSON *et al.*, 1960).

In fact, boron is more abundant in the deposits of Nanao Bay rich in clay minerals than in those of detrital sands obtained at small islands. This is probably due to the adsorption of boron by clay minerals such as illite, montmorillonite and kaolinite, whose presence are confirmed by X-ray diffraction method.

As to the relation of boron to other elements, there are positive correlations between the contents of boron and those of sulfur, organic carbon and nitrogen, as is shown in Figs. 1, 2 and 3. It can be also found that boron and vanadium are in close relationship, as Fig. 4

Fig. 1. Relationship between the contents of boron and sulfur in deposits of Nanao Bay.

Fig. 2. Relationship between the contents of boron and organic carbon in deposits of Nanao Bay.

shows. Sulfur, organic carbon, nitrogen and vanadium which are closely related to boron have a close correlation with organic matter, derived from a part of marine organisms which adsorbed concentrated boron from sea water.

2) The boron contents of the shallow-water deposits from Kasaoka Bay and Oki Island

In order to find the relation between the boron

Fig. 3. Relationship between the contents of boron and nitrogen in deposits of Nanao Bay.

Fig. 4. Relationship between the contents of boron and vanadium in deposits of Nanao Bay.

Table 4. Boron contents of the shallow-water

Locality	Geology**	Type of deposits
Hiroshima, Kagawa-ken	Granites	grayish white sand
Nakashima, Ehime-ken	"	light brown sand
Ogishima, Kagawa-ken	" (Sanukite)	"
Momoshima, Hiroshima-ken	"	"
Yokoshima, Hiroshima-ken	"	"
Okinoshima, Kōchi-ken	"	grayish brown sand
Kogoshima, Ehime-ken	"	brown sand
Kōnoshima, Okayama-ken	Quartz-porphyry	light brown sand
Tashima, Hiroshima-ken	"	greenish sandy mud
	(Granites, Ryoke metamorphics)	
Heigunshima, Yamaguchi-ken	Pyroxene-andesite	grayish brown sand
Kajishima, Ehime-ken	Norite	light blackish gray sand
Kasatoshima, Yamaguchi-ken	Ryoke metamorphics (Granites)	grayish brown sandy mud
Ōtsushima, Yamaguchi-ken	Sangun metamorphics (Granites)	blackish green sand
Takashima, Ōita-ken	Sanbagawa metamorphics	grayish blue sand
Nushima, Hyōgo-ken	Greenschist, Black phyllite	grayish white sand
Shishishima, Kagawa-ken	Upper Paleozoic formations	light brown sand
Mutsukishima, Ehime-ken	Upper Paleozoic formations (Granites)	yellowish brown sand
Ōnyūshima, Ōita-ken	Mesozoic formations	brown sand
Shimoniizu-mura, Ōita-ken	"	"
Sugari, Owashishi, Mieken	"	blackish gray sand
Tobishima, Yamagata-ken	Tertiary formations	"
Higashitonda-mura Wakayama-ken	"	light blackish gray sand
Himagashima, Aichi-ken	"	light grayish brown sand

* Three capes are also included.

** Only the predominant rocks and formations are shown. The parentheses are for the rocks which

*** The experiments were carried out within 10 % of error in the case of boron, and within 2 % of error

Table 3. Boron content in the deposits of Kasaoka Bay and Oki.

Kasaoka Bay, Okayama Prefecture			
Depth (m)	Number of samples	Type of deposits	B content (ppm)
1.7—3.4	3	mud	16
9.2—13.1	2	mud	27
15.8—17.3	3	mud	17
39	1	mud	29
Oki, Shimane Prefecture			
Depth (m)	Number of samples	Type of deposits	B content (ppm)
8.3	1	mud	28
11.8	1	mud	29
27	1	mud	36
41	1	mud	40

deposits collected from various small island*.

Composits of	B*** ppm	SiO ₂ *** %	Fe ₂ O ₃ *** %	Al ₂ O ₃ *** %	MnO*** %	CaO*** %	MgO*** %	CO ₂ *** %
5 deposits	17	82.92	0.56	9.23	trace	0.74	0.33	—
5 "	15	79.28	1.26	11.01	0.01	1.09	0.34	—
5 "	17	77.49	1.97	12.16	0.03	2.23	0.24	—
4 "	16	75.81	2.34	12.21	0.04	1.69	0.40	—
5 "	16	76.21	2.49	14.77	0.03	1.32	0.25	—
5 "	26	73.96	3.08	10.40	0.04	3.76	0.46	2.33
3 "	17	70.62	4.28	12.98	0.11	2.85	1.14	1.66
5 "	27	79.24	1.56	9.74	0.02	2.57	0.56	1.28
5 "	25	75.87	2.02	11.52	0.03	0.90	0.49	—
2 "	13	71.20	2.98	13.49	0.04	2.92	1.87	—
5 "	11	52.64	8.25	20.06	0.18	9.69	4.58	0.52
4 "	18	79.36	3.05	6.82	0.11	2.82	1.12	1.58
2 "	15	47.48	6.14	12.31	0.12	15.95	2.74	8.28
5 "	22	70.02	2.87	9.51	0.06	7.05	1.86	4.01
5 "	27	74.26	2.16	7.07	0.06	5.62	0.74	3.86
5 "	18	87.54	1.00	5.77	0.04	1.19	0.21	—
2 "	16	79.25	1.02	10.05	0.01	2.13	0.52	—
4 "	35	76.42	2.99	10.95	0.03	1.80	0.26	0.50
5 "	44	70.67	5.21	13.37	0.08	0.76	1.10	—
4 "	48	72.20	3.38	11.27	0.04	3.45	0.65	1.20
4 "	25	57.69	3.69	14.82	0.05	8.56	2.20	5.14
4 "	29	56.25	2.76	7.15	0.01	15.27	1.25	11.28
5 "	28	77.54	1.79	8.77	0.01	3.83	0.51	2.18

distribute in land areas relatively far from the location sampled.
in other elements.

Table 5. Boron content and the geology.
(summary of Table 3)

Geology	Number of samples	B content (ppm)	
		Range	Average
Igneous rocks			
Acidic rocks	9	15—27	20 ± 5
Basic rocks	2	11—13	12 ± 1
Metamorphic rocks			
Gneisses	1	—	18
Crystalline schist	3	15—27	21 ± 6
Sedimentary rocks			
Upper Paleozoic formations	2	16—18	17 ± 1
Mesozoic formations	3	35—48	42 ± 7
Tertiary formations	3	25—29	27 ± 2

content and the depth, the deposits in Kasaoka Bay, Okayama Prefecture, and at Oki Islands, Shimane Prefecture, were analysed. Table 3 shows the analytical results obtained in these samples. No systematic variation of boron contents with respect to the depth was found in the deposits Kasaoka Bay and Oki, although boron has a tendency to increase to some extent with depth in the latter. Therefore, it seems necessary to analyse a much larger number of deposits taken at various depths at many more places to find such relations.

3) The boron content of the shallow-water deposits collected at several small islands around Honshu, Japan

The analytical results are presented in Table 4 and summarized in Table 5, and these figures are given on the sea-salt-free and dry basis.

The boron contents of 11—48 ppm and the average of 23 ± 10 ppm are found in these deposits derived mainly from detritus which is approximately one-third of 67 ± 20 ppm, the average of Nanao Bay deposits. It is probably that a considerable variation in boron contents of these deposits is attributed to the difference in geology of the land adjacent to the location of sampling. As is shown in Tables 4 and 5, the average boron content of 20 ± 5 ppm in the deposits of Hiroshima—Tashima where igneous acidic rocks predominate, is approximately two times greater than the average of 12 ± 1 ppm in the deposits of Heigunshima and Kajishima where igneous

basic rocks are predominant. Such a variation in boron content in these deposits agrees well with the tendency that boron content is higher in igneous acidic rocks, such as 15 and 20 ppm reported by SAHAMA (1945) and WASSERSTEIN (1951) respectively, than that in igneous basic rocks, which is 9 (SAHAMA, 1945) and 10 ppm (VINOVSADOV, 1956). It is one of interest that the values of boron contents of igneous rocks are close to the values of 20 ± 5 and 12 ± 1 ppm in the deposits described above, suggesting that the deposits is derived mainly from igneous rocks.

Boron, generally, is contained more abundantly in sedimentary rocks than in igneous rocks. SAITO (1965) stated that the average boron content in sedimentary rocks is 85 ppm, which is approximately eight times the value in igneous acidic rocks. A similar tendency can be expected to occur in these deposits, too. Actually, the

Table 6. Average boron for shallow-water deposits from Nanao Bay, Kasaoka Bay and various small islands and comparison with boron figures derived by other workers.

	B(ppm)
21 Muds from the Nanao Bay (This work)	67 ± 20
4 Muds from Kasaoka Bay (This work)	22 ± 7
4 Muds from Oki, Shimane Prefecture (This work)	33 ± 6
23 Sands from various small islands around Japan Proper (This work)	23 ± 10
6 Greenish muds from Gulf of Paria (HIRST, 1962)	81
3 Delta sands from Gulf of Paria (HIRST, 1962)	51
14 Modern marine argillaceous sediments (POTTER <i>et al.</i> , 1962)	89.6
19 Modern fresh-water argillaceous sediments (POTTER <i>et al.</i> , 1962)	45.6
22 Deep-sea sediment from the Pacific (GOLDBERG and ARRHENIUS, 1958)	300
25 Silurian shales (SPENCER, 1957)	102
Recent marine clays (GOLDSCHMIDT and PETERS, 1923d)	93
Marine hydrolyzates (LANDERGREN, 1945)	150
Bottom sediment, Tyrrhenian Sea (LANDERGREN, 1948)	50
Volcanic rocks (HARDER, 1959)	17

boron contents of the deposits of Shishishima—Himagashima composed mainly of sedimentary rocks are higher than those of other islands formed predominantly by igneous rocks, especially high in the deposits in mesozoic formations showing the average of 42 ± 7 ppm. This is probably due to the shales rich in boron, which are characteristic of the mesozoic formations and considered to be deposited in rather deep sea.

4. Summary

From the above results and discussions the following conclusions were derived: 1) The boron contents of Nanao Bay deposits are affected considerably by the sedimentary environments and the amounts of clay minerals such as illite, montmorillonite and kaolinite; 2) No clear relationship of boron content to depth is found in the deposits from Kasaoka Bay and Oki Island; 3) the average boron content of the deposits from Hiroshima—Tashima, where igneous acidic rocks are predominant, is approximately 2 times higher than that of the deposits from Heigunshima and Kajishima, where igneous basic rocks predominate; 4) boron is more abundant in the deposits derived from sedimentary rocks, particularly mesozoic formations, than in those from igneous and metamorphic rocks.

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浅 海 底 土 の ホ ウ 素 含 量

山 本 善 一

要旨 石川県七尾湾の浅海底土のホウ素含量をしらべ、更にホウ素含量と水深ならびに沿岸の地質との関係をみるために、岡山県笠岡湾、島根県隠岐ならびに本州周辺の各種の島嶼から採取した浅海堆積物を分析した。

七尾湾海底土のホウ素含量は $16 \sim 103$ ppm の範囲にわたり、その平均値は 67 ± 20 ppm であった。外洋の影響を受けやすい七尾湾北湾の海底土のホウ素含量（平均値 56 ± 12 ppm）は、比較的その影響の少ない七尾湾南湾のもの（平均値 90 ± 9 ppm）よりかなり低い。これらの浅海底土のホウ素含量は有機物含量の増大と共に増加する。ホウ素含量とイオウ、有機炭素、窒素およびバナジウム含量との間には正の相関関係が存在する。

笠岡湾および隠岐から採取した試料のホウ素含量はそ

れぞれ $16 \sim 29$ および $28 \sim 40$ ppm の範囲にわたるが、この結果だけでは水深との相関は明瞭でない。

本州周辺の比較的均一な地質から成る小さな島嶼（23か所）から採取した。主に碎屑岩源の砂よりなる浅海堆積物のホウ素含量は $11 \sim 48$ ppm で、平均 23 ± 10 ppm である。これは上述の七尾湾海底土の平均値 67 ± 20 ppm のほぼ $1/3$ である。また、これらの試料のホウ素含量は沿岸の地質と関連が深く、酸性火成岩類の主に分布している島から採取した試料には比較的ホウ素が多く（平均値 20 ± 5 ppm）、塩基性火成岩に由来する試料には少ない（平均値 12 ± 1 ppm）。これに対して、上部古生界を除く主に堆積岩よりなる島から採取した試料は $25 \sim 48$ ppm にわたる、比較的高いホウ素含量を示す。